Risk assessment of chlorine dioxide storage facilities

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Abstract
Chlorine dioxide (ClO_2) is universally used as a bleaching agent in the manufacturing of pulp for paper production. ClO_2 is very reactive and hazardous, and one of the largest risks associated with production of ClO_2 is the storage facilities. The intent with this master thesis was to develop a method for risk assessment of the ClO_2 storage facilities at pulp mills.

From methodical scientific work comprising literature searches and interviewing professionals has resulted in a thorough identification of the risks associated with ClO_2 storage facilities.
The gas release in case of several different scenarios has been simulated using the software ALOHA. The software unfortunately cannot account decaying concentrations in the liquid releasing the gas and also not account the fact that chlorine dioxide decomposes in air. Consequently, the extent of the gas release as well as the concentration gradients is exaggerated. Never the less, the simulation work allows distinguishing between various scenarios.

Based on the identification of risks and the simulations of various scenarios, an "ideal" ClO_2 storage facility can be defined. A method for comparing a real storage to this ideal facility has been developed. The result is very promising; the method allows the user to efficiently identify the gap between an actual storage facility and the "ideal" storage. The method also indicates, through an easy to comprehend colour coding, in which areas improvement is most imperative.

Whilst improvement of the simulations of gas release and adoption of the method to reflect also internationally conceivable risks would even further extend the result from this master thesis, the overall result is still very satisfactory and indicates an efficient route for safe ClO_2 storage facilities.

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Sammanfattning

Klordioxid (ClO_2) används som blekmedel vid tillverkningen av pappersmassa för papperstillverkning. Kemikalien är mycket reaktiv och skadlig och en av de största riskerna kopplad till produktion av ClO_2 är lagringsutrymmena. Eka Chemicals, en av de ledande leverantörerna av råvaror och teknik för produktion av ClO_2, startade därför detta examensarbete för att ytterligare stärka och förbättra den totala säkerheten. Avsikten var att utveckla en metod för riskbedömning av lagringsanläggningen för ClO_2 vid massabruken.

Ett metodiskt och vetenskapligt arbete bestående av litteratursökningar och intervjuer med branschfolk har resulterat i en grundlig kartläggning av riskerna kring lagringsanläggningar för ClO_2. De identifierade riskerna har rankats, och för de största riskerna har bakomliggande orsaker, konsekvenserna och sannolikhet bedömts. De största riskerna var läckage från rör, brott på rör, läckage från lagringstank, brott på lagringstank samt mindre spill.

De utsläpp av gasformig ClO_2 som är förknippat med dessa olika risker har simulerats med programmet ALOHA. Programvaran kan dessvärre inte räkna med minskade koncentrationer i vätskan från vilken gasen frigörs och inte heller det faktum att ClO_2 bryts ned i luften. Följaktligen är omfattningen av utsläppen och koncentrationsgradienterna överdrivna. Icke desto mindre ger simuleringarna en tydlig fingervisning om skillnaderna mellan olika scenarier. Simuleringarna bekräftar också att en olycka har potential att sprida gasmoln med koncentrationer över de rekommenderade tröskelvärdena för arbetshälsa långa sträckor. Nära utsläppskällan kan halterna vara mycket höga, ibland så höga att de uppnår den undre explosionsgränsen (LEL) eller till och med dödliga.

Baserat på identifieringen av risker och simuleringarna av olika scenarier, kan den "ideala" ClO_2 lagringsanläggningen definieras. En metod för att jämföra verkliga lagringsanläggningar med denna ”ideala” lagringsanläggning har sedan utvecklats. Under utvecklingsarbetet har metoden använts på tre olika ClO_2 lagringsanläggningar, alla vid svenska massabruk. Resultaten är mycket lovande. Metoden ger användaren möjlighet att effektivt identifiera skillnader mellan sin lagringsanläggning och den "ideala". Metoden visar, genom en lättförståelig färgkodning, inom vilka områden förbättringar i säkerheten är nödvändiga. Metoden är också viktig i det avseende att den ger användaren ett förtroende för den rådande säkerhetsnivån.

Även om förbättring avseende simuleringarna och utveckling av metoden för att återspegla även internationellt tänkbara risker skulle ytterligare förbättra resultatet av detta examensarbete, är det övergripande resultatet fortfarande mycket tillfredsställande. Den utvecklade metoden visar en effektiv väg till säkrare ClO_2 lagringsanläggningar.

Det kan slutligen noteras att grundtanken bakom denna metod kan visa sig vara effektiv och uppskattad även i andra områden, exempel inom annan kemisk industri.

Abstract

Chlorine dioxide (ClO_2) is universally used as a bleaching agent in the manufacturing of pulp for paper production. ClO_2 is very reactive and hazardous, and one of the largest risks associated with production of ClO_2 is the storage facilities. Therefore, Eka Chemicals, one of the leading providers of ClO_2 technology, initiated this master thesis in order to further strengthen and improve the overall safety in the ClO_2 manufacturing plants. The intent was to develop a method for risk assessment of the ClO_2 storage facilities at pulp mills.

From methodical scientific work comprising literature searches and interviewing professionals has resulted in a thorough identification of the risks associated with ClO_2 storage facilities. The risks have been ranked, and for the most important risks the cause, severity of the consequences and magnitude of the probability has been assessed. The most important risks are; pipe leakage, pipe rupture, tank leakage, tank rupture and spills.

The gas release in case of several different scenarios has been simulated using the software ALOHA. The software unfortunately cannot account decaying concentrations in the liquid releasing the gas, neither account the fact that chlorine dioxide decomposes in air. Consequently, the extent of the gas release as well as the concentration gradients is exaggerated. Never the less, the simulation work allows distinguishing between various scenarios. It also confirms that an accident has the potential to create a long range extending gas plume with concentrations above the recommended threshold limit values for occupational health. Close to the source, the concentrations can be very high; concentrations could occasionally reach as high as the lower explosion limit (LEL) or even be mortal.

Based on the identification of risks and the simulations of various scenarios, an "ideal" ClO_2 storage facility can be defined. A method for comparing a real storage to this ideal facility has been developed. During the development of the method it has been applied at three different ClO_2 storage facilities, all at Swedish pulp mills. The result is very promising; the method allows the user to identify the gap between an actual storage facility and the "ideal" storage. The method also indicates, through an easy to comprehend colour coding, in which areas improvement is most imperative. Importantly, the model also allows the user to have confidence in the security level for the facility analyzed.

Whilst improvement of the simulations of gas release and adoption of the method to reflect also internationally conceivable risks would even further extend the result from this master thesis, the overall result is still very satisfactory and indicates an efficient route for safe ClO_2 storage facilities.

It may finally be noted that the applied concept of the method can be efficient and appreciated also in other areas, for example the chemical industry.

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Christoffer Käck
Daniel Lundberg

Lund, 2010-03-20

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1. Introduction

This introduction will give an overall description of the background, limitations and the intentions with this master thesis. The overall goal is to create and develop a method for risk assessment of ClO_2 storage facilities at Swedish pulp mills for Eka Chemicals. The need for such a method is growing as the concern and focus on safety, driven by internal as well as commercial aspects, increases. The developed method should not only be easy to use, but also give comprehendible results.

1.1 Background

Chlorine dioxide (ClO_2) is universally used as a bleaching agent in the manufacturing of pulp for paper production. ClO_2 is very reactive with properties enabling cost efficient and environmentally friendly processes. However, the reactive properties and the fact that the chemical is hazardous make it necessary to take cautions, employ strict management and design of the systems used for manufacturing and storage.

Due to the reactivity, ClO_2 is highly unstable. Therefore, produced ClO_2 are always stabilized in weak water solutions. Considering the amount of ClO_2 that is used at the pulp mills each day, transportation of the solution to the pulps mills is inconceivable and uneconomic. Furthermore, such transports are potentially very dangerous. Therefore, all production of ClO_2 is carried out continuously at each pulp mill.

The fact that ClO_2 has hazardous and dangerous properties is well known by the pulp mills, and because of this, the overall safety at the pulp mills is in generally good. Nevertheless, there is an increasing concern and focus on the area of safety, driven from internal, external and commercial aspects. As the pulp mills continuously strive to improve the overall safety and knowledge around ClO_2, it has been noticed that one of the largest risks associated with production of ClO_2 is in the storage facilities.

Eka Chemicals is a part of the larger company Akzo Nobel. Eka Chemicals is foremost a producer of different chemicals for the pulp- and paper industries, such as bleaching agents and paper chemicals. The company has approximately 3000 employees and currently has production at 36 locations in 19 countries all over the world (Eka Chemicals 2009b). Besides supplying chemicals, Eka Chemicals is one of the leading suppliers of technology for manufacturing ClO_2. In most of the cases, these production facilities are sold to and operated by the pulp mills. However, Eka Chemicals offer help with the operating as well as process optimization and a number of other services linked with these. The above-mentioned increasing concern and focus on the area of safety is noticed by Eka Chemicals. Being a major supplier of technology, Eka Chemicals has better possibilities to meet these concerns than their clients have. As the interest in improving and enhancing the already good safety at the pulp mills is common for both Eka Chemicals and their clients, this is an area where resources and work are focused.

Therefore, Eka Chemicals initiated this master thesis, in order to further strengthen and improve the overall safety at pulp mills. The intent was to develop a method for risk assessment of the ClO_2 storage facilities at pulp mills.

1.2 Goal

The overall goal for this master thesis is to create and develop a method for risk assessment of ClO_2 storage facilities at Swedish pulp mills. Fundamental is the requirement for the method to be useful and suitable for Eka Chemicals, and indirect their clients. To reach this requirement the method should be:

- easy to use
- fast to use
- present results easy to comprehend

To be considered easy and fast to use, the workers at the pulp mills should be able to conduct the method themselves, without support from Eka Chemicals or without any previous experience in risk assessments or risk analyses. The workers performing the method should only need the knowledge and understanding of their own ClO_2 storage facility, overall pulp mill and the conditions there.

The result can be considered being a gap analysis, illustrating potential improvement. It should alert whether one might need to perform further risk assessments and risk analyses in different areas. The method will not generate specific recommendations for eliminating risks; it is aiming to indicate different areas of concern and thereby directing the future work for an improved overall safety.

1.3 Limitations

There are several overall limitations surrounding this master thesis, these are going to be presented below. However, there are several other limitations, which are not overall, but specific. These limitations are not presented here, but at different places throughout the master thesis. Nevertheless, these limitations are as important as the overall ones.

The most apparent and important overall limitation is the definition of the system. As stated earlier, the method is focused on the assessment of the risks arising from the ClO_2 storage facility. However, it is uncertain what the ClO_2 storage facility includes. In this master thesis, this system is defined as the storage tank or the storage tanks, the inbound and outbound pipes, the inbound and outbound pumps and the surroundings of the storage tanks. The exact length of the inbound and outbound pipes is not exactly defined, neither the distance of the surroundings. The length should be considered 10-50 meters for the pipes and the distance 10-100 meter for the surroundings. This definition excludes the process and the process equipment and thereby the risks arising from this, even when located within the distances mentioned above. However, certain aspects concerning administration and such that are overall for the entire pulp mill is included into the model.

Another important limitation is the fact that the method is developed for ClO_2 storage facilities at Swedish pulp mills and the special conditions at those. Although documentation from some international pulp mills has been used, the main sources of information are documentation from the Swedish pulp mills and study visits at these. This limitation can also be noticed throughout the analysis of risks and the probabilities for those. Earthquakes, terror attacks and extreme weather have not been brought forward as important, solely because they are not that important in Sweden. Should the method appeal to a wider range of countries and ClO_2 storage facilities, these properties need to be re-evaluated.

1.4 Method

When presenting the method for this master thesis, there are foremost two aspects that need to be put forward. The first aspect is the theoretical and scientific approach to this master thesis and the second aspect is the more "straight- forward" description of the working process.

1.4.1 Scientific approach

A scientific research need to be objective, unbiased and balanced in order to gain credibility. Being objective means that the information is true and correct. To assure that this criterion is met, the author should turn to primary sources or sources that are subject to extensive review. The reason for this is that secondary sources can contain misconceptions or misinterpretations that might spread and lower the credibility of the research (Ejvegård, 2003). Hansson (2007) also points at the importance of reviewing different sources critically. Knowledge from a low quality source might propagate in to the research, limiting its usefulness.

The research should also be unbiased. This means that the author must not let his preconceptions color the choice of sources or words. If the research considers hot topics, the author must assure that his sources covers all viewpoints. This said, the author might still argue for his point of view, but should always point out that it is subjective reasoning (Ejvegård, 2003).

Last, the research should be balanced, meaning that the different parts of the research should get an appropriate amount of space and focus. The research should for example focus more on significant reasoning than on rather irrelevant details (Ejvegård, 2003).

The methods used by the author of a scientific research are tools to meet these criterions. In this master thesis, the method will be what Ejvegård (2003) refers to as "*modellbildande*", freely translated into English as "the formation of a model". Ejvegård (2003) states that the more detailed a model is, the better a reflection of the reality it is. Hansson (2007) however points out that one should never forget that a model, no matter how detailed it is, always is a simplification of reality. The model can otherwise lead to an inappropriate conclusion. The level of detail should be determined by the intended use of the model (Ejvegård, 2003). The model created in this master thesis is intended to model the level of risk emerging from the storage of ClO_2 at pulp mills. It is important that the risk assessment is detailed enough to give a good measure of the risk, but since it is designed to be a simple method, it cannot be too detailed either. To get this right will require some balance, and it will be hard not to lean towards one way or the other.

To be able to create this model, relevant information must be gathered. This master thesis will use literature studies, field studies and interviews as techniques to do so. A literature study is preceded by a literature search. When searching for relevant literature it is important to find trustworthy sources. Scientific databases are a great help to accomplish this. Thereafter, a scientific summary of the gathered literature is compiled. The objective of this summary is to gain insight in to the subject (Ejvegård, 2003).

Field studies are not covered in the literature about scientific methodology, but the technique seems to be similar to what Ejvegård (2003) refers to as "*deltagande observation*", freely translated into "participating observation". This technique has the disadvantage that the results might be colored by the preconceptions and feelings of the authors. Another disadvantage is that presence might influence the situation (Ejvegård, 2003). For example, workers might act differently if they know that they are observed.

Interviews are used when information are gathered from experts whom might, due to their experience, be able to answer questions that are not readily answered through literature studies. To be able to conduct an efficient and rewarding interview, it should be carefully prepared. By doing this, relevant questions might be asked and the need for a second interview might be avoided. It is also important to take notes or record the interview since the memory of the interview fades quickly (Ejvegård, 2003).

The execution of these techniques will color the resulting model. The model should have high reliability and validity. Hence, it is important that the methods used produce information that also has high validity and reliability. High reliability means that the model will give the same answer every time it is applied at the same CLO_2 storage facility. High validity means that it measures the right parameter, in this case the risk level of the storage facility (Ejvegård, 2003).

1.4.2 The working process

The working process of this master thesis and the development of the method for risk assessment began with two separate literature studies. The first one looked at definitions within the area of risk management and different methods for risk assessment and risk analysis. The second one looked at the properties of ClO_2. The reason for these literature studies was to gain knowledge of these subjects as a foundation for the rest of the master thesis.

During the autumn, there was the opportunity to conduct study visits at three different pulp mills. The intent was partly to get an insight in the production and storage of ClO_2, partly to gain knowledge and information about possible risks affecting the ClO_2 storage facilities and the safety at these.

From the information obtained at these study visits, a representative ClO_2 storage facility was developed. The representative ClO_2 storage facility is the model of a typical Swedish. A risk analysis was performed on the model, combined with consequence calculations. This gave further insight in to which possible risks affecting the ClO_2 storage facility, without being colored by other sources of information or opinions.

The result from the risk analysis was followed by a third literature study, looking at precedent risk assessments, incident reports and articles in the media about accidents at ClO_2 storage facilities. This extent risk identification was then compared with the conclusions from the risk analysis and the calculations on the representative ClO_2 storage facility. From this broad spectrum of possible risks, the most important were identified. In this context, important meant risks with either high probability and/or high consequence.

All of the different risks were then broken down into parameters. These parameters were conditions or actions affecting either the probability or the consequences, both increasing and decreasing. Some of these parameters were obtained from the literature, while others were stated by the authors and observed in the consequence calculations.

Based on the parameters identified and with support from literature, an “ideal” ClO_2 storage facility in aspects of safety was stated. This “ideal” ClO_2 storage facility was then used as the foundation for the development of the actual risk assessment method. The method was created as a checklist with questions. The questions in the checklist was inspired and based on the “ideal” ClO_2 storage facility, thereby indirectly on some of the parameters indentified earlier. The questions and the checklist were designed to obtain information of which safety measures that exist in the ClO_2 storage facility and at the pulp mill. Should answers indicate that these properties differed from the ones stated at the “ideal” ClO_2 storage facility there is deduction of points. The size of these deductions was determined from the risk selection and the stated consequences and probabilities. The result after the deduction of pints is compared with a fixed scale. The input to this scale came from the impressions of the visits and from testing the method on actual ClO_2 storage facilities.

2. Theory

This chapter will present the theoretical aspects of risk management and information about ClO_2. A broad and brief understanding of these subjects is needed as a base for the continuation of this master thesis.

2.1 Risk

Risk, as well as risk management and risk assessment, is somewhat ambiguous concepts. To be able to follow the discussions in this master thesis, a basic understanding of these concepts is helpful, if not even necessary. Therefore, the different concepts and aspects of risk will be discussed in short.

2.1.1 Different perspectives on risk

There are many different ways to define risk. Historically, the most common definition of risk includes the elements consequence and probability. The measurement of the risk is obtained from multiplication of these elements (Kelman, 2003). This perspective defines risk technically and ignores human emotions and anxieties, only seeking to give risk an objective numerical value (Nilsson, 2003).

Slovic (1999) and Renn (1998), among others, have criticized this strictly technological definition and perspective of risk. They argue that it is too much of a scientific perspective, consequently disregarding the risk perception of common people. According to Slovic (1999), people perceive risks differently depending on their age, sex, social status and previous experiences. The expression, "*the truth lies in the eye of the beholder*", is suitable. The implication of this is that the concept of risk is a social construct that can differ between different cultures but also between different individuals in the same culture.

Professionals try to analyze risks according to objective probabilities and consequences, common people look at the likelihoods and the consequences subjective. Therefore, common people tend to overestimate the risk of unlikely accidents with big consequences. In the same way, they tend to underestimate the risk for common accidents with small consequences (Enander, 2006). While the advocates for the social perspective argue that it is mostly important to regard the worries of common people, the professionals with the technical perspective argue that it is a waste of money to mitigate such risks, since they are not as dangerous and severe as people think (Slovic, 1999).

The intent with this master thesis is however not to investigate such a compromise. Hence, in this master thesis the technological perspective will be used. Maybe the technological perspective is not completely objective, but the authors find it more objective than the social perspective.

2.1.2 Risk management and risk assessment

The concepts of risk management and risk assessment are broad and the aspects included differ from time to time. However, the International Electrotechnical Commission (IEC) has defined the concept and process of risk management as well as the concept of risk assessment. These definitions are presented in figure 2.1.

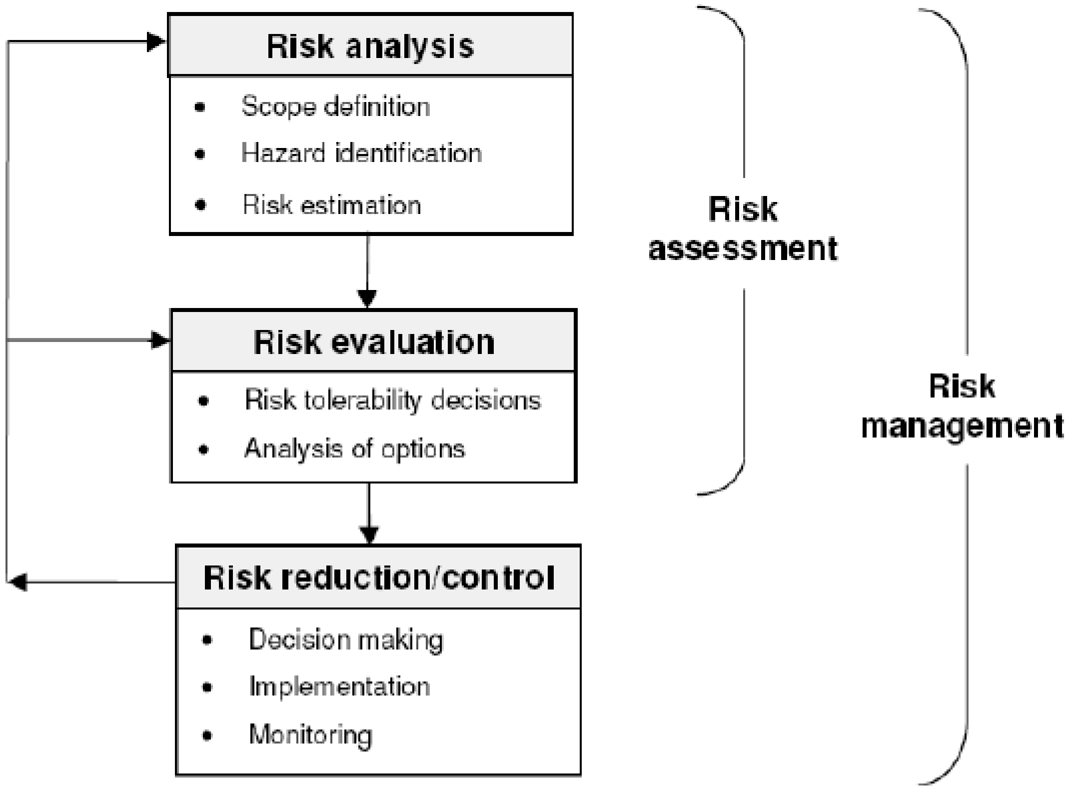

Figure 2.1, Risk management and risk assessment as defined by the International Electrotechnical Commission (IEC, 1995)

Risk analysis is the process of identifying hazards within a defined system and then estimate the risk imposed by these hazards.

Risk evaluation investigates the tolerability of the risks from the risk analysis and analyses different risk mitigating actions.

Risk reduction/control includes the decision of which mitigating action to perform, the implementation of these and monitoring of the effects.

Risk assessment is described as a part of risk management, namely the process of risk analysis and risk evaluation. This master thesis will use these definitions when mentioning risk management and risk assessment henceforth.

Risk management is described as the continuous process to direct and control an organization with regard to risk, for example risk analysis, risk evaluation and risk reduction/control.

2.2 Different methods for assessing risk

There are many different methods for risk assessment and risk analysis, and all methods have their own scope of use, strengths and weaknesses. One distinguishing element between these methods is the ability to make quantifiable assessments. The different methods for risk assessment are often arranged on a scale according to their quantitative properties (Nystedt, 2000). The exact placing of the methods on the scale varies between different literatures. The authors have made their own scale, based on their knowledge and experiences using these methods. This scale is presented in figure 2.2.

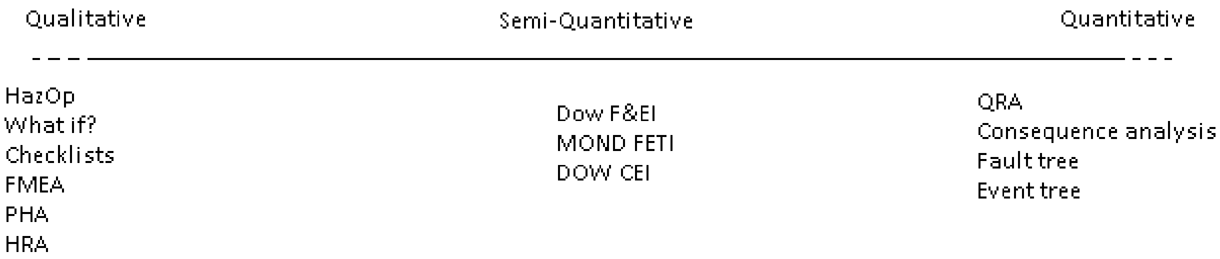

Figure 2.2, Different risk assessment methods ordered by how much of a quantitative result they give.

Which method one should use depends on the objective of the risk assessment and the amount of information available (Nilsson, 2003). If the purpose is to identify the risks, one of the qualitative methods will suffice. On the other hand, if the purpose is to compare the risks between two options of where to place a chemical process industry, a quantitative method is better. To give a better understanding of the methods and their scope of use as well as strengths and weaknesses, a short presentation of the methods will follow.

2.2.1 Qualitative methods for risk assessment

The qualitative methods for risk assessment have the main purpose of identifying what different risks and unforeseen events that can occur under the given circumstances, within the defined system. The methods are most useful during the beginning of the risk assessment process, the beginning of a project or as a foundation for the more thorough semi-quantitative or quantitative methods (Nilsson, 2003).

The qualitative methods are simple in their implementation. Sometimes the methods are challenged as being too simple. The reason is the sometimes vague and imprecise result. This is of course a matter of discussion. Nevertheless, the qualitative methods should not be underestimated or considered as less functional, since they fulfill their intended use. Furthermore, they can easily be adapted to different situations and operations (Nilsson 2003), which should be considered as a strength.

Besides identifying the different risks, some of the qualitative methods also take steps to measure those risks. The measurement is basic and cannot be compared with the quantitative methods. Often the measurement extends to grade the consequence as small, big or various in between. The same goes for the probabilities (Nilsson 2003). There is not any great distinction between those kinds of qualitative methods and the more basic semi-quantitative methods.

There are many different qualitative methods for risk assessment, for example HazOp, What if? and checklists. A more thorough review of these methods and other common qualitative methods are presented in Appendix A.

2.2.2 Semi-quantitative methods for risk assessment

When the qualitative methods at best manage to give a vague measurement of the risks together with the mapping of the risks, the semi-quantitative methods can present information that is more comprehendible. Yet the semi-quantitative methods are not nearly as detailed as the quantitative methods (Nilsson, 2003).

In conformity with all methods for risk assessment, the semi-quantitative methods investigate what different risks and unforeseen events that can occur under the given circumstances. What distinguishes those methods from the others is the fact that they try to rank those unforeseen events based on their individual risk. However, the method is not depending on the exact measurements of consequences and probabilities of those different events. It is not necessary to know the damage from the explosion in accident A or the duration of fire in accident B. The only thing needed is the knowledge and experience to be able to grade these different accidents according to each other. There will be larger consequences with the accident A than the accident B. Of course, the same reasoning complies with probabilities. Because of this, the semi-quantitative methods can only present a relative measurement of the risk of different events, unlike the quantitative methods that present an actual number for the greatness of the risk. That is the limitation of the semi-quantitative methods (Nilsson, 2003).

There are many different kinds of semi-quantitative methods for risk assessment. There are even more methods that under certain conditions could be considered as semi-quantitative. The differences between semi-quantitative and qualitative on the first hand, and semi-quantitative and quantitative on the other hand are sometimes not clear. A more thorough review of the semi-quantitative methods is presented in Appendix A.

2.2.3 Quantitative methods for risk assessment

The quantitative methods are numerical, and as that implies, estimate the risk through calculations. The measurements of the risk are therefore also numeric. This makes it possible to compare the risks between different locations and activities in a more exact way. It is important not to confuse this overall label with the specific method called quantitative risk assessment (QRA).

The numerical value obtained is often expressed as number of deaths per year or the likelihood of dying per year. Other frequent measures are the number of deaths or damages in monetary terms (Nilsson, 2003).

Numerical methods are associated with uncertainties. Uncertainties are introduced in to the assessment through several ways, for example the models that are being used to calculate consequences or through the data used for probabilities and the calculation of the consequences. The model uncertainties arise due to the complexity of modeling the nature or complex technological systems. The data uncertainties often arise because the lack of historical data or due to assumptions made by experts. These uncertainties then propagate through the calculations. To reduce this problem, a sensitivity analysis can be made to identify which parameters are most sensitive to uncertainty and thereafter concentrate on minimizing uncertainty for those parameters

(Abrahamsson, 2000). Another way is to use distribution functions instead of a solitary numerical value when calculating the probabilities (Kaplan & Garrick, 1981). As with all risk assessment methods, the numerical methods are not completely objective. For example, the selection of risks to consider will always be made by persons and is therefore somewhat subjective (Slovic, 1999).

Quantitative methods are often divided in to two subsequent categories, deterministic and probabilistic methods. The deterministic methods only give a measure of the consequences while the probabilistic approach weight the consequences by multiplying them with their probabilities (Nystedt, 2000). A more thorough review of the quantitative methods is presented in Appendix A.

2.3 Chlorine dioxide

Pure ClO_2 (CAS 10049-04-4) has a boiling temperature of 11˚C and therefore exists as gas in room temperature and at normal pressure. The gas is yellow to reddish-yellow and has an unpleasant smell, similar to that of elemental chlorine (Cl_2) (Budavari, et al., 1996). The gas has a density of 1600 g/m^3, and is therefore heavier than air. The chemical is highly soluble in water, which gives a yellow to greenish-yellow solution. The solution might be stored for long periods without any dramatic changes of concentration, given the right conditions (Kirk, et al., 1993).

ClO_2 is commonly used as a bleaching agent in the pulp industry and as a biocide, typically in water treatment systems, where it is used to disinfect potable water (Kirk, et al., 1993). According to Environmental Protection Agency, EPA (1999), ClO_2, unlike Cl_2, oxidize without chlorinating. To chlorinate means that chlorine atoms (Cl) become attached to organic molecules. The fact that ClO_2 do not chlorinate is a valuable advantage since chlorination might form potentially harmful compounds that is not readily decomposed in the environment (Richardson, et al., 2007). Together with the facts that ClO_2 has biocidal properties over a wider pH-range and is a more selective oxidant, ClO_2 have replaced Cl_2 as the leading bleaching and disinfection agent (OxyChem, 2009).

Because of the leading position, large amounts of ClO_2 are produced. Every year, approximately 2 million tons are being used for pulp bleaching alone. This amount is divided over approximately 300 pulp mills of different sizes. In addition to these large facilities, there are several thousands of smaller used for producing ClO_2 for biocide applications in mostly water treatment plants (Pelin, 2009).

2.3.1 Processes

In the industry, ClO_2 is formed in large scale by reducing the chlorate ion (ClO_3^-) in a highly acidic medium by the general reaction:

$$ClO_3^- + \text{acid} + \text{reducing agent} \rightarrow ClO_2 + H_2O$$

There are several commercial processes for large scale producing of ClO_2. All of these use sodium chlorate ($NaClO_3$) as raw material. In most of the processes sulfuric acid (H_2SO_4) is used to make the medium acidic, while some uses hydrochloric acid (HCl). What really distinguishes the commercial processes from each other is the choice of reducing agent and under which conditions the reaction is run (Fredette, 1996). For small-scale production, typically for biocidal applications, many different processes exist, often using sodium chlorite ($NaClO_3$) as raw material. The product from these processes is typically consumed immediately, why such installations are not relevant to this master thesis.

Since this master thesis considers the storage of ClO_2 and the product of all the large-scale processes are similar, what follows is only a short review of three of the available processes. The following briefly describes processes using the three reducing agents most typically employed in the pulp mill industry.

The Mathieson process

The Mathieson process was one of the first continuous processes to be used commercially. Newer processes have successively replaced it, but the process is still in use at many pulp mills. It uses sulfur dioxide (SO_2) as a reducing agent and runs at atmospheric pressure. The specific reaction is:

$$2\ NaClO_3 + SO_2 \rightarrow 2\ ClO_2 + Na_2SO_4$$

A disadvantage with the process is a Cl_2 producing side reaction occurring when the medium is not acidic enough. Therefore, an excess of H_2SO_4 is fed to the reactor, creating an abundance of spent acid that must be handled. Because of the side reaction and the fact that some of the SO_2 are washed out of the reactor by the excess acid, the yield is limited to about 87% (Fredette, 1996). Other disadvantages with the Mathieson process are the fact that the process is dependent on SO_2 and forms Cl_2 as a byproduct. The storing and handling of SO_2 might be considered a higher risk than ClO_2 itself (Prevent, 2008).

SVP-LITE

In this process methanol (CH_3OH) is used as the reducing agent and the process is run in vacuum. The specific reaction is:

$$9\ NaClO_3 + 2\ CH_3OH + 6\ H_2SO_4 \rightarrow 9\ ClO_2 + 3\ Na_3H(SO_4)_2 + \tfrac{1}{2}\ CO_2 + \tfrac{3}{2}\ HCOOH + 7\ H_2O$$

The advantages of this process compared to processes run under atmospheric pressure are the fact that the formation of Cl_2 is heavily reduced and therefore the yield is increased to about 97% (Fredette, 1996). A negative aspect is that the reaction produces an acidic salt cake that has to be disposed off and that it produces organic byproducts in the form of formic acid (HCOOH). SVP-LITE is a registered trademark of Eka Chemicals (Eka Chemicals, 2009a).

SVP-HP and HP-A

The reaction with hydrogen peroxide (H_2O_2) as a reducing agent can be run either under vacuum (SVP-HP) or at atmospheric pressure (HP-A). The stoichiometry and products of the reaction are different depending on the conditions (Fredette, 2006 and Eka Chemicals, 2009a). If the reaction is run in vacuum, the stoichiometry is:

$$2\ NaClO_3 + H_2O_2 + H_2SO_4 \rightarrow 2\ ClO_2 + O_2 + 2\ H_2O + Na_2SO_4$$

This vacuum process is called SVP-HP, and is like SVP-LITE a registered trademark of Eka Chemicals. Some of the advantages, among others, are that the reaction, compared to SVP-LITE, produces 30 % less salt cake and that the salt cake is neutral rather than acidic. The formation of organic byproducts and Cl_2 are also completely eliminated (Eka Chemicals, 2009a)

If the reaction is run at atmospheric pressure, the reaction is:

$$2\ NaClO_3 + H_2O_2 + H_2SO_4 \rightarrow 2\ ClO_2 + O_2 + 2\ H_2O + Na_2SO_4$$

This process is called HP-A, and is a registered trademark of Eka Chemicals. The difference in the process yield between the two processes is the higher amounts of H_2SO_4 required in HP-A, which is a consequence from the process set up. One advantage of the HP-A process is that pulp mills that are currently running the Mathieson process can upgrade to the HP-A process for a relatively small cost (Eka Chemicals, 2009a).

2.3.2 Reactivity

ClO_2 is a free radical-like molecule. This means that it has an unpaired electron, a state that is not ideal for the stability of a molecule. Therefore, it readily reacts, trying to reach a more stable state. This is what gives ClO_2 the oxidizing power. In the strive to reach a more stable electron configuration it steals electrons from other molecules, thereby oxidizing them (Atkins & Jones, 2000). According to the Agency for Toxic Substances and Disease Registry (2004), this makes ClO_2 so unstable that it is only able to exist for short times in the immediate vicinity of where it is produced or released. The molecule quickly decomposes due to thermal decomposition, photolysis and reactions with oxidizable materials in the surroundings.

Due to the instability in its gaseous state, ClO_2 are always diluted in water. The chemical does not hydrolyze, why it exists as a dissolved gas in the solution. Because of the uneconomic to transport diluted solutions of chemicals, ClO_2 is always produced at the site of application and dissolved in water. The typical solution consists of concentrations of 10 g/dm^3 (Fredette, 1996).

Thermal decomposition

The thermal decomposition is a heterogeneous, exothermic and autocatalytic reaction. This reaction might be rather violent given high partial pressures of ClO_2 in the air, exceeding 10.1 kPa. The decomposition is often referred to as a “puff”. The general reaction is:

$$ClO_2 \rightarrow \frac{1}{2} Cl_2 + O_2 + 26.3 \text{ kcal / mole}$$

The thermal decomposition becomes more violent the higher the partial pressure of ClO_2 is. At partial pressures of above 40 kPa, ignition of the gas might even cause it to detonate (Masschelein, 1979).

Decomposition of the gas might be initiated for various reasons, for example heat, dust particles, electric sparks, sunlight or sudden pressure fluctuations (Eka Chemicals, 2008a). Contact with certain chemicals might also cause decomposition. These chemicals include hydrocarbons (C_xH_x), carbon monoxide (CO), mercury (Hg), sulfur (S), phosphor (P) and potassium hydroxide (KOH) (Lewis, 2000).

Photolysis

Sunlight is another factor that causes ClO_2 to decompose. This mechanism is called photolysis and is present both in air and in solution. The exact process, mechanisms and product are dependent on type of media, for example dry air or aqueous solution (Masschelein, 1979).

Decomposition through reduction

The reaction with oxidizable materials also causes ClO_2 to decompose. Masschelein (1979) states that ClO_2 oxidizes organic material through the following reaction:

$$ClO_2 + e^- \rightarrow ClO_2^- \rightarrow (+ 4 e^- + 4 H^+) \rightarrow 2 H_2O + Cl^-$$

In the reaction, the electrons (e^-) are taken from organic materials or metals, which are thereby oxidized, as ClO_2 are reduced to chlorite (ClO_2^-). ClO_2^- is then further reduced to the stable product water (H_2O) and chloride ion (Cl^-). The second part of the reaction is fast but not as fast as the initial reduction of ClO_2 (Masschelein, 1979).

Corrosion

The oxidizing properties of ClO_2 make it corrosive. Therefore, the process and storage equipment are required to withstand this. In most of the cases, fiber-reinforced plastic (FRP) are used. The material is reinforced with corrosive resistant layers. This system is cheaper than storage tanks made out of corrosive resistant metals, for example titanium (Ti) (Bergman, 2009).

2.3.3 Degassing rate

When gas is soluble in water, equilibrium will always develop between the amount in the solution and the gas above the solution. When storing ClO_2, it is important that the concentrations of gas above the solution be controlled. Should the partial pressure reach above 10.1 kPa, the gas might undergo thermal decomposition.

A study made by Eka Chemicals (1998b) show that the degassing rate is foremost dependent on the concentration of ClO_2 in the solution. A subsequent study by Eka Chemicals (1998a) shows that the degassing rate of ClO_2 is limited by the mass transport from inside the medium to the interface between the medium and the gas phase. This means that a concentration gradient is formed inside the solution, because of the limitations in the diffusion speed of the gas. Another factor that influences the degassing rate is the temperature of the ClO_2 solution. This is evident from the relationship between temperature and the solubility of gases, first formulated by William Henry (Atkins & Jones, 2000).

2.3.4 Health effects

There are several possible health effects from exposure to ClO_2. Under this heading, the wide range of different health effects will be reviewed. Furthermore, the mechanism and toxicokinetics as well as existing regulations concerning the exposure will be presented.

2.3.4.1 Toxicokinetics

The fact that ClO_2 is highly reactive, and due to this undergo decomposition, reflects the toxicokinetic properties. Ingested ClO_2 quickly reduces in the aqueous environment in the body, by the saliva as well as gastric juices from the stomach. The products from this metabolism are thought to be mainly ClO_2^- and Cl^-. The reactions and process of the metabolism differs slightly depending on the concentration of ClO_2 in the solution entering the body. At high concentrations, ClO_2^- is the principal metabolite. However, the metabolism does not stop there, but continues with slowly degrading some of the ClO_2^- into Cl^- (Environmental Protection Agency, 2000). At low concentrations, Cl^- is the principal metabolite. Bercz et al. (1982), however suggests that the product after the metabolism is non-oxidizing elements, foremost Cl_2. Another source states that the information concerning the metabolites is unclear, but it is unlikely that intact ClO_2 could last long enough for being absorbed from the gastrointestinal tract. It is however possible that the metabolites mentioned above could be absorbed, foremost Cl^- (World Health Organization, 2002).

Several sources, among them World Health Organization (2002), are univocal in the assumption that the metabolites are being secreted principally through the urine. The sources are however at variance concerning the half time of metabolites. The Environmental Protection Agency (2000), states that the metabolites are slowly cleared from the system, not defining slowly in hours or days.

There is little known about the metabolism after inhalation of ClO_2 and no studies available from which to draw conclusions. However, literature ascertains that the metabolic pathways are likely to differ from the ingestion. ClO_2 in air dissociates and forms among others Cl_2, oxygen (O_2), hydrogen chloride (HCl) as well as other chemicals. The distribution between these different chemicals is depending on temperature and humidity. It is a fact that ClO_2^- is not formed during this degradation, because it cannot persist in the dry atmosphere, since it is an ion. Nor is ClO_2^- likely to be formed in any greater amounts in the upper respiratory tract, although the humidity here enables the right conditions. The right conditions refer to that the humidity is high enough, making the reactions similar to the once occurring in the aqueous environment after ingestion. Since ClO_2^- is not formed in any greater amount, it is unlikely that the same toxic effects seen after ingestion will occur after inhalation. However, like mentioned before, too little is known about this metabolism (National Research Council, 2007).

There are also gaps in the knowledge concerning the dermal absorption and the subsequent metabolism. ClO_2 is rapidly degraded to Cl^- and ClO_2^- on the surface of the skin, due to the contact with oxidizable substances like tissue, bacteria and dirt. The absorption of these chemicals is considered very limited. However, the corrosive properties of the ClO_2 can increase this absorption due to damage of the protective skin and tissues (Eka Chemicals, 2008a).

2.3.4.2 Acute health effects

Chlorine dioxide has numerous acute health effects from ingestion, inhalation and physical contact.

Solutions of ClO_2 are acutely toxic when ingested. However, the dangers do not come solely from ClO_2 as such, but also the metabolites and by-products of the metabolism. Typical symptoms and effects are irritation to the digestive tract (Agency for Toxic Substances and Disease Registry, 2004). Exposure to higher doses can also cause hematologic effects such as methemoglobinemia (National Research Council, 2007). Methemoglobinemia is a disorder characterized by an increased level of methemoglobin (metHb) in the blood (National Library of Medicine, 2009). The methemoglobin lacks the ability to carry O_2, which can lead to both general hypoxia as well as tissue hypoxia (National Institute of Standards and Technology, 2005).

Vapours from ClO_2 are acutely toxic when inhaled. Animal experiments as well as documented exposures from accidents have shown that exposure for high doses can be mortal. Mutually for the whole range of exposure for gaseous ClO_2 is the attack on respiratory tract. Low exposure is characterized by lacrimation, irritation to the eyes, salivation, pallor, coughing and wheezing. With higher exposure, the consequences and symptoms become more severe, dyspnoea going over into pulmonary congestion and edema (National Research Council, 2007).

Schorsch (1995) conducted experiments resulting in the statement that ClO_2 is very toxic by inhalation. The experiment exposed rats for 4 hours to 16 ppm, 25 ppm, 38 ppm and 46 ppm. All groups of animals showed signs of toxicity, including respiratory distress, pulmonary oedema and emphysema, increasingly severe with the higher exposure. The lower exposure level did not claim any mortality. The three higher exposure levels however resulted in several mortalities each.

Since ClO_2 is corrosive, the chemical can damage skin as well as other tissues at contact. Of course, this also gives damages due to the corrosive properties when ingested and inhaled as well. The degradation of ClO_2 into Cl^- and ClO_2^- on the surface of the skin is mentioned earlier. Thereby you can ascertain that the skin will be exposed to other corrosive and reactive chemicals besides ClO_2 (Eka Chemicals, 2008a).

2.3.4.3 Repeated dose health effects

Several different studies have been carried out in order to monitor the long-term health effects from repeated exposure to ClO_2. There are many differences between these studies, concerning results, approach and implementation. The exposures have been characterized by both inhalation and ingestion. Levels of exposure as well as the duration of the exposure or the frequency of the exposures differ. Furthermore, different kinds of animals have been used in the studies. Since there is no consistently result or conclusion concerning the possible negative effects to health, these studies are not summarized in this thesis. If the reader should want more information and a more thorough look at these studies, the following literature among other is available: Abdel-Rahman et al. 1985, Bercz et al., 1982, Dalhamn, 1957, Daniel et al., 1990, Lubbers et al., 1984, Paulet et al., 1970, Paulet et al., 1972 and Paulet et al., 1974.

2.3.4.4 Actual cases of exposure

Searching the literature, the authors have been able to find several reports and studies concerning actual incidents, with both short time and long time exposure to ClO_2. However, most of these reports are associated with uncertainties and should be looked upon with skepticism. The reports are often unclear with the levels of exposure, the duration of the exposure and the definitive health effects. Since there is no consistent result or conclusion concerning the possible negative effects to health from these reports, they will not be presented further here. If the reader should want more information and a more thorough look at these studies, the following literature among other is available: Elkins, 1959, Exner-Freisfeld et al., 1986 and Meggs et al., 1996.

2.3.4.5 Cancerogenic effects

The Environmental Protection Agency (1996) has not found a satisfactory study of the carcinogenic potential of ClO_2 conducted among humans or animals. World Health Organization (2002) agrees to this, and states that there is no conventional carcinogenicity study available. Neither has the National Research Council found data concerning the carcinogenicity of ClO_2 in humans (National Research Council, 2007). No other studies from those years and forward were found.

2.3.4.6 Reproductive effects

The Environmental Protection Agency states that a number of studies consistently have found developmental effects following exposure before birth and direct upon birth. However, the Environmental Protection Agency points out that the effects and their severity differ between different studies and that no overall conclusion about the reproductive effects could be drawn (Environmental Protection Agency, 2000). The National Research Council state that there are no data concerning developmental or reproductive effects of ClO_2 inhalation in humans (National Research Council, 2007).

2.3.4.7 Genotoxical effects

Inconclusive results are found throughout the genotoxicological studies. Some of the studies find negative effects such as increased occurrence of reverse mutations, while others could not ascertain any effects (Environmental Protection Agency, 2000). The National research Council somewhat agree to this, pointing out that there are currently no conclusive data concerning the genotoxicity of ClO_2 in humans (National Research Council, 2007).

2.3.4.8 Conclusion about the health effects

The conclusion that the authors themselves can draw from the literature taken part of is that exposure to ClO_2 has a negative effect on the health. The acute, and sometimes lethal, effects from shorter and large exposure are documented. Even though the documentation made concerning the longer and minor exposures, reproductive effects and genotoxical effects are not conclusive, the occurrence of studies stating that these effects do occur is reason enough for caution.

2.3.5 Threshold limit values and guideline value

Many of the studies presented above, as well as other studies concerning the health effects, present some kind of threshold limit value for a distinguished negative effect. Along with these different values, there are governments, lobbying groups, officials and authoritativeness stating their recommended threshold limit values. Some of these different values will be presented below. It is important to recognize that all of the different types of values are looking at different effects as well as consisting of different situations and durations of exposure.

NOAEL and LOAEL

No-observed-adverse-effect-level (NOAEL) is frequently used today. The threshold is often resulting from animal experiments, other experiments or observations. The NOAEL is defined: "*Greatest concentration or amount found by experiment or observation, which causes no detectable adverse alteration of morphology, functional capacity, growth, development, or life span of the target organism under defined conditions.*" (International Union of Pure and Applied Chemistry, 2009).

Lowest-observed-adverse-effect-level (LOAEL) is frequently used and obtained alongside the NOAEL. The LOAEL is defined: "*Lowest concentration or amount of a substance, found by experiment or observation, which causes an adverse alteration of morphology, functional capacity, growth, development, or life span of a target organism distinguishable from normal (control) organisms of the same species and strain under defined conditions of exposure*." (International Union of Pure and Applied Chemistry, 2009).

A summary of some of the different NOAEL and LOAEL found in literature is presented in table 2.1.

Type	Level	Effect/Endpoint	Report
NOAEL	0.1 ppm	Respiratory	Dalhamn (1957)
NOAEL	5 ppm	Lung damage	Paulet and Desbrousses (1974)
NOAEL	0.1 ppm	not stated	Bercz et al. (1982)
LOAEL	1 ppm	Respiratory	Paulet and Desbrousses (1972)
LOAEL	2.5 ppm	Respiratory	Paulet and Desbrousses (1970)
LOAEL	10 ppm	Lung damage	Paulet and Desbrousses (1974)
LOAEL	10 ppm	Respiratory	Dalhamn (1957)
LOAEL	0.1 ppm	not stated	Daniel et al. (1990)

Table 2.1, Summary of different NOAEL and LOAEL.

AEGL

The developments of the Acute Exposure Guideline Level (AEGL) for different elements and substances are a collaborative international project with participation from public sectors as well as private sectors. The guidelines intend to describe the risk to humans resulting from exposure to airborne chemicals. Hopefully, the guidelines will help authorities as well as private companies dealing with all kind of different exposures, ranging from the small every day spills to the emergencies with catastrophic exposure (Environmental Protection Agency , 2009).

There are three levels of the AEGL, named AEGL-1, AEGL-2 and AEGL-3. For each one of these levels there are five different exposure periods: 10 minutes, 30 minutes, 1 hour, 4 hours and 8 hours (National Research Council, 2007).

AEGL-1 is defined: "*AEGL-1 is the airborne concentration (expressed as parts per million (ppm) or milligrams per cubic meter (mg/m^3)) of a substance above which it is predicted that the general population, including susceptible individuals, could experience notable discomfort, irritation, or certain asymptomatic, non-sensory effects. However, the effects are not disabling and are transient and reversible upon cessation of exposure.*" (National Research Council, 2007).

AEGL-2 is defined: "*AEGL-2 is the airborne concentration (expressed as ppm or mg/m^3) of a substance above which it is predicted that the general population, including susceptible individuals, could experience irreversible or other serious, long-lasting adverse health effects or an impaired ability to escape.*" (National Research Council 2007).

AEGL-3 is defined: "*AEGL-3 is the airborne concentration (expressed as ppm or mg/m^3) of a substance above which it is predicted that the general population, including susceptible individuals, could experience life threatening health effects or death.*" (National Research Council, 2007).

A summary of the different AEGL-1, AEGL-2 and AEGL-3 is presented in table 2.2.

Classification	Duration				
	10 min	30 min	1 hour	4 hours	8 hours
AEGL-1	0.15 ppm	0.15 ppm	0.15 ppm	0.15 ppm	0.15 ppm
AEGL-2	1.4 ppm	1.4 ppm	1.1 ppm	0.69 ppm	0.45 ppm
AEGL-3	3.0 ppm	3.0 ppm	2.4 ppm	1.5 ppm	0.98 ppm

Table 2.2, Summary of the different AEGL-1, AEGL-2 and AEGL-3 (National Research Council, 2007).

ERPG

The Emergency Response Planning Guidelines (ERPG) has much resemblance with the AEGL values and is frequently used (Oak Ridge Institute for Science and Education, 2009). The ERPG values will be used when performing consequence calculations further into this master thesis.

ERPG-1 is defined: *"The ERPG-1 is the maximum airborne concentration below which it is believed that nearly all individuals could be exposed for up to 1 hr without experiencing other than mild transient adverse health effects or perceiving a clearly defined, objectionable odor."* (Oak Ridge Institute for Science and Education, 2009).

ERPG-2 is defined: *"The ERPG-2 is the maximum airborne concentration below which it is believed that nearly all individuals could be exposed for up to 1 hr without experiencing or developing irreversible or other serious health effects or symptoms which could impair an individual's ability to take protective action."* (Oak Ridge Institute for Science and Education, 2009).

ERPG-2 is defined: *"The ERPG-3 is the maximum airborne concentration below which it is believed that nearly all individuals could be exposed for up to 1 hour without experiencing or developing life-threatening health effects."* (Oak Ridge Institute for Science and Education, 2009).

A summary of the ERPG-1, ERPG-2 and ERPG-3 is presented in table 2.3

Classification	Level
ERPG-1	-*
ERPG-2	0.5 ppm
ERPG-3	3 ppm

Table 2.3, Summary of the ERPG-1, ERPG-2 and ERPG-3 (American Industrial Hygiene Association, 2009).

*****The ERPG-1 is referred to as "not appropriate" (American Industrial Hygiene Association, 2009).

Other threshold limit values and guideline values

The World Health Organization has stated the occupational exposure limits for ClO_2 as follows. The time-weighted average (TWA) for an 8 hours working day, giving a 40 hours working week, is 0.1 ppm (0.28 mg/m^3). The short-term exposure level (STEL) for 15 minutes is 0.3 ppm (0.84 mg/m^3) (World Health Organization, 2002).

The Swedish authoritativeness "Arbetsmiljöverket" has also stated some occupational exposure limits. The "Takgränsvärde" (TGV), exposure during 15 minutes, is determined to 0.3 ppm

(0.8 mg /m3), while the “Nivågränsvärde”, exposure during 8 hours, is determined to 0.1 ppm (0.3 mg/m^3) (Arbetsmiljöverket, 2005).

There are several others, often on national basis, threshold limit values and guidelines values available all over the world. However, since many of these have great resemblance with these already mentioned, they will not be presented here.

2.3.6 Environmental fate

As mentioned before, ClO_2 is very reactive and persists only for a short period in the environment. However, limited detailed information is available concerning the speed of which ClO_2 is decomposed in the environment. The half-life is 2.4 days in air and 15 minutes when dissolved in water. These figures do however only take in account the degradation by photolysis, when in reality reduction and thermal decomposition as well has an effect on decomposition rate.

The authors think that it is reasonable to assume that the decomposition will be faster the more oxidizable materials the medium contains and the more direct sunlight it is exposed to. If this assumption is appropriate, the decomposition rates for the three principally different mediums in the environment should follow the pattern (Eka Chemicals, 2008a): air < water < soil

The reason for this is that soil contains more oxidizable materials, like organics and metals, than water, which in turn contains more of these components than air (Eka Chemicals, 2008a).

Since ClO_2 behave like a radical, one could suspect that it potentially could deplete the ozone (O_3) layer. However, for a substance to deplete stratospheric O_3 it must have an expected half-life of at least one year. The expected half-life for ClO_2 is much smaller. Exact information about the role of ClO_2 in depletion of troposphere O_3 is though unknown. ClO_2 does not absorb light in the atmospheric window, why it is not classified as a greenhouse gas (Eka Chemicals, 2008a).

ClO_2 are considered very dangerous to aquatic organisms, causing the death of fish, invertebrates and algae at concentrations of about 1 mg/dm^3. Its residual degradation products, ClO_2^- and ClO_3^-, are also very reactive and are readily further reduced to Cl^-. However, the partition coefficients, log P_{ow}, for ClO_2, ClO_2^- and ClO_3^- are all negative (Eka Chemicals, 2008a and Health Canada, 2008). This is evidence that the chemicals do not bioaccumulate. The log P_{ow} value specifies whether a chemical are more readily dissolved in octanol or in water. Since ClO_2 readily dissolves in water it will not adsorb to particles in the soil, neither is it accumulated in the fatty tissue in organisms (Miyamoto, 1996). Furthermore, ClO_2 do not chlorinate (Richardson, et al., 2007).

The conclusion that the authors can draw about the environmental effects of ClO_2, is that ClO_2 will have large effects. The chemical will probably wipe out all aquatic organisms in the immediate vicinity of the leakage, which also holds true for organisms living in the soil. However, because it does not chlorinate, not bioaccumulate and are highly unstable, it will not cause any long-term adverse effects, only short-term.

3. Developing a method for risk assessment

This chapter contains the main part of this master thesis. The chapter will systematically move through the working process of developing the method for risk assessment of ClO_2 storage facilities at Swedish pulp mills. In the end of this chapter, the method itself will be presented. The chapter will contain the following parts:

- A risk identification, in which the possible risks affecting the ClO_2 storage facility is identified
- A risk selection, in which the most prominent risks will be selected
- A parameter identification, in which all identified risks, but the selected risks in particular, are broken down in to parameters influencing the probability and/or the consequences
- A contexture of an "ideal" ClO_2 storage facility in which the necessary levels of safety within different areas are stated
- A description of the develop method for risk assessment, in which the authors explain the thoughts behind the method and the features of this
- A presentation of the developed model for risk assessment of ClO_2 storage facilities at Swedish pulp mills

3.1 Risk identification

Essential for the development of the new method for risk assessment are a consistent and broad understanding of the possible risks arising from the ClO_2 storage facility and the surroundings of this. To gain this understanding, several sources will be used for identifying as many of the risks as possible. The first source is the contexture of a representative ClO_2 storage facility and the following risk analysis of this. This risk analysis is complemented with a consequence analysis. Other sources of information consist of precedent risk assessments and risk analyses, incident reports and accident reports as well as articles from media.

3.1.1 Representative ClO_2 storage facility

There are foremost two reasons for the contexture of a representative ClO_2 storage facility. The first reason is the fact that study visits have been made to three different pulp mills currently using ClO_2 for bleaching. However, the pulp mills and the companies behind them wish to stay anonymous. In order to use the information and impressions from these study visits, the creation of a representative ClO_2 storage facility is one solution. The representative ClO_2 storage facility will be a product of the three different storage facilities and their specific properties. The second reason is the fact that a risk analysis made by the authors before studying precedent material will not be preconceived by other sources of information or views. The authors of this master thesis will be able to look upon the situation and potential risks solely on the base of their specific knowledge and experience.

The authors will not claim to have pieced together the most representative ClO_2 storage facility possible. However, it is one possible representative ClO_2 storage facility.

3.1.1.1 Representative ClO_2 storage facility

The representative ClO_2 storage facility is not a model in the traditional sense, but more of a summary and context of the impressions and information from the different study visits. Several conditions and properties were common for these visited pulp mills. These common denominators are the base for the representative ClO_2 storage facility. The representative ClO_2 storage facility can be compared with the "ideal" ClO_2 storage facility in chapter 3.4.

The typical Swedish ClO_2 storage facility is located close to a body of water (sea or lake) and less than one kilometer away from residence areas. The ClO_2 storage facility itself consists of two FRP storage tanks working as "communicating vessels". These storage tanks are located in an area where heavy traffic is close by. Despite the traffic, the storage tanks are not fully protected from collisions and might even lack any collision protection. In the same area, there are several other chemical storage tanks, for example strong acids and oxidizing agents.

The storage tanks are equipped with redundant safety features consisting of, for example ventilation and level meters to avoid thermal decompositions and overfilling. The storage tanks are also equipped with consequence limiting features consisting of, for example explosion lids. A safety feature that the typical ClO_2 storage facility lacks is a dike that is able to contain the entire amount of ClO_2 stored.

Inspections of the corrosion inside the storage tanks and the inbound and outbound pipes are done every sixth year. An accredited inspection company carries out the inspections. The workers at the pulp mill take care of the continuous maintenance of the ClO_2 storage facility. This work includes for example repairing leaking valves and replacing old seals.

The smell of ClO_2 is often perceptible in and around the ClO_2 storage facility. This indicates that the concentration have reached and most likely exceeded the "Nivågränsvärde", stated by the Arbetsmiljöverket (2005). There are gasmasks readily available, but often these are not used. There are gas detectors placed in the surroundings, warning if the concentration of ClO_2 is too high. Overall, the safety awareness among the workers has shortages. More information and details about the typical Swedish ClO_2 storage facility is presented in Appendix B.

3.1.1.2 Risk analysis on the representative ClO_2 storage facility

A risk analysis, more exact a preliminary hazard analysis, will now be performed on the representative ClO_2 storage facility, and thereby indirect on the base of the information and impressions from the study visits. The method was chosen on behalf of its simplicity and wideness. More information about the method is presented in Appendix A.

The preliminary risk analysis is based on the template presented by Kemikontoret (2001). However, this model has been somewhat modified. Kemikontoret (2001) have already come up with fixed scales for the consequences for human life and health (H), environment (M) and property (E) as well as definitions of the different probabilities. These different scales used in the method are presented in table 3.1 to table 3.4. The authors themselves have translated the Swedish scales presented by the Kemikontoret (2001) into English.

Consequences on the life and health of humans	
Class	Description
1 Small	Slight transversal discomfort
2 Light	Occasional wounded, permanent discomfort
3 Large	Occasional severely wounded, severe discomfort
4 Very Large	Occasional deaths, several severely wounded
5 Catastrophic	Several deaths, tenths of severely wounded

Table 3.1, Scale of the consequences on the lift and health of humans.

Consequences on the environment	
Class	Description
1 Small	No real damage. Small extension.
2 Light	Temporary transversal damage. Small extension.
3 Large	Long term damage.
4 Very Large	Permanent damage. Small extension.
5 Catastrophic	Permanent damage. Large extension.

Table 3.2, Scale of the consequences on the environment.

Probability	
Class	Description
1 Very unlikely	Once per 1000 years or more seldom
2 Remote	Once per 100-1000 years
3 Occasional	Once per 10-100 years
4 Probable	Once per 1-10 years
5 Frequent	More than 1 per year

Table 3.3, Scale of the probability.

Consequences on the property Total cost (mill. SEK)	
Class	Description
1 Small	Less than 0.1
2 Light	0.1-1.0
3 Large	1.0-5.0
4 Very Large	5.0-20.0
5 Catastrophic	More than 20.0

Table 3.4, Scale of the consequences on the property.

The potential for the authors to estimate the costs of the consequences on the property is low. This is due to the lack of experience concerning the costs of process equipment or the costs of reconstruction. Furthermore, the costs and prices could have changed during the years after this publication. Based on these facts, the authors have chosen to walk out on the definitions of consequences on property stated by Kemikontoret (2001). Instead of the scale presented in table 3.4, a simplified scale made by the authors will be used. This new scale is presented in table 3.5.

Consequences on the property	
Class	Magnitude
1	Small
2	Large
3	Catastrophic

Table 3.5, Scale of the consequences on the property.

There are most certainty advantages as well as disadvantages using this simplified scale. The foremost advantage is the simple usage, while the foremost disadvantage is the difficulties separating consequences from each other with only these levels on the scale. The later point could also be explained by the fact that the scale is qualitative unlike the scale from Kemikontoret.

The definition of the concept of property is also wider in this risk analysis then the definition stated by Kemikontoret (2001). The idea of company brand value is incorporated in the definition used in this master thesis. Consequences on the property do not only consist of damage to equipment, loss of production and costs for rebuilding. The concept of property needs to be put in a wider definition, not limited to material aspects. Therefore, also the public opinion and effects to the trademark are included.

The assessed probabilities for the different causes are presented in table 3.6. The result from the preliminary risk analysis is presented in table 3.7. For further information and motivations to the assessed consequences and probabilities presented, see Appendix C.

Cause	Initiating events	Probability
Leaking process equipment	Summary	5
	Leakage from pump	4
	Leakage from valve	4
	Leakage from packing, seal or joint	4
	Leakage from sample-taking equipment	5
Corrosion	Summary	3
	Insufficient maintenance	3
	Insufficient controls/inspections	3
	Error in process	2
	External corrosion	2
	Improper choice of material	2
Falling object (large)	Summary	2
	Failure when lifting equipment	1
	Debris from explosion	1
	Weather conditions	2
Falling object (small)	Summary	3
	Dropping equipment	3
	Debris from explosion	1
	Weather conditions	3
Collision (pipe)	Summary	3
	Losing control over vehicle	3
Collision (tank)	Summary	3
	Losing control over vehicle	3
Freezing	Summary	2
	Weather conditions + insufficient isolation	2
Overfilling	Summary	3
	Technological failure	2
	Operational failure	3
Thermal decomposition – “Puff”	Summary	2

	Error in process	2
	Malfunctioning ventilation	2
	Fire	1
Undermining	Summary	2
	Leaking pipe	2
	Weather conditions	2
	Corrosion on foundations	2
Sabotage	Summary	1
	Personal conflict	1
	Organizational conflict	1
Earthquake	Summary	1
	Design of tank or pipe not strong enough	1
Vibrations	Summary	2
	Construction work	2
	Traffic	1
	Process equipment	1
Explosion	Summary	1
	Error in process	1
	Other chemicals	1

Table 3.6, The assessed probabilities for the different causes.

Scenario	Cause	Probability		Consequence	
			Health	Environment	Property
Pipe leakage			2	1	1
	Collision (pipe)	3			
	Corrosion	3			
	Falling object (large)	2			
	Freezing	2			
	Sabotage	1			
	Falling objects (small)	3			
	Earthquake	1			
	Vibrations	2			
	Explosion	1			
	Leaking process equipment	4			
	Undermining	2			
Pipe rupture			3	2	1
	Collision (pipe)	3			
	Corrosion	3			
	Falling object (large)	2			
	Freezing	2			
	Sabotage	1			
	Falling objects (small)	2			
	Earthquake	1			
	Vibrations	2			
	Explosion	1			
	Undermining	2			
Tank collapse			5	4	2
	Corrosion	3			
	Thermal decomposition –"Puff"	2			
	Collision (tank)	3			
	Undermining	2			
	Falling objects (large)	2			
	Sabotage	1			

	Earthquake	1			
	Vibrations	1			
	Explosion	1			
Tank leakage			4	4	2
	Corrosion	3			
	Thermal decomposition –"Puff"	3			
	Collision (tank)	3			
	Overfilling	3			
	Falling objects (large)	2			
	Sabotage	1			
	Undermining	2			
	Earthquake	1			
	Vibrations	1			
	Explosion	1			
Spill			2	1	1
	Leaking process equipment	5			

Table 3.7, The results from the preliminary risk analysis.

3.1.1.3 Consequence calculations on the representative storage facility

Consequence calculations have been conducted in order to investigate the consequences from different scenarios. The scenarios included are:

- Storage tank rupture
- Storage tank leakage
- Pipe rupture
- Pipe leakage

The results from these calculations are used as input to the preliminary risk analysis in chapter 3.1.1.2. Note that the small spillages, mentioned in the risk analysis, is not included in these calculations because of the small amount of ClO_2 released on each occasion.

The consequences for the different scenarios vary. It must first be noted that the calculated results are subject to uncertainty and two especially important such is the fact that the decomposition by solar radiation and the decreasing of the concentration in the source are not taken into account. This has not been accounted, and thus the calculated plume lengths are highly exaggerated. A summary of some different consequences are presented in table 3.8.

Scenario, source strength, wind speed, stability class and duration of the release (surface depletion and decomposition by solar radiation not accounted)	Distance to ERPG-3	Distance to ERPG-2
Tank leakage, 1.99 kg/s, 2 m/s, E, 30 min	5.3 km	>10 km
Tank leakage, 1.99 kg/s, 5 m/s, D, 30 min	2.6 km	6.7 km
Tank leakage, 4.09 kg/s, 5 m/s, D, 30 min	3.8 km	9.8 km
Pipe leakage, 0.08 kg/s, 2 m/s, E, 30 min	1.0 km	2.6 km
Pipe rupture, 0.50 kg/s, 2 m/s, E, 30 min	2.6 km	6.8 km

Table 3.8, A summary of the most important consequences.

Not included in this table is the calculation of at which distance the concentration reaches 0.3 ppm, corresponding to the Swedish "Takgränsvärde". This distance has only been calculated for one scenario and might be viewed in Appendix D.

These consequence calculations are as indicated associated with great uncertainties and many assumptions. Therefore, the numbers should be looked upon with skepticism. The numbers should not be taken literally, but more as measuring rod from which the different scenarios can be put into context. For more information concerning the uncertainties, assumptions, sources of errors and discussions of the results, see Appendix D.

Anyway, the consequence calculations have focused on the effects on human health, which of course is the first priority. No consequence calculations have been made on the effects on the environment or property. In the case of environmental consequences, this is because information in the literature search stated that the consequences to the environment are not irreversible or long term. Because of this, the consequences to the environment are not seen as severe as the health consequences and are therefore based on the approximate amount of ClO_2 released in each scenario. This largely follows the health consequences, but because of the different scales, the environmental consequences are somewhat lower. The consequences to the property are very difficult to calculate and are therefore approximated in the same way.

3.1.1.4 Discussion concerning the risk analysis on the representative ClO_2 storage facility

A risk analysis is normally conducted like an ongoing discussion with representatives from different areas of interest and knowledge. In this case, the authors only had limited opportunities to collaborate and discuss with knowing workers or management. Of course, this limits the discussion and thereby possibly the result.

The authors have relied on foremost three sources of information for this risk analysis:

- The first source is the model of the representative ClO_2 storage facility based on information and impressions from the study visits.
- The second source is literature concerning among others probabilities of failure.
- The third source of information is the contact with workers on the visited pulp mills. These different persons have been able to answer some of the questions that were not answered during the study visits.

There are no doubt sources of errors within these three sources of information. However, by detecting and presenting these sources of errors the result from the risk analysis could be put into a better context. The representative ClO_2 storage facility are nothing but an example of a storage ClO_2 facility and do not claim to represent all conceivable versions. When it comes to the information and answers from workers at the pulp mills, contacts have been made with only one person at each pulp mill. The answers from these persons are of course based on their personal experiences and opinions. The answers to the questions asked were probably not backed up by documentation or statistics. If another person had been interviewed, there is a chance that he or she would give another different answer. Furthermore, each individual has a limited memory and events and accidents in the past are unlikely to be known by these persons. Perhaps there were accidents with overfilling 30 years ago that the workers do not know of and therefore not include into their estimation. On the other hand, the situation and safety at the pulp mills have much likely improved during the years. Perhaps one should not include accidents and events into an estimation based on historical conditions. Nevertheless, the interviewed persons knowledge and honesty are not questioned. Contrary to the cooperation has proven to be an efficient and fast way to gather reliable information.

Problems have been experienced with combining the different risk measures from the different sources of information. Part of the measures is qualitative and part of the measures is quantitative. Which is the most reliable? How do you combine them? As if this was not enough, there is always the problem of putting your personal opinions and impressions against the others views and the cold facts from literature.

The consequence calculations are subject to many assumptions and approximations that make them uncertain. This discussion has already been brought up somewhat in Appendix D, and will therefore be held short. One of the most affecting assumptions is the approximation that the released gaseous ClO_2 does not decompose due to solar radiation. Another important assumption is that the source strength is constant in time and not decreasing due to depletion. Furthermore, no consideration has been taken of the concentration gradient emerging in the solution. These assumptions make the calculated plume length highly exaggerated and because of this, the calculated plume lengths should not be taken literally. Instead, they should be viewed as a way to compare the magnitude among different scenarios. For more information concerning the uncertainties and assumptions, see Appendix D.

The division of risks, in aspect of both probability and consequences, into different scales was also a difficult assignment, especially when the definitions of the scale varied between too defined or in other cases unclearly defined. Events that occur once every 110 year are put in the same category as the event that occurs once every 990 years. The level of details in the scale is always a matter that is going to be up for questioning. Furthermore, there is the difficulty with translating the stated probability “low” or “medium” provided by the pulp mill representatives into levels of the scales. The same applies when the numerical results from the consequence analysis is translated into scales.

The observant reader has seen that initiating events have been given different probabilities for different causes. For example, extreme weather condition is given higher probability for causing small objects to fall than for large. The authors have also stated causes with different probabilities on different scenarios. For example, collision (tank) is given higher probability for storage tank leakage than storage tank collapse. This is solely on the base of the authors own thoughts. For example, it is assumed that a collision with the storage tank will be more likely to cause leakages than ruptures. The values presented in table 3.7 should be seen as guidelines more than exact statements.

One category containing scenarios causing or initiating events named “other” have not been implemented in the risk analysis. Many other risk analyses use this broad definition to include all the possible factors not taken into account and clearly stated. The reason for not doing so is the broadness of the definition. It is difficult to assess the probability and consequences, when it is not even stated what different situations or events included. At the end of the day, what is the point of pointing out to the pulp mills that the possible largest risk comes from something not even the participants in the method can define?

The risk analysis is based on the Swedish conditions observed at the visited pulp mills. Should this master thesis come to use in an international perspective, it is important to be aware of this fact and the fact that the outcome might be different for pulp mills abroad.

Finally, the relationship between the cause, the scenario and the consequence will be discussed. In the risk analysis it is assumed that there is a direct relationship between these. If the cause happen then the scenario will occur and it will always and inevitable lead to the consequence. This matter could of course be discussed and questioned. The collision between a truck and the storage tank might not lead to a direct tank rupture, but cracks and tensions might be created which considerably shortens the lifetime of the storage tank and which can be difficult to correctly detect and repair. The force from the falling toolbox will maybe not break the pipe beneath. These thoughts have not been deliberate and outspoken, but looking back on to the risk analysis emerges as clear.

3.1.2 Precedent risk assessments

During the contacts with Eka Chemicals and the pulp mills, existing risk assessments and risk analyses from different pulp mills in Sweden as well as international have been obtained. This information is valuable and important in the strive to map all possible risks affecting the ClO_2 storage facility. However, since the pulp mills and the companies behind those wish to stay anonymous, this literature cannot be revealed in is full extent. In order to be able to use these risk assessments, they are anonymized. Therefore, the pulp mills visited and other pulp mills existing in this literature obtained will be referred to as ALFA, BETA and so on. Of course, risk assessments and risk analyses available from the public Internet will not be surrounded with the same secrecy.

These different risk assessments and risk analyses are presented in short below. For more information, see Appendix E.

Risk assessment of pulp mill ALFA from 1999

This risk assessment was carried out in-house with supervisors from different sectors and operators. The risk analysis focused on the possible large leakages from the storage tanks. There were four different causes, leading forward to storage tanks ruptures. Consequences were calculated as high, while probabilities medium (Eka Chemicals, 1999a).

The full result of this risk assessment is presented in table E.3 in Appendix E.

Preliminary hazard analysis of pulp mill BETA from 2000

This preliminary hazard analysis was carried out in-house with supervisors from different sectors and operators as well as representatives from Eka Chemicals. The focus was not specifically the ClO_2 storage facility, but the entire pulp mill was analyzed. Therefore, there was only one scenario regarding the ClO_2 storage facility. This scenario was an explosion, "puff", inside the storage tanks due to high concentration of gaseous ClO_2. The probability for this scenario was assessed medium to high. Consequences were calculated medium to high (Eka Chemicals, 2000a).

The full result of the preliminary hazard analysis is presented in table E.4 in Appendix E.

Preliminary hazard analysis of pulp mill GAMMA from 2002

This preliminary hazard analysis was carried out in-house with supervisors from different sectors and operators. For some reason, the risk assessment has not assessed the probabilities, thereby only presenting scenarios and estimation of their consequences. Despite the fact that probabilities are not available, it is interesting to see what kind of scenarios that have been deemed as possible by others. The scenarios presented are storage tank rupture caused by collision, corrosion or thermal decomposition as well as leakages of ClO_2 caused by rupture of pipes. The estimated consequences are high for storage tank rupture and medium for pipe rupture (Eka Chemicals, 2002a).

The full result of the preliminary hazard analysis is presented in table E.5 in Appendix E.

Risk assessment of pulp mill GAMMA from 2008

Consultants from a consultant company with help from supervisors from different sectors carried out this risk assessment. This risk assessment grades two scenarios with high probabilities. The first scenario is that paper rolls overturn on the storage tanks, thereby causing rupture. The probability is estimated to be high. The other scenario is that corrosion inside the storage tanks leads to a leakage of ClO_2. The probability for this scenario is medium. Both of the scenarios consequences were estimated medium to high (Eka chemicals, 2008b).

The full result of the risk assessment is presented in table E.6 in Appendix E.

Preliminary hazard analysis of pulp mills DELTA from 2004 and ETA from 2003

These preliminary hazard analyses were carried out in-house with supervisors from different sectors and operators as well as representatives from Eka Chemicals. For some reason, both of them are identical in every aspect. The exact same risks have been identified and both the probabilities and consequences are assumed with the exact same numbers. It is probable that the same persons have been involved in the working process with both the analyses. However, it is almost impossible that the exact same situation concerning the risk could exist at the both pulp mills, especially since they are located in different parts of the world. The most notable thing about these risk assessments is that storage tanks ruptures due to a thermal decomposition or vacuum inside the storage tanks are assessed with high probabilities. Consequences were estimated high (Eka Chemicals, 2004 and Eka Chemicals, 2003a).

The full result of the preliminary hazard analysis is presented in table E.7 in Appendix E.

Hazard identification on the Bell Bay pulp mill in Australia from 2006

This investigation was carried out as a HAZID (Hazard Identification) with supervisors from different sectors and operators and representatives from the consultant companies of GHD and Quest (GHD, 2006).

The HAZID methods have not been presented before in this master thesis. It is a systematic procedure, starting with the definition of the system. Following is the identification and definition of hazards within this system, possible preventive measures and finally the dangers that will occur if the preventive measures are insufficient (GHD, 2006).

This risk analysis points out some scenarios, but does not estimate any probabilities or consequences. It does however give suggestions of risk mitigating safeguards. The risks identified are leakage of ClO_2 due to catastrophic storage tank failure, impact with pipe bridges and contamination of ClO_2 with organic materials (GHD, 2006).

The full result of the HAZID is presented in table E.8 in Appendix E.

3.1.3 Incident reports and accident reports

As for the existing risk analyses and risk assessments obtained in the contacts with Eka Chemicals and different pulp mills, the incident and accidents reports are anonymized. Therefore, the visited pulp mills and other pulp mills existing in this literature will be referred to as ALFA, BETA and so on.

Incident report from pulp mill EPSILON from 2002

The incident was caused by a manual drain valve inside the reserve outbound pump failing or breaking, allowing solution of ClO_2 to pass. Approximately 2 m^3 of concentrated ClO_2 solution escaped into the containment and was then further spread when degassing (Eka Chemicals, 2002b).

When the bleaching plant operator saw the cloud of ClO_2, he thought that the storage tank had ruptured. Therefore, he switched off the production, sending solution of ClO_2 from the reactor and absorber down in the drain. This action leads to even larger degassing and spreading (Eka Chemicals, 2002b).

The containment areas vapor suppressing system, consisting of foam, was deployed twice directly after the incident. Workers equipped with breathing masks entered the containment area and tried to isolate the storage tank from the leak. Finally, water was flushed through the pipes to clear out the remaining ClO_2 (Eka Chemicals, 2002b).

The cloud of gaseous ClO_2 spread over the pulp mill forcing large parts of the pulp mill to shut down their operations and started evacuations. Other parts were put in standby for evacuations based on the wind and spreading of the cloud (Eka Chemicals, 2002b).

The incident report was quite clear in their statement that this broken valve was the single cause for this event (Eka Chemicals, 2002b).

Incident report from pulp mill ZETA from 1998

This ClO_2 storage facility had two storage tanks, each one with the capacity of 200 m^3. One of these storage tanks suffered from an abrupt and severe pressure decrease leading to damage on the top of the storage tank. Since the storage tanks were linked as "communicating vessels", this pressure fluctuation transferred to the second tank, damaging this one as well (Eka Chemicals, 1998c).

The consequences of this incident were limited, extending to material and property damages. No leakage of ClO_2 was detected (Eka Chemicals, 1998c).

The incident report was not able to establish the cause for this incident. The most plausible cause for this pressure decrease however, was thought to be decomposition in the first storage tank. When this decomposition started, it rapidly spread through the connecting pipe to the second storage tank. The incident report state that such events have been reported many times, however not in combination with this type of damages. For this actual ClO_2 storage facility, there had been reports of smaller decompositions the week before as well as the weeks after this event (Eka Chemicals, 1998c).

The decomposition produced large amounts of energy, heating the solution, resulting in a sudden development of gas inside the storage tank. The large development of gas and the high pressure lead forward to disengagement of the explosion hatches. Thereby, the high pressure was released and the hatches fall back into place. This theory is supported by the fact that the pressure inside the storage tank does not show any significant peaks during this period. However, the theory is questioned by the fact that none of the workers noticed the decomposition characteristics, the smell from the ClO_2 cloud or the sound (Eka Chemicals, 1998c).

The solution surface, the tank walls and splashes quickly cooled the remaining gas inside the storage tank. Thereby, the pressure quickly decreased and the storage tank started to curve in. The storage tanks both had vacuum breakers, but these could not cope with the quick decrease of pressure and prevent the damages (Eka Chemicals, 1998c).

Although the incident report could not establish that the incident was caused by decomposition, the report states some other causes for decomposition. The report particular brought forward the fact that the storage tank lacked the ability to strip of gaseous ClO_2. The further investigation of the causes of this event is made in the report, but it is too technically demanding and irrelevant to deal with in this master thesis. Beside the cause mentioned above, the storage tanks were only filled up to 30% capacity and it was a sunny and warm day. These two reasons lead forward to the fact that the development of gas inside the storage tank was high already from the beginning. The conditions for decomposition were good and any initiator present as rust, organic material, oil, sunshine or electrostatic sparks could start the reaction (Eka Chemicals, 1998c).

3.1.4 Other literature of interest

As for the existing risk assessments and incident reports obtained in the contacts with Eka Chemicals and different pulp mills, the other literature of interest are anonymized. Therefore, the visited pulp mills and other pulp mills existing in this literature will be referred to as ALFA, BETA and so on. Of course, literature available from the public Internet will not be surrounded with the same secrecy.

Consequence calculations concerning spreading of gas at ClO_2 at pulp mill GAMMA from 2003

These consequence calculations have been carried out by an external consultant company.

The consequence calculations are based on two different scenarios. The first scenario is a large leak of ClO_2 where the gas leaves the pool during the period of 10 minutes. The second scenario is a large leak of ClO_2 where the gas leaves the pool instantaneously. In both of the cases, 700 m^3 of ClO_2 solution with a concentration of 8 g/dm^3 is leaked. In both cases, it is assumed that 20 % of the total amount of ClO_2 is released to the atmosphere, why the consequence calculations assume that 1120 kg of ClO_2 are released in to the air (Eka Chemicals, 2003b).

The first scenario is thought to be more probable than the second one. Even if the solution containing ClO_2 will leave the storage tank instantaneously, gaseous ClO_2 will not leave the solution all in once, making the second scenario not physically possible. Causes for these leakages of ClO_2 are identified as vehicle colliding with storage tanks, storage tanks worn down by internal corrosion and storage tanks damaged by vacuum or overpressure (Eka Chemicals, 2003b).

When the leakage is treated as continuous, a plume is formed in the direction of the wind. This plume reaches a constant shape after approximately 4 minutes and 40 seconds. The concentration in this plume is dependent on the distance from the source, but one can detect concentrations of 5 ppm up to 1.6 km from the source. The concentration is 100 ppm in a radius of about 200 meters from the source. However, the concentration in plume does not reach the lowest explosion limit (LEL). As soon as the continuous source are depleted, the plume will be diluted and quickly reach non-toxic concentrations. What exact numbers these non-toxic concentrations refer to are however not stated (Eka Chemicals, 2003b).

When the leakage is treated as instantaneous, a concentrated cloud of gaseous ClO_2 will form. This cloud will move in the direction of the wind and could contain concentrations above the LEL. The cloud is however quickly diluted, and thereby the risk for explosion will only exist for about 10 seconds, before the concentration decreases. The dilution also affects the toxicity of the cloud, lowering the concentration to 5 ppm in between 6 to 8 minutes (Eka Chemicals, 2003b).

In summary, the consequence calculations show that the consequences to human health due to a large leak of ClO_2 are limited because of the quick dilution. However, it is probable that persons residing in the immediate vicinity of where the leak occurs will obtain serious damage, if not lethal damages, either from toxic effects or by explosions. It is important to stress the necessity of alarms warning for a gas leakage since there might be sufficient time to take shelter (Eka Chemicals, 2003b).

One must keep in mind that the simulations are dependent on factors like wind speed, atmospheric stability and temperature. These factors are location and time specific and have to be given a single value, why the calculations might be both an underestimation and an overestimation. However, these calculations give the impression that a continuous leakage is generally more dangerous and more probable than an instantaneous (Eka Chemicals, 2003b).

Risk assessment of industries in Karlshamn municipality from 2005

The local emergency services in Karlshamn, Sweden, in 2005 performed a risk assessment of the industries in the municipality. One of the industries located in the municipality is the Södra Cell Mörrum pulp mill. This pulp mill produces and uses ClO_2 for bleaching. In the past, the Mathieson process was used, but partly because of the great risks associated with storing and handling SO_2, the mill have switched to the HP-A process.

The local emergency services identified and then simulated and calculated two scenarios. The first scenario was that a pipe would rupture or the tank collapse while storing ClO_2. The hole through which the ClO_2 solution escaped was assumed to be 0.5 m in diameter. The second scenario was that a pipe ruptures when the solution are pumped from the storage tanks to the bleaching facility. The hole through which the ClO_2 solution escaped was assumed to be 0.15 m in diameter. The consequences were specified as the distance from the source where the concentration was at least 500 ppm (Karlshamns Kommun, 2005). For calculated probabilities for the different scenarios and their consequences, see table 3.9.

Scenario	Consequence (meters)	Probability (per year)
Pipe rupture or tank collapse (0.5 m)	200	$5.1*10^{-7}$
Pipe rupture (0.15 m)	65	$1.75*10^{-5}$

Table 3.9, Probabilities and consequences for the different scenarios.

Consequence calculations concerning spreading of gas and concentrations

According to Alp and Boughner (2005), a dike is fundamental for decreasing the degassing after a leakage of ClO_2 solution. This is shown through comparisons of consequence calculations for two different scenarios. The first scenario consists of a leakage that is contained in the dike. The second scenario consists of the same leakage, but without the existence of a dike. The amount of solution leaking is not specified. The only thing stated is the fact that three storage tanks together withhold about 250 m^3 (Alp & Boughner 2005).

The SLAB model, developed by Laurence Livermore National Laboratory and Environmental Protection Agency, is used to perform the consequence calculations. The consequence calculations look at the distance to different concentrations. The concentration looked at is 5 ppm. For the first scenario, the distances are 120 meters and 280 meters. The first calculation is made with a wind speed of 5 m/s and the atmospheric stability class D, while the second calculation is made with a wind speed of 1.5 m/s and the atmospheric stability class F. For the second scenario, without the dike, the distances are 1800 meters and 8100 meters (Alp & Boughner 2005).

It is noted that ClO_2 decomposes rapidly upon exposure to solar radiation, forming Cl_2 gas. This natural decomposition reduces the hazard distances, and assuming no decomposition will result in conservative estimates of hazard zones. Under strong insolation conditions (bright sunshine at noon in July), the time it would take dissociate to about 10% of the initial concentration is approximately 30 seconds. At 5 m/s winds, this would imply approximately 150 m of travel, within which most of the ClO_2 would dissociate. At 1.5 m/s, the distance would be about 45 m. Therefore, assumption of complete conversion to Cl_2 under such high insolation conditions would be justifiable. On the other hand, under clear skies shortly after sunrise in January, the time it would take for ClO_2 to dissociate to about 10% of the initial concentration is around 500 s. This would imply travel distances of 2500 m and 750 m for 5 m/s and 1.5 m/s winds, respectively. Therefore, neglecting dissociation is more reasonable and justifiable (Alp & Boughner 2005).

3.1.5 Incidents or accidents reported in the media

There are several incidents and accidents at pulp mills involving ClO_2, which have been noticed by media. The articles from the media are of course not as qualitative as the incident and accident reports, yet useful.

Most of the articles in media mention leakages from pipes, either because of damages or because of total rupture. These leakages are mostly limited in quantity, typically not more than some hundred liters. In some articles, there have been more severe leakages linked to damages to the storage tank or rupture of the same. In these cases, the leakages have consisted of hundreds of m^3. Consequences considering the health and environment are rare.

More information concerning the articles in the media and the events described there are presented in Appendix F.

3.1.6 Discussion concerning the risk identification

A large number of sources have been used for gaining knowledge and information about the different risks existing at the pulp mills. There is always a balance between the benefits of using multiple sources of information and the disadvantage of synonymous information. What is the point of presenting the same type of information repeatedly? In this case, it would have been easy to continue finding new sources of information. However, the line have to be drawn somewhere. Gaining 90% knowledge in a short period is perhaps sometimes better than gaining 99% knowledge in a very long period. After all, focus of this master thesis should be on the thinking and working process around developing the new method.

The sources of information are solely in Swedish or English and originating mostly from Sweden, U.S.A. and Canada. Of course, this narrowing is an important source of error to discuss. Many sources of information are not presented in Swedish or English and therefore automatically excluded. Since this master thesis will focus on Swedish storage facilities, it might have been better to exclude information from abroad pulp mills and only studying information from Sweden.

There is reason to believe that much useful information, foremost concerning accident and incidents are hidden. Companies with pulp mills involved in accidents or incidents are probably not keen to brag about this fact and display it on the public Internet. Furthermore, there could be details in design or processes that the companies want to keep secret. The same reasoning might apply for documentation with risk assessments as well.

Some of the articles from media are clearly biased by political views. In order to counteract those standpoints the focus has been on the chain of events and not the outcome. In many cases, the outcome is blown up in these articles.

There are a number of databases and registers of incidents and accidents within the chemical industry on the Internet. However, the accesses to these are far restricted. In some cases, you have to be a member of a participating company or employed at some kind of authoritativeness to gain access. Other databases only enable one to view small abstracts. This is unfortunate, since there probably is much useful information within these. Some of the attempts to reach this information have been rejected while others have not been responded. Although many of the registers talk about the importance of sharing information and gaining global knowledge, the reality is another.

Several precedent risk assessments have been brought up as sources of information. The efforts put into these and the quality varies. Some of the risk assessments appear to be very solid and thorough, while others just scrape on the surface. It is hard to know whether these risk assessments are poor in quality or if they deliberately have excluded several of the causes and scenarios. These might have been excluded on the base of logical reasoning, for example if they are too unlikely. Nevertheless, there is reason to suspect that most of the internal risk assessments have a limited quality. Looking at the risk assessments made with external help clearly reveals the differences in quality. Furthermore, many of the risk assessment are made on the entire pulp mill, giving the ClO_2 storage facility little space in the documentation. The risk assessments focusing on the manufacturing of ClO_2 or even better, the ClO_2 storage facility, are much more detailed and useful. There is also the fact that many of the risk assessments and their scenarios partly exist outside the system defined in this master thesis. This is a fact that needs to be considered when looking at these scenarios and even more when studying the stated consequences and probabilities.

3.2 Risk selection

On the background of the risk analysis and the consequence calculations, the most important risks and the causes of these has been identified and selected. This selection is supported by the precedent risk assessments as well as all the other literature presented under the risk identification chapter.

The most “important” risks refer to the risks and causes that have been classified with high probability, high consequences or a combination of these. These risks are the ones that the pulp mills need to focus on. Of course, there are other risks as well as other causes, but with less magnitude considering both probability and consequences. The selected risks and causes most relevant to ClO_2 storage facilities are presented in table 3.10.

Scenario	Consequence	Cause
Pipe leakage	Small continuous leakage	Collision (pipe)
		Corrosion
		Freezing
		Falling objects (small)
Pipe rupture	Medium continuous leakage	Collision (pipe)
		Corrosion
		Freezing
		Falling objects (small)
Tank collapse	Big instantaneous leakage	Corrosion
		Thermal decomposition -“Puff”
		Collision (tank)
		Undermining

Tank leakage	Big continuous leakage	Corrosion
		Thermal decomposition - “Puff”
		Collision (tank)
		Undermining
Spill	Small continuous leakage	Leaking process equipment

Table 3.10, The selected risks and causes.

3.2.1Discussion concerning the risk selection

Comparing the authors risk analysis with the risk analyses and risk assessments found in literature one could find great resemblance, which made the selection easier. Of course, there were some discrepancies. This is however not remarkable, considering the fact that the different assessment are looking at different ClO_2 storage facilities with different properties.

The tank leakages and the tank ruptures were at all times assessed with large consequences. The most frequent causes for these events were corrosion, thermal decomposition, “puff”, and collision (tank). The probability for a thermal decomposition, “puff”, was often assessed higher than what the authors had anticipated. On the other hand, corrosion was sometimes assessed with lower probability than the one assigned for the representative ClO_2 storage facility. Collision (tank) was assessed with medium probability both in our risk analysis and by the literature. There was one particular risk assessments found in literature differing from this, stating the probability as low. The most probable cause for this is the fact that the storage tanks might have sufficient collision protection, unlike the situation at many of the other pulp mills. This is however not proved or known, simply assumed.

Undermining was assessed with low probability for the representative ClO_2 storage facility. On the sole base of this, undermining would not be included in the selection. However, some of the risk assessments in literature brought this cause forward and even assigned it with medium probability. Therefore, it was included as well. The situation is the opposite when mentioning overfilling. In the risk analysis of the representative ClO_2 storage facility, overfilling was assigned a medium probability. On the other hand, when mentioned in literature, this cause had very low or low probabilities. Therefore, overfilling was excluded from this selection. Another cause excluded was the falling objects (large). There was only one of the references stating this cause with high probability. However, at the specific pulp mill large storages of paper rolls were stacked near the storage tanks, risking overturning.

For the pipe leakages and the pipe ruptures, corrosion is the most frequent cause. Beside this, collision (pipe), freezing and falling objects (small) are mentioned and assessed with medium probability. The authors agree with the assessing of collision (pipe) and falling objects (small), but had assessed freezing as less probable. However, since the literature was univocal with this, freezing was included in the selection.

In the risk analysis of the representative ClO_2 storage facility there were several other causes assessed with the same, or slightly less, probability as some of the above-mentioned causes.

Vibrations and falling objects (large) are examples of these. Since these was not assessed with medium probabilities or pointed out in any of the assessments in the literature, they were excluded.

Looking at the articles in media, accidents involving pipes are the most frequent. The reasons mentioned in these articles are foremost leaking process equipment, falling objects (small) or corrosion. These articles have also influenced the selection of causes for pipe leakages and pipe ruptures.

The leaking process equipment causing spill has not been mentioned anywhere in literature. Nevertheless, this cause is included in the selection, partly on the base of this being assessed with high probabilities and partly on the base of the uncertainties concerning the effects to the health from these minor long-term exposures.

3.3 Parameter identification

Looking at the selected risks and their causes, one can find several different parameters affecting the probability and consequences of these. These effects consist of both increase and decrease of the probabilities and the consequences. By knowing and understanding the effects from these parameters, one could better understand the measures that need to be taken to ensure safety at the ClO_2 storage facility.

The focus of the parameter identification has been on analyzing the parameters of the selected risks and the selected causes. The following text is only a shorter summary. This compilation does not claim to have found all possible affecting parameters.

3.3.1 Parameters affecting probability

Under this heading, different parameters that could increase or decrease the probability will be presented. In order to ease the overlook, the parameters are sorted according to the different causes. For more parameters and more information concerning all of the parameters, see Appendix G.

Falling objects (small)

- Stockpiling close to the storage tanks
- Removal of scattered material close to the storage tanks
- Enhancements and controls of surrounding constructions and buildings
- Rules for construction and reparation at height
- Whether the storage tanks are in use when construction and reparation are made
- Physical protection of the storage tanks and pipes
- Location of the storage tanks

Corrosion

- The frequency of controls, looking for damages due to corrosion
- The experience and knowledge among the inspecting companies
- Whether the advices from the inspections are followed
- Frequency of errors in the process
- Location of the storage tanks
- Correct choices of FRP and similar material

Human error

- The technological interface
- The work load of the employees
- Preparation and training
- Developed routines for work tasks

Collision

- Whether the stated speed limits are followed
- Limitations in where vehicles are allowed
- Maintenance with snow clearing
- Location of the storage tanks
- Collision protection, considering both storage tanks and pipes

Undermining

- The occurrence of underground piping systems
- Proper drainages around the storage tanks
- The foundation of the storage tanks

Freezing

- Whether there are passive measures, heating systems and isolation

Thermal decompositions - "Puff"

- The ventilation of the storage tanks
- Number of errors in the process
- Location of the storage tanks in aspects of heating from the sun

Leaking process equipment

- Close monitoring and maintenance of process equipment

3.3.2 Parameters affecting consequences

Under this heading, different parameters that could increase or decrease the consequences will be presented. For more parameters and more information concerning all of the parameters, see Appendix G.

- The existence of breathing masks and the frequency of use
- Relations to emergency services and general accident preparedness
- Safety culture
- Attitude towards small spills and the localization of potential sources of these

3.3.3 Parameters identified in the consequence calculations

Under this heading, different parameters noticed in the consequence calculations affecting the consequences will be presented. For more parameters and more information concerning all of the parameters, see Appendix D.

- Systems for suppressing or stopping degassing
- Drainage system around the storage tanks with the ability to enclose and thereby contain leakages
- Dikes around the storage tanks
- Storage tanks working as "communicating vessels"

- Location of the storage tanks
- Solution temperature
- Solution concentration
- Reinforcement of lower parts of storage tanks to withstand collision

3.4 "Ideal" ClO_2 storage facility

Throughout the working process, several features have been noticed, that could enhance the safety and minimize the risks affecting the ClO_2 storage facility. These different pieces of information have successive grown together. Together with insights and thoughts gained during the working process, this "ideal" has become more and more extent. To make use of this information and thoughts, an "ideal" ClO_2 storage facility will be presented in aspects of safety. This "ideal" will henceforth play an important role when developing the method for risk assessment of ClO_2 storage facilities. Below are some brief points that the authors want to put forward. These have been arranged in to two categories according to necessity and in two categories according to type: technical/physical and organizational. More information and points are presented in Appendix H.

Important

Technical/physical

- The storage tanks should be surrounded with dikes that are able to contain at least 100% of the volume in the largest storage tank and 10% of the volume in the other storage tanks. The dike should be built in a corrosion resistant material.
- There should be systems installed to reduce the degassing of ClO_2 in case of a release. There are several different methods and systems. Such methods include spreading oil or foam over the ClO_2 solution, diluting it with water or neutralizing the ClO_2 solution by adding sodium thiosulfate ($Na_2S_2O_3$) or sodium bisulphate (Na_2S). Neutralizing should be preferred.
- The storage tanks should be equipped with explosion lids.
- There should be gas detectors localized around the ClO_2 storage facility. These should be programmed to react at concentrations of 0.1 ppm. There should also be the possibility to manual activate the alarm.
- The storage tanks should be equipped with technological as well as physical systems for protection against overfilling. This system should be connected with the enclosed drainage.
- The storage tanks should have proper collision protection constructed around them.
- The inbound and outbound pipes should have isolation valves installed, to stop sudden leakages.
- The storage tanks should be ventilated, and with systems for backup.
- There should be reserve power systems and preparations to keep important safety systems like ventilation of the storage tanks running at outages.
- The storage tanks should be constructed with suitable material and according to the latest knowledge and proper design.
- The temperature and concentration of the ClO_2 solution should be maintained at below 11 °C and 11 g/dm^3 at all times.
- Protective equipment like gas masks must be readily available and regularly controlled for function.

Organizational

- An accredited control company should inspect the internal corrosion on the storage tanks and the inbound and outbound pipes at least once every six years.
- Preventive maintenance, overall supervision and control of functions should be performed frequently on the equipment at the ClO_2 storage facility. These actions should be regulated through written rules and clear instructions.
- A safety management system should be implemented and frequently reviewed and improved. The areas of human errors and safety culture are areas that need special attention.
- The preparedness for accidents should be reviewed regularly. Cooperation with emergency services and other authorities should be encouraged.
- Strengthen the workers knowledge about the storage facility and their ability to operate it safely, under both normal conditions as well as emergencies.

Preferred

Technical/physical

- The ClO_2 storage facility should consist of two or more storage tanks. These should work as communicating vessels and have the possibility to both automatically and manually shut down the interconnection.
- The drainages around the storage tanks should be possible to close and thereby enclose a leakage of ClO_2.
- The storage tanks should be placed indoor, in a building with the sole purpose of containing the storage tanks.
- There should be protection and reinforcements of the inbound and outbound pipes, to prevent falling objects or collision from traffic causing damages. Such protection and reinforcement could consist of pipe bridges.
- The ClO_2 storage facility should be located away from storage tanks of other chemicals.
- The presence of underground pipes under or around the ClO_2 storage facility should be investigated. If necessary, these pipes should be moved to avoid undermining in case of one of these breaking.
- The surroundings of the ClO_2 storage facility should not be the stockpile of building material or other objects. These objects might fall or blow and cause damages and could obstruct possible actions taken on emergencies and leakages.

Organizational

- The traffic at the pulp mill should be directed so that it does not pass close to the ClO_2 storage facility.
- The storage tanks and the inbound and outbound pipes should be marked with labels stating the contents and properties of the chemical.
- The monitoring of the ClO_2 storage facility should be around the clock. The systems for monitoring should be easy to comprehend and overlook.
- The working routines as well as special emergency routines should be written down and regularly reviewed.

Finally, two things should be pointed out. First, this “ideal” ClO_2 storage facility is made without consideration of the economics. Second, the features presented in this “ideal” ClO_2 storage facility are a selection. Several other aspects and features than the ones mentioned here could be brought up, but since the focus is on the development on the new method, this has to do.

3.5 Description of the method

The developed method have been formed by the knowledge and information gained up to this point. The literature study concerning different methods for risk assessment gave ideas that in the end led to the structure of this method. The structure can best be described to resemble a checklist with questions. These questions are foremost inspired by the parameters and properties presented in the description of the "ideal" ClO_2 storage facility, which in turn are largely based on the parameter identification and the risk identification. One should see the entire working process and all of the different parts of this master thesis as sources of inspiration.

Systematically, one will have to answer the different questions in the method. The alternatives for answers will be held simple and consist largely of "yes" and "no" alternatives. While the general checklist is referred to as a qualitative method for risk assessment, this method will somewhat differ from this. The method has features of semi-quantitative elements. In fact, the method could be seen as a mixture between a qualitative and a semi-quantitative method.

The semi-quantitative elements are included into the method through the points linked with each question. When starting to answer the questions, one will have a sum of points corresponding to the sum of the "ideal" ClO_2 storage facility, according to the properties mentioned in the chapter above. Depending on the answer to the questions, one might have to deduct points from this sum because of defects in safety and differences from this "ideal". The deduction of points for each question is based on subjective thoughts, which are foremost based on the risk selection and the preparatory work of this. The number of points deducted is an integer from 1 to 5.

When all the questions are answered, the remaining points are counted. The sum is then compared with fixed scales. Thereby, one can see how close to the "ideal" ClO_2 storage facility the ClO_2 storage facility is, concerning the safety. The scale and the thoughts behind this will be described in another chapter below.

Into the method, several "keys" will be included. These "keys" summarize the answers and points of chosen questions. These chosen questions are all connected to a special category. The "keys" proposed are organizational safety, physical safety, preparedness and maintenance. From these chosen "keys", one can perhaps better understand what was earlier referred to as questions connected to a special category. These different "keys" were chosen for different reasons. Organizational safety is an important component when looking at the underlying causes for accidents and incidents. The pulp mills need to have clear regulations, planning and routines. Such features are included into the organizational safety. Physical safety includes both physical and technological aspects. This means both physical systems, like dikes and collision protection, and technological systems like monitoring systems and level transmitters. The different systems included might lower the probability, mitigate the consequence or achieve both. Preparedness tries to point out how the pulp mills have prepared themselves for possible accidents, emergencies and incidents. Parameters included here are both practical preparations, like the access to breathing masks, and theoretical, evacuation planning and risk analysis. The last "key" included was maintenance. This "key" looks at the frequency of the maintenance and defects in this. A high standard of maintenance is needed to ensure safety and avoid incidents and accidents. Of course, one could come up with more “keys” or create more questions to incorporate into the “keys” and the overall method. The proposed “keys” are assumed to cover the larger areas of safety, without being too detailed, thus keeping the method simple.

The sum of points for the different “keys” is compared with separate scales. One advantage of introducing these different “keys” is the fact that the method could present more precise and extent information, without growing larger or becoming more complicated.

The different results, both the overall and the specific, will alert the pulp mill, whether it might need to perform further risk assessments and risk analyses in different areas. The method will not present any result that clarifies exactly what risks existing or what mitigating actions to take, but to point at different areas of concern.

3.5.1 The scale

The scales are based on the questions and the points deducted from these. Counting the different points included into the method and the different “keys” gave the maximal points. Thereby, the highest and lowest point on the scales was fixed.

The scales consist of three different levels, referred to as “green”, “yellow” and “red”. “Green” is defined: the safety is good. “Yellow” is defined: the safety is sufficient. “Red” is defined: the safety is insufficient. These definitions apply for both the overall result and the results within the “keys”. For the overall result, there is the addition to the “yellow” level: However, one should look at the different “keys” for more information about the weaknesses in the overall safety.

A preliminary method was sent to the three pulp mills visited during the autumn. The scales in this preliminary method were established without any closer thoughts. Receiving the answers from the different pulp mills turned out to be both interesting and helpful. Not only was there feedback concerning the form of the method and the formulation of the questions received, but also clear information in the form of answers and results. The thoughts and impressions from the study visits were compared with the answers and the calculated sums of points. This comparison lead forward to the statement that about 85% of the points corresponded to “green” and about 60% of the points corresponded to “yellow”. Since the impression from the study visits was that most of the ClO_2 storage facilities had some shortcomings, this corresponded well with what the pulp mills had answered. Furthermore, the method was repeatedly applied on fictitious ClO_2 storage facilities, looking at the points and the placement on the scale. These repetitions lead forward to some fine grounding of the scale.

3.6 Result

The finished method is preceded and sent with a draft instruction and description. The thoughts behind this one are to explain the intent, limitations and somewhat the features of the method. The actual method is presented after this, in table 3.10.

Risk assessment of ClO_2 storage facilities at Swedish pulp mills

Introduction

Chlorine dioxide (ClO_2) has emerged as one of the most dangerous chemical stored at many Swedish pulp mills. Even though the most ClO_2 storage facilities and pulp mills have sufficient safety levels, the awareness of the risk from ClO_2 and the demand for improvements in safety are ever increasing. This method is developed for risk assessment at ClO_2 storage facilities at Swedish pulp mills, hopefully leading to improvements of the current situation. The method strives to be quick and easy to use. The method can be conducted internally without any involvement of external experts or previous experience.

Instructions

The method resembles a checklist and consists of 84 questions. There is no need for previous experience or knowledge about this method or other methods for risk analysis or risk assessment. However, thorough knowledge about the situation and conditions at the specific ClO_2 storage facility and the overall pulp mill is needed. Some of the questions aim towards the technical aspects of the ClO_2 storage facility as well as the organizational aspects of the pulp mill. Therefore, before starting the method, make sure that any data, documentation or human resources that might be necessary to answer the questions is available.

This risk assessment method does not give concrete advices about what safety measures or mitigating actions to take. The result from the risk assessment should rather be considered as guidance to whether the ClO_2 storage facility is in need of a more thorough risk assessment or risk analysis or not. The risk assessment also points at different areas, beside the overall safety, that might be neglected in respect to safety. This is to help focus the pulp mills resources on the proper area.

For the result to reflect the real situation and safety level at the ClO_2 storage facility, it is of great importance that all questions are answered truthfully and objectively.

Limitations

This method is intended to be used for the assessment of the total risk arising from different ClO_2 storage facilities at Swedish pulp mills. The method might be applicable at Western European and Northern American conditions as well, due to the similarities, but no tests have been conducted to assure this.

Even though the method is based on a foundation of thorough research, the method cannot take into account all the location and situation specific parameters and risks that might exist at different ClO_2 storage facilities.

	The questions	The points linked to each answer	
1	Is the ClO_2 storage facility located within 800 meters from residential areas?	Yes -4	No 0
2	Are there dikes installed around the storage tanks?	Yes 0	No -5
3	If answer yes on question 2: Are the dikes able to contain more than the maximum volume stored in the largest storage tank plus 10% of the volume stored in the other tanks?	Yes 0	No -3
4	If answer yes on question 2: Are the dikes built with corrosion resistant material, for example concrete with a surface treatment?	Yes 0	No -1
5	Are the inbound pipes to the storage tanks located under the surface of the solution?	Yes 0	No -2
6	Is the ClO_2 solution stored at above 11° and 11 g/dm^3?	Yes -3	No 0

7	Does the pulp mill have an action plan for dealing with possible leakages and such, for example decontamination and removal?	Yes 0	No -3

8	Is the pulp mill aware of the term "human errors"?	Yes 0	No -3

9	Does the pulp mill conduct controls of the conditions of surrounding constructions and buildings, in order to locate weaknesses and loose objects?	Yes 0	No -1

10	Does the pulp mill have cooperation, exercises and dialogue with local emergency services and other authoritativeness?	Yes 0	No -3

11	Are the inbound and outbound pipes controlled for damages from internal corrosion once every sixth year?	Yes 0	No -4

If answer yes on question 11:

12	Are different parts of the pipes controlled?	Yes 0	No -3

13	Are the storage tanks marked with labels stating the contents and proper danger symbols?	Yes 0	No -1

14	Does the ClO_2 storage facility have safety nets or other protection installed over the storage tanks to protect from smaller falling objects?	Yes 0	No -1

15	Does the ClO_2 storage facility risk suffering from a landslide?	Yes -4	No 0

16	Is the ClO_2 storage facility located away from traffic?	Yes 0	No -2

If answer no on question 16:

17	Do the workers have to go through education in order to drive vehicles inside the pulp mill?	Yes 0	No -2

If answer no on question 16:

18	Does the pulp mill have clearly displayed speed limits?	Yes 0	No -1

If answer yes on question 18:

19	Does the pulp mill control that these speed limits are followed?	Yes 0	No -1

If answer no on question 16:

20	Does the pulp mill conduct sufficient maintenance of the roads, foremost snow clearing and salt spreading?	Yes 0	No -2

21	Does the ClO_2 storage facility have collision protection around the storage tanks, for example dikes or reinforced poles?	Yes 0	No -3

If answer yes on question 21:

22	Is it possible for a vehicle to pass over, in between or on the side of the collision protection?	Yes 0	No -2

23	Are the storage tanks equipped with level transmitters to detect and alert of possible overfilling or leakages?	Yes 0	No -4

If answer yes on question 23:

24	Are these detectors able to automatic shutdown the inbound flow to the storage tanks?	Yes 0	No -2

25	Do errors in the process frequently occur, causing increased concentrations, temperature or decontamination in the ClO_2 solution transported to the storage tanks?	Yes -3	No 0

26	Does the pulp mill have written instructions for all operations and work tasks performed on daily basis?	Yes 0	No -3

27	Does the ClO_2 storage facility have prohibitions against lifting objects over the inbound and outbound pipes?	Yes 0	No -2
28	Does the pulp mill have workers monitoring the ClO_2 storage facility and the process at all times, visually or technological?	Yes 0	No -4
29	Do the inbound and outbound pumps have dikes installed around them for containing potential leakages?	Yes 0	No -3
30	Are the storage tanks isolated?	Yes 0	No -2
31	Does the ClO_2 storage facility risk suffering from flooding?	Yes -3	No 0
32	Are the storage tanks frequently controlled for damages from external corrosion?	Yes 0	No -1
33	Are there systems installed for reducing the degassing rate after a leakage, for example foam or neutralizing agents?	Yes 0	No -4

34	Is the filling degree of the storage tanks frequently less than 80%?	Yes -3	No 0

35	Are the inbound and outbound pipes from the storage tanks marked with labels stating the content and proper danger symbols?	Yes 0	No -2

36	Does the ClO_2 storage facility have reserve power to restore important features around the storage tanks in the event of outage?	Yes 0	No -3

37	Do the workers that frequently maintain close to the ClO_2 storage facility have access to breathing masks and other protective equipment?	Yes 0	No -5

38 If answer yes on question 37:

Do the workers at the ClO_2 storage facility use their breathing masks when ClO_2 is smelled or anticipated or when the gas detectors signals levels above the accepted level?	Yes 0	Sometimes -3	No -5

39	Does the pulp mill have an evacuation plan for dealing with possible accidents and exercise this?	Yes 0	No -3

40	Are there regulations concerning the work done at height? Regulations referring to limitations in the number of tools, the amount of materials brought, the usage of safety nets and so on.	Yes 0	No -2

41	Does the pulp mill have programs for preventive maintenance considering conditions of pumps, valves, instrumental equipment and so on?	Yes 0	No -5

42	Does the ClO_2 storage facility have isolation valves on the pipes around the storage tanks and the inbound and outbound pumps?	Yes 0	No -4

43 If answer Yes on question 42:

Are these isolation valves automatic or easy accessible, even in the case of a possible accident?	Yes 0	No -4

44	Is there ventilation installed in the storage tanks?	Yes 0	No -4

45	Do the storage tanks have overfilling protection, for example piping system?	Yes 0	No -2

46 If answer Yes on question 45:

Is this piping system leading to an enclosed drainage or storage?	Yes 0	No -2

47	Is the ClO_2 storage facility located within 100 meters from waters?	Yes -3	No 0

48

Is there a single storage tank or multiple storage tanks?	Single -3	Multiple 0

49

If answer Multiple on question 48:

Are these working as communicating vessels with the ability to close the interconnection between them?	Yes 0	No -3

50

If answer Yes on question 49:

Are the closing automatic or easy accessible, even in the case of a possible accident?	Yes 0	No -3

51

Does the pulp mill know whether there are piping systems beneath the ClO_2 storage facility?	Yes 0	No -2

52

If answer Yes on question 51:

Are the conditions of these piping systems known?	Yes 0	No -2

53

Does the ClO_2 storage facility have collision protection for inbound and outbound pipes, for example reinforced pipe bridges?	Yes 0	Partly -1	No -2

54

Does the ClO_2 storage facility have redundancy in their technological as well as mechanical systems, for example pumps, ventilation, detectors and level transmitters?	Yes 0	Partly -3	No -4

55

Are there automatic gas detectors (0.1-0.3 ppm detection level) installed in the vicinity of the ClO_2 storage facility?	Yes 0	No -4

56

If answer Yes on question 55:

Are these connected with well audible and visible alarms?	Yes 0	No -4

57

Does the pulp mill have storages of gas tubes (flammable or explosive) close to the ClO_2 storage facility?	Yes -2	No 0

58

Does the pulp mill repeatedly educate and rehearse the workers in the properties and dangers of ClO_2?	Yes 0	No -3

59

Does the pulp mill schedule construction work and repair work in the surroundings to periods when the ClO_2 storage facility are not in use?	Yes 0	Partly -1	No -2

60

Are the inbound and outbound pipes frequently controlled for damages from external corrosion?	Yes 0	No -1

61	Do the storage tanks have enclosing fences?	Yes 0	No -1	
62	Does the pulp mill use accredited inspectors to control the corrosion?	Yes 0	No -4	
63	If answer Yes on question 62: Does the pulp mill follow the recommendations from the inspections?	Yes 0	No -4	
64	Are the storage tanks equipped with valves dimensioned for coping with large pressures fluctuations, for example vacuum breakers and explosion lids?	Yes 0	No -4	
65	Are the storage tanks protected from wind by neighboring constructions or indoor placement?	Yes 0	Partly -2	No -3
66	Has the pulp mill thought about how future climate changes might affect the pulp mill?	Yes 0	No -1	
67	Are the storage tanks controlled for damages from internal corrosion once every sixth year?	Yes 0	No -4	

68

Does the ClO_2 storage facility have measures for preventing freezing in inbound or outbound pipes, for example isolation, heating coils or regular inspections?	Yes 0	No -2

69

Does the ClO_2 storage facility have drainages around the storage tanks, for example street drains?	Yes 0	No -2

70

If answer Yes on question 69:

Are the drainage system enclosed or designed with the ability to enclose, and thereby contain ClO2?	Yes 0	No -3

71

Do the workers try to locate and fix the sources of small leakages detected by smell or automatic gas detectors?	Yes 0	Sometimes -3	No -5

72

Does the pulp mill have control over which persons entering the pulp mill?	Yes 0	No -1

73

Does the pulp mill have routines and encourage workers to report incidents, accidents, defects and so on?	Yes 0	No -3

74

Does the pulp mill stockpile in the surroundings of the ClO_2 storage facility? Stockpiling referring to active storage, objects left behind and so on.	Yes -2	No 0

75	Does the pulp mill have a safety management system or relevant features in their overall management system?	Yes 0	No -4	

76 If answer Yes on question 75:

Does the pulp mill revise this management system?	Yes 0	No -3

77	Does the pulp mill have storages of chemicals close to the ClO_2 storage facility?	Yes -2	No 0	
78	Are the storage tanks located indoors?	Yes 0	Partly -2	No -3

79 If answer Yes on question 78:

Does this building have the sole purpose of containing the storage tanks?	Yes 0	No -2

80	Does the pulp mill have an enclosing fence?	Yes 0	No -1
81	Does the ClO_2 storage facility have prohibitions against lifting objects over the storage tanks?	Yes 0	No -2

82	Does the pulp mill conduct risk analyses in case of reconstruction, new construction or changing of process?	Yes 0	No -3
83	Are the storage tanks located in the shadow for most of the day?	Yes 0	No -1
84	Does the pulp mill have in house knowledge about and defined choices of material, for the storage tanks?	Yes 0	No -2

Table 3.10, The complete method, with all the questions and the points linked with each question.

The definitions of the different colors, results, in the method are presented in table 3.11.

Definitions

The safety is good.

The safety is sufficient. However, one should look at the "keys" for more information about weaknesses in the safety.

The safety is insufficient.

Table 3.11, The definitions of the different colors in the method.

The scales for the overall result and the different "keys" are presented in table 3.12.

Scale

Overall safety:	183-152	151-110	109-0
Organizational safety:	42-34	33-24	23-0
Physical safety:	86-71	70-50	49-0
Preparedness:	21-18	17-13	12-0
Maintenance:	27-23	22-16	15-0

Table 3.12, The scales for the overall result and the different "keys".

The definitions of which questions included into which "key" are presented in table 3.13.

Keys

Overall safety:	Include questions 1-84.
Organizational safety:	Include questions 8-9, 17-19, 26-28, 40-41, 58-59, 73-76, 81-82 and 84.
Physical safety:	Include questions 2-6, 13-14, 16, 21-24, 28-30, 33-36, 42-46, 48-57, 61, 64, 68-71 and 77-80.
Preparedness:	Include questions 7, 10, 37-39, 55-56 and 82.
Maintenance:	Include questions 9, 11-12, 20, 32, 41, 60, 62-63, 67 and 71.

Table 3.13, The definitions of which questions included into which "key".

4. Discussion

This discussion is an opportunity for the authors to enlighten their thoughts and present their reflections concerning not only the developed method, but also the master thesis as a whole. However, the discussion will not only consist of loose thoughts and reflections. The discussion will also be an opportunity to step back and critically and thoroughly review the developed method and the working processes leading up to this. Fundamental for this review is the question whether the intended goals are fulfilled or not.

The working process of developing the method has been discussed earlier in this master thesis. The chapters of risk analysis of the representative ClO_2 storage facility as well as the risk selection included such discussions. Bringing about the same points of discussion again is therefore not needed and these parts will be held short. The authors have instead decided to let the scientific approach presented under the introduction stand as the centre for the following discussion.

Fundamental for any kind of scientific research and work, is the need to be objective, unbiased and balanced. The authors think that all of these needs have been achieved in this master thesis. To keep the scientific research balanced could sometimes be difficult. Information is sometimes hard to find. Chapters with accessible and extended sources of information, unintended often become more extent. Even though the information that is hard to find, more often is the most interesting. For example, to find risk analysis concerning the pulp mill is easy, but to find risk analysis specifically pointed at the ClO_2 storage facility is hard.

That the scientific research should be unbiased as well as objective appears as two sides of the same coin. In the scientific researches, where risk and the related concepts are fundamental, the objectiveness could somewhat be questioned. Risk is in large parts subjective, not only when it comes to perception. This master thesis is no exception. The authors subjective deciding and thoughts has been notable on several locations, from the risk analysis of the representative ClO_2 storage facility to the risk selection. On the other hand, objective information about these is not available. Since the situations concerning both the quantitative and qualitative properties of risk differ between different places and situation, there is no chance of finding useful and accurate information. Therefore, one has to build most of the reasoning on subjective thoughts. Perhaps, one could establish that the parts of this master thesis that can be built on reliable and objective information have been so.

References and information will always be questioned, and should be questioned. However, the authors are firm in their belief that reliable information has been used. When addressing the area of information and trustworthiness of this, one could also look at the methods for gathering this information. As mentioned before, the literature studies have been of great importance. This information is considered as information from secondary sources. The authors themselves have gathered information from primary sources through direct interviews and direct visits. Although primary sources, there is always the chance that these are being coloured and biased. Either from the interpretations and opinions of the authors or thoughts and opinions of the persons interviewed. On the other hand, there is no information that is not in risk of becoming biased from this point of view.

Beside the overall goal to create and develop a new method for risk assessment, which will be discussed later on, several secondary goals were established for the method. Among others, the method should be easy to use, not require any previous experience or knowledge about risk assessments and present results that are easy to comprehend. All of these goals are quite simple, looking at them, yet hard to accomplish.

Since the alternatives to the questions furthermore most consist of affirmative or negative alternatives, the simplicity of the method cannot be questioned. Questions from which one might choose different alternatives must be considered as simple to answer. Of course, there could be some minor problems with formulations of the questions, misunderstanding of the questions or other kind of difficulties. However, since the method has been successfully tested among workers at different pulp mills, without any greater complications, this should not be the case.

The authors state that there is no need for previous experience of risk assessments or risk analyses, which goes hand in hand with the simplicity. One could question whether one need some basic overall understanding of risk assessments and the purpose of such. The authors state that such understanding and experience is unnecessary. The actual method comes with a short description that should be sufficient for giving that understanding. Nevertheless, one does need knowledge about the ClO_2 storage facility and the situation at the whole pulp mill to answer the questions. However, since the method is most appropriate to be carried out as a cooperation, in a group, one do not need to have all the knowledge oneself.

There are more points to discuss about the comprehension of the result. The description of the method stated that the result would not clarify what risks affecting the storage of ClO_2 or what mitigations actions to take. The method has the sole purpose to enlighten shortages in the overall safety as well as within certain chosen areas, referred to as the “keys”. The overall result as well as the results within these certain “keys” are presented as a sum of points out of a staring sum. The result will also be displayed with a color, depending on the sum of points. These colors are “green”, “yellow” and “red”, similar to the traffic lights. At this stage, the comprehension of the result should not be a problem. What could be a problem in terms of comprehension is the question of what follows the result. What should the user do with these results? Although stated, that the result should be the fundament for where to conduct more thorough risk assessments and risk analyses, this might be unclear and cause problems. The problems probably linger more in the question of how to proceed than the question about which areas to proceed within. Which risk assessment methods or risk analysis methods should one use? Should external help be required? Unfortunately, these questions cannot be answered by the result of the method. These questions are outside the scope and intentions of the method. However, through this master thesis and the working process of this, one might find useful tips of how to increase the safety level of the ClO_2 storage facility.

Other than reviewing the secondary goals and the achievement of these, the method could also be reviewed in other aspects. The first thing that the authors want to bring forward is the questions in the method. Several things could be discussed concerning these. The formation of the questions is one such thing. The authors have afterwards noticed that most of the questions are asked so that the “same” alternatives always correspond to the same outcome. The “yes” alternative is in most of the questions the “good” alternative, not leading to deduction. This fact and the awareness of this fact, could perhaps influence the user of the method, either unconsciously or consciously, thereby misleading the result. Looking back on this fact, some of the questions should have been reformulated.

The formulation of the questions could also be reviewed in other aspects. Some of the questions contain exact numerical values, for example the temperature of 11 °C and the distance of 800 meters. These numerical values could most certainly be discussed. Some of these are based exclusively on external sources of information. The temperature mentioned above is based on such information. The information came from a graph showing the partial pressure of gaseous ClO_2 at different temperatures. From that graph, the authors concluded that the partial pressure above this temperature, easily could lead to explosions, and therefore choose that value. The distance mentioned above is not based on external sources of information. In this case, the authors stated the distance. The distance is based on their thoughts and results from the consequence calculations presented in this master thesis. These formulations of the questions unfortunately make them rather blunt. One way of making these questions sharper is too assign different numerical values as answers to the questions, rather than formulating questions around specific numerical values. This matter will also be discussed when discussing improvements for the method.

The number of questions is also something that needs to be discussed. There are approximately 80 different questions. Should there be more questions or should there be fewer questions? It is important to clarify that more questions not necessarily gives a better method. There is no point of involving all possible risks into the method and the questions of this. As the authors previously stated, some risks could be disregarded due to small consequences or low probabilities. There are also the aspect of simplicity, previous mentioned in this discussion. More questions could make the method both sharper and blunter, depending on the point of view. More precise and detailed information can be gathered through more questions. On the other hand, more questions could also make the method blunter, when gathering more and more information in aspects of different risks. The balancing between these points of view is hard. The authors have settled with approximately 80 questions, because they think that these questions include the most important risks affecting the storage of ClO_2 and the details of those. Should someone else have different thoughts, there is nothing preventing the addition of questions to the method. This matter will also be discussed when discussing improvements for the method.

In linkage with the discussion concerning the numbers of questions in the method, one could also think about whether the right questions are included. Of course, this is something that always will be discussed. In order to evaluate this fact one probably have to look at the whole working process and gathering of information leading up to the method and the questions in this. Furthermore, one has to evaluate the subjective statements that the authors have made in their risk selection. At bottom, the questions are based on this working process. The including of the different questions in the different “keys” could also be questioned. Questions perhaps should be included into another “key” or perhaps in more “keys”. Time after time, the discussion returns to the fact that subjective decisions are the base for the method as well as the whole area of risk.

There are also other aspects then the questions that need to be brought forward for discussion when reviewing the method. The deduction of points is one such thing. This aspect has importance both considering the actual points linked with each question as well as the sum of points linked with the results.

The deduction of points has been simplified through the introduction of integers reaching from 1 to 5. The advantage from this simplification is foremost to ease the awarding of points. To have 5 alternatives instead of perhaps 10 or 100 is obviously easier. However, the purpose of this master thesis was not to ease the working process and awarding of points for the authors, but to create and develop a functional method. One could somewhat believe that this simplified system is more comprehendible than a more detailed system. On the other hand, there are some disadvantages as well. The more simplified system will not give the same precise information and resolution. Actually, the points might not reflect the reality, looking at the deduction at points between questions and the severity of the parameter asked about. There are differences in the effects on the overall safety that will not be displayed and properly addressed with this simplified system. This matter will also be discussed when discussing improvements for the method.

The points could also be discussed regarding to the scales and the result. This discussion has somewhat been dragged up before, and are therefore held brief. The scales were established during a period of testing. Different pulp mills tested the method and their results were noted. Furthermore, the authors themselves tested the method on the base of their notes and impressions from visits. In the most cases, the results were the same, which gave a good starting point for discussing the levels. In short, the scales were established as a cooperation between the pulp mills view of their safety and the comparison with our view of their safety.

Although not directly connected with the points, but with the scales, is the discussion whether "yellow" should be defined as "sufficient". This might give the wrong signals and perhaps lead the user and the pulp mill to believe that no more actions or improvement is needed. Improvement is always possible and one should strive after this. Even upon an already good or "sufficient" situation.

To review and discuss the whole concept of the method is difficult, since the method does not match any other method, what the authors have seen. However, one could list strengths and weaknesses in the method and the concept of the method, and thereby somewhat be able to review and discuss.

One of the greater strengths of the developed method is the simplicity. As been discussed above, the method does not require previous experience in risk assessments or risk analyses. Neither does the method require previous experience conducting such methods, since both the concept and the conducting of the actual method are simple. Unlike many other methods for risk analysis and risk assessment, this method does not require much work from the user. The different risks and scenarios has already been mapped and sorted. The simplicity is also in focus when talking about the presented result from the method. Although held simple, the method is still able to perform the high qualitative work for which it is developed.

Another strength of the method is the fact that the method and the questions in this is built on thorough work and scientific research. Not only have large amounts of literatures and knowledge been incorporated through literature studies and references in text. Furthermore, the professional knowledge and experience of the authors within the field of both chemistry and risk have been included. The selected risks are the one most frequently occurring or the most severe according to these sources of information. Not all methods for risk assessment or risk analysis have this solid scientific fundament. Many of these instead count and lean on the user for much knowledge, with variation in results.

The method has some weaknesses beside the strengths. These weaknesses are equally, if not even more important, to take into consideration. The fact that the method and the question are based on a solid scientific fundament was called strength. However, in another perspective this could be seen as a weakness. Although the research behind the selection has been thorough, the method and the questions will not be able to take allowance to properties specific for the different ClO_2 storage facilities. The method and the questions might be suitable for the general ClO_2 storage facility, but could not cover all the specific features that might exist. From time to time, these specific properties and risks might be large, but still not reflected over, since they are excluded from the method. Obviously, this is a problem and a weakness.

Another weakness is the fact that the user can have impact on the result. The authors are not claiming that the user otherwise do not have influence over the result of the risk assessment or risk analysis. The difference from other methods is the fact that this method presents a result that evaluates the ClO_2 storage facility, and perhaps indirect the user. The most of the other methods do not make this judgment. From the other methods, the result is often listing of possible risks, some assessment of the consequences and probabilities or suggestions of mitigating actions. The possibility that trouble the authors is the fact that the user might unconscious or conscious strive to achieve great result rather than answering truthful on the questions. The problem with formulation of questions was mentioned earlier in this discussion. This might conspire with this strive. The user might wish to reach the “green”, rather than “yellow” or “red”. There are few things that the authors can do to prevent such actions. One must have trust in the users and hope that they take on the method with good intentions and want improvement, rather than good results. After all, the method is trying to improve and help their situation.

The last weakness to bring forward is the fact that the result of the method is not substantial in the same way as other methods for risk assessment and risk analysis. First, one must be aware of the fact that this has never been the goal with the method, as stated earlier. The result do not give the user much information concerning what risks affecting the ClO_2 storage facility, although some could be read from the result within the different “keys”. Neither does the method give any suggestions on mitigating actions, nor for that matter state, how the user should proceed upon the result. This weakness might give the method less usefulness in the eye of the user, which might be the cause for not using it or being neglectful when using it. The authors have therefore been clear when presenting the intention of the method in the brief instruction that follows the actual method.

The authors started the working process of this master thesis with the outspoken goal to create and develop a method for assessing risks at ClO_2 storage facilities at Swedish pulp mills. One has to ask oneself whether this goal has been achieved or not. During the working process, the authors have realized what an extent and ambitious strive and effort this was. This is the first time the authors make use of their knowledge and methods from their education. Eka Chemical and the mentors have throughout the working process pointed out that the opinion of the authors are the core of this master thesis and that these are as important as other sources of information. This encouragement has strengthened, and we today feel satisfied with our effort and strive, and feel like we have succeeded in this achievement of developing a new method.

This developed method is functional and ready to be used. However, there are several points of improvements to shape the method into perfection. Producers of ClO_2 and Eka Chemicals now have great possibilities and opportunities to continue working on improving this method and the applications. The authors have thought about some improvements that can be important. Due to the limited time of this master thesis, these improvements have not had the chance to be included into the current method.

Although based on both Swedish and international sources of information, the method is made considering Swedish properties and adapted for use at Swedish pulp mills. One might think that the method should be able to work decent on Scandinavian, North European and perhaps North American pulp mills, even though not intended. Nevertheless, Eka Chemicals is working internationally with facilities and customers all over the world. To adapt the method to international aspects would be much useful, if not even necessary. This adoption might seem small, but the authors fear that there is much work to be done. First, one must understand that one will have to deal with differences between different parts of the world. To include all these differences are difficult and the authors do not have a solution on how to achieve this. One will most likely have to conduct the complete and thorough process of risk assessments and risk identifications for several different parts of the world, if not single countries. In other words, conduct the same working process that lead forward to this method time after time again. The load of work will be great. Perhaps one could take an easier way and choose to include or exclude questions into the method based on the properties of the different parts of the world. Take the question about earthquakes for example. This question might not be needed in Sweden. Maybe not in Italy either. However, pulp mills in Japan most certainly risk suffering from this and the question therefore should be included into a method suited for Japan. One might also think about changing the deduction of points. There are probably many other solutions to adapt the method to work international and with the variation this requires.

The method does not have any restrictions when it comes to the numbers of questions. One could add more questions as well as remove questions. There will most certainly be some work in changing the scales of the result, the summarization of the points and such things, but nothing difficult. The fact that one could add more questions gives room for introducing not selected risks and questions about these into the method. The same way, one might add detailed questions about the already selected risks and advance the questions already existing in the method. The addition of questions and the possibility to remove such might be seen as an easy way to adept the method international, as stated above. The same way, there might be more “keys” added to the method as well as removed. Eka Chemicals might think that some other area of safety is more important than the ones already mentioned. The “key” might be created through using already existing questions as well as introducing new questions. The method is very flexible.

Continuing on the questions, there are several other ways of improvement. First, the authors believe that the possibility to answer with exact values and answers would be to prefer instead of simple positive or negative alternatives, at least for some of the questions. The questions thought about is foremost the questions involving some kind of numerical value. Instead of stating whether the distance is greater or less than 800 meters, one could choose whether the distance is approximately 400 meter, 600 meters or 800 meters. On the other side, this formulation presents different problems. How should one answer when one have the distance of 500 meters? Of course, there are solution for this problem as well, stating alternatives like <400 meters, 400-600 meters or >800 meters. What could be even more preferable is the possibility for the user to solely answer with an exact numerical value rather than choosing an alternative. The questions could be linked with flexible deduction of points. Second, which was briefly discussed above, is the possibility to specify the points for the different questions. The system with integers reaching between 1 and 5 has low resolution. The introduction of a system of points reaching from 1.0 to 5.0 would be more resolute, which according to the authors, is to prefer. Third and final, the current linkage between the points deducted and the questions could be analyzed. The points deducted with each question are in large based on the subjective thought of the authors and could be questioned.

Improvement could also be made to the scales of the result. The authors have had the opportunity to test the method on three different ClO_2 storage facilities and some other fiction. Although the authors fell confident in their stated scales, there could be improvements by testing the method at more ClO_2 storage facilities. That way, one might increase the resolution, and the scales and the result could more precise reflect the reality.

Finally, the authors also want to bring up the possibility to use this overall concept of the method at other types of storages of chemicals. Eka Chemical as well as Akzo Nobel handle and sell a great variation of chemicals, not all of them with the same dangerous properties as ClO_2, but still dangerous. The comprehensibility and simplicity of this overall concept could most certainly appeal to other customers within different areas as well.

5. Conclusion

A methodical scientific research comprising literature searches and interviewing professionals has resulted in a thorough identification of the risks associated with ClO_2 storage facilities.

The identified risks have been ranked, and for the most important risks the cause, severity of the consequences and magnitude of the probability has been assessed. The most important risks are; pipe leakage, pipe rupture, tank leakage, tank rupture and spills. Probable causes for the pipe leakage and the pipe rupture are collisions, corrosion, freezing and falling objects. For the tank leakage and tank rupture, probable causes are corrosion, thermal decomposition ("puff"), collision and undermining. Concerning spills, the only probable cause found are leaking process equipment. It is important to be aware of the fact that there are several other risks, scenarios and causes existing beside the ones mentioned here.

The gas release in case of several different scenarios has been simulated using the software ALOHA. The software unfortunately cannot account decaying concentrations in the liquid releasing the gas, neither account the fact that ClO_2 decomposes in air. Consequently, the extent of the gas release as well as the concentration gradients is exaggerated. Never the less, the simulation allows distinguishing between various scenarios. It also confirms that an accident has the potential to create a long range extending gas plume with concentrations above the recommended threshold limit values for occupational health. Close to the source, the concentrations can be very high; concentrations could occasionally reach as high as the lower explosion limit (LEL) or even be mortal.

Based on the identification of risks and the simulations of various scenarios, an "ideal" storage facility was defined. A method for comparing a real ClO_2 storage facility to this "ideal" has been developed. The key features of such "ideal" ClO_2 storage facility are, among others, the use of parallel storage tanks, which can be individually sealed, explosion relief lids on the storage tanks, sufficient dikes, a building surrounding the storage tanks, protection preventing collisions, systems for preventing degassing and neutralizing leakages, systematic inspections and alarm systems. During the development of the method it has been applied at three different ClO_2 storage facilities, all at Swedish pulp mills. The results are very promising. The method allows the user to identify the gap between an actual storage facility and the "ideal" storage facility. The method also indicates, through an easy to comprehend colour coding, in which areas improvement is most imperative. Importantly, the model also allows the user to have confidence in the security level for the storage facility analyzed.

Whilst improvement of the simulations of gas release and adoption of the method to reflect also internationally conceivable risks would even further extend the result from this master thesis, the overall result is still very satisfactory and indicates an efficient route for safe ClO_2 storage facilities. It may finally be noted that the concept used in the method and the master thesis can be efficient and appreciated in other areas within, for example the chemical industry.

References

Abdel-Rahman, M. S. et al., 1985. Toxicity of chlorine dioxide in drinking water. *Journal of Environmental Pathology, Toxicology and Oncology*. Volume 6.

Abrahamsson, M., 2000. *Treatment of Uncertainty in Risk Based Regulations and Standards for Risk Analysis.* [pdf] Available at: http://130.235.7.155/publikationsdb/docs/3116.pdf [Accessed 5 September 2009].

Agency for Toxic Substances and Disease Registry, 2004. *Toxicological profile for chlorine dioxide and chlorite.* [pdf] Available at: http://www.atsdr.cdc.gov/toxprofiles/tp160.pdf [Accessed 29 Sep 2009]

Akselsson, R., 2008. *Människa, Teknik, Organisation och Riskhantering*. Lund: Institutionen för Designvetenskaper

Alp, E. & Boughner, T., 2005. *Risk Assessment for Chlorine Dioxide Systems*. [pdf] Avalaible at: http://psm.chemeng.ca/2005papers/CSChE_PSM_ClO2RiskManagement_AlpBoughnerPaper.pdf [Accessed 9 October 2009]

American Composites Manufacturers Association, 2007. *ABC's of FRP*. [webpage] Available at: http://www.acmanet.org/fgmc/abc_frp.htm [Accessed 19 January 2010]

American Industrial Hygiene Association, 2009. *Current AIHA ERPG Values (2009)*. [pdf] Available at: http://www.aiha.org/insideaiha/volunteergroups/Documents/ERP-erpglevels.pdf [Accessed 19 November 2009]

American Institute of Chemical Engineering, 1994a. *Dow's Fire & Explosion Index Hazard Classification Guide*. New York: American Institute of Chemical Engineering

American Institute of Chemical Engineering, 1994b. *Dow's Chemical Exposure Index*. New York: American Institute of Chemical Engineering

Andreasen, P. & Rasmussen, B., 1990. Comparison of methods of hazard identification at plant level. *Journal of Loss Prevention in the Process Industries*. Volume 3 (4), pp 339-344.

Apostolakis, G., 2004. How useful is quantitative risk assessment? *Risk Analysis.* Volume 24(3), pp 515-520.

Arbetsmiljöverket, 2005. Arbetsmiljöverkets författningssamling AFS 2005:17 – Hygieniska gränsvärden och åtgärder mot luftföroreningar. [pdf] Available at: http://www.av.se/dokument/afs/AFS2005_17.pdf [Accessed 28 September 2009]

Atkins, P. W. & Jones, L., 2000. *Chemistry: molecules, matter, and change*. New York: Freeman

Bercz, J. P. et al., 1982. Subchronic toxicity of chlorine dioxide and related compounds in drinking water in nonhuman primate. *Environmental Health Perspectives*. Volume 46, pp 47-55.

Bergman, G. (gunnar.bergman@swerea.se), 2009. Re: *Fråga angående lagring av klordioxid i GAP-tankar.* [e-mail] Message to C., Käck (bt05ck9@student.lth.se). Sent Thursday 24 September 2009, 12:40. [Accessed 29 Sep 2009]

Budavari, S. et al., 1996. *The Merck index.* New Jersey: Merck & Co

CBC News, 2009. *Chlorine dioxide leak at mothballed B.C. pulp mill spurs evacuation*. [webpage] Available at: http://www.cbc.ca/canada/british-columbia/story/2009/02/22/bc-mackenzie-mill-chlorine-dioxide-leak.html [Accessed 9 October 2009]

Center for Chemical Process Safety, 1999. *Guidelines for Process Equipment Reliability Data-With Data Tables*. New York: Center for Chemical Process Safety

Cornwell, J. B. & Marx, J., D., 2009. *The Significance of Hazard End Points In Quantitative Risk Analysis.* [webpage] Available at: http://www.questconsult.com/hazard.html [Accessed 8 Oct 2009]

Dalarnas Tidning, 2009. *Misstänkt sabotage på SSAB*. [webpage] Available at: http://www.dt.se/nyheter/borlange/article453600.ece [Accessed 19 October 2009]

Dagens Nyheter, 2009. *Industriexplosion i Skoghall*. [webpage] Available at: http://www.dn.se/nyheter/sverige/industriexplosion-i-skoghall-1.911518 [Accessed 17 November 2009]

Dalhamn, T., 1957. Chloride dioxide: Toxicity in experimental animals and industrial risks. *American Medical Association Archives of Industrial Health.* Volume 15, pp 101-107.

Daniel, F. B. et al., 1990. Comparative subchronic toxicity studies of three disinfectants. *Journal of the American Water Association*. Volume 82(10), pp 61-69.

Davidsson, G., Haeffler, L., Ljundman, B. & Frantzich, H., 2003. *Handbok för riskanalys*, Karlstad: Räddningsverket.

Ejvegård, R., 2003. *Vetenskaplig metod.* Lund: Studentlitteratur

Eka Chemicals, 1998a. *Internal Eka Chemicals documentation-Degassing (Häggström&Fontes)*. [doc] [Accessed 19 October 2009]

Eka Chemicals, 1998b. *Internal Eka Chemicals documentation-Degassing (Häggström)*. [doc] [Accessed 19 October 2009]

Eka Chemicals, 1998c. *Internal Eka Chemicals documentation-Incident report*. [Accessed 4 November 2009]

Eka Chemicals, 1999. *Internal Eka Chemicals documentation-Risk assessment*. [Accessed 20 November 2009]

Eka Chemicals, 2000a. *Internal Eka Chemicals documentation-Preliminary Hazard Analysis*. [Accessed 14 November 2009]

Eka Chemicals, 2002a. *Internal Eka Chemicals documentation-Preliminary Hazard Analysis*. [Accessed 20 November 2009]

Eka Chemicals, 2002b. *Internal Eka Chemicals documentation-Incident report*. [Accessed 20 November 2009]

Eka Chemicals, 2003a. *Internal Eka Chemicals documentation-Preliminary Hazard Analysis*. [Accessed 17 November 2009]

Eka Chemicals, 2003b. *Internal Eka Chemicals documentation-Consequence calculations*. [Accessed 17 November 2009]

Eka Chemicals, 2004. *Internal Eka Chemicals documentation-Preliminary Hazard Analysis*. [Accessed 14 November 2009]

Eka Chemicals, 2008a. *Internal Eka Chemicals documentation-Information about ClO_2*. [doc] [Accessed 20 November 2009]

Eka Chemicals, 2008b. *Internal Eka Chemicals documentation-Risk assessment*. [Accessed 20 November 2009]

Eka Chemicals, 2009a. *Chlorine dioxide generation*. [webpage] Available at: http://www.akzonobel.com/eka/products/pulp_and_paper_industry/plant_equipment_it/eka_engineering/products_services/chlorine_dioxide_gen.aspx [Accessed 29 Sep 2009]

Eka Chemicals, 2009b. *Akzo Nobel Pulp and Paper Chemicals*. [webpage] Available at: http://www.akzonobel.com/eka/ [Accessed 10 December 2009]

Elkins, H. B., 1959. *The chemistry of industrial toxicology*. New York: Wiley and Sons.

Enander, A., 2006, Människors behov och agerande vid olyckor och samhällskriser, in: *Ledning av räddningsinsatser i det komplexa samhället*, Fredholm, L. (red.), Göransson, A. (red.), Karlstad: Räddningsverket, pp 31-75.

Environmental Protection Agency, 1996. *Proposed guidelines for carcinogen risk assessment.* Washington D.C: U.S. Environmental Protection Agency. [pdf] Available at: http://www.epa.gov/nceawww1/cancer.htm [Accessed 28 September 2009]

Environmental Protection Agency, 1999. *Alternative Disinfectants and Oxidants Guidance Manual.* [pdf] Available at: http://www.epa.gov/safewater/mdbp/alternative_disinfectants_guidance.pdf [Accessed 29 Sep 2009]

Environmental Protection Agency, 2000. *Toxicological Review of Chlorine Dioxide and Chlorite*. [pdf] Available at: http://www.epa.gov/iris/toxreviews/0496-tr.pdf#page=39 [Accessed 9 December 2009]

Environmental Protection Agency, 2009. *Acute Exposure Guideline Levels (AEGLs)*. [webpage] Available at: http://www.epa.gov/oppt/aegl/index.htm [Accessed 28 September 2009]

Exner-Freisfeld, H., Kronenberger, H. & Meier-Sydow, J., 1986. Intoxication from bleaching with sodium chlorite. *Deutsche Medizinische Wochenschrift*. Volume 111(50), pp 1927-1930.

Ferweda, G., 2004. Upgrades to Storage and Procedures Ensure Safe Use at Chlorine Dioxide, *Pulp & Paper*, Volume 78(6), pp 54-58.

FOA, 1998. *Vådautsläpp av brandfarliga och giftiga gaser och vätskor.* Tumba: Försvarets forskningsanstalt.

Fredette, M. C., 1996. Bleaching chemicals: Chlorine dioxide, In: C., W., Dence, D., W., Reeve, eds. *Pulp bleaching: principles and practice*, Atlanta: TAPPI, pp 60-69.

GHD, 2006. *Bell Bay Pulp Mill Project – Preliminary Hazard Analysis*. [pdf] Available at: http://www.gunnspulpmill.com.au/IIS/V15/V15_A48.pdf [Accessed: 12 October 2009]

Gupta, J. P. et al., 1997. Application of DOW's fire and explosion index hazard: classification guide to process plants in the developing countries. *Journal of Loss Prevention in the Process Industries*. Volume 10 (1), pp 7-15.

Gupta, J. P. et al., 2003. Calculation of Fire and Explosion Index (F&EI) value for the Dow Guide taking credit for the loss control measures. *Journal of Loss Prevention in the Process Industries*. Volume 16 (4), pp 235-242.

Hansson, S. O., 2007. *Konsten att vara vetenskaplig*. [pdf] Available at: http://www.infra.kth.se/~soh/konstenatt.pdf [Accessed 2 November 2009]

Health and Safety Executive, 2003. *Transport fatal accidents and FN- curves: 1967-2001*. [pdf] Available at: http://www.hse.gov.uk/research/rrpdf/rr073.pdf [Accessed 9 December 2009]

Health and safety executive, 2009. *An independent review of HSE methodology for assessing societal risk.* [PDF] Available at: http://www.hse.gov.uk/societalrisk/review.pdf [Accessed 8 Oct 2009]

Health Canada, 2008, *Proposed re-evaluation decision: Sodium chlorate and sodium chlorite*. [pdf] Available at: http://www.hc-sc.gc.ca/cps-spc/alt_formats/pacrb-dgapcr/pdf/pest/part/consultations/prvd-pdrv/prvd2008-09-eng.pdf [Accessed 29 Sep 2009]

IEC, 1995. International Standard - Dependability management part 3: application guide - section 9 Risk Analysis of technological systems. Geneva: International Electrotechnical Commission

International Union of Pure and Applied Chemistry, 2009. *IUPAC Compendium of Chemical Terminology - the Gold Book.* [webpage] Available at: http://goldbook.iupac.org/index.html [Accessed 28 September 2009]

Jönköpings Län, 2003. *Vägledning och policy för kemikalielagring vid tillsyn enligt Miljöbalken*. [pdf] Available at: http://www.lst.se/NR/rdonlyres/8D609025-7530-4832-BA31-AE0474705A64/151742/Jonkopings_lans_kemikaliepolicy.pdf [Accessed 24 November 2009]

Kaplan, S. & Garrick, B., 1981. On the quantitative definition of risk, *Risk Analysis*, Volume 1(1), pp 11-27.

Karlshamns Kommun, 2005. *Riskanalys för det geografiska området Karlshamns kommun*. [pdf] Available at: http://www.karlshamn.se/upload/9649/Riskanalys%20Khamn%202005.pdf [Accessed 12 October 2009]

Karlsson, H. T., 1993. *Processriskanalys*. Lund: Studentlitteratur

Kellman, I., 2003. *Defining risk.* [pdf] Available at: http://www.ilankelman.org/abstracts/kelman2003frn.pdf [Accessed 9 December 2009]

Kemikalieinspektionen, 2009. *Säker kemikaliehantering*. [webpage] Available at: http://www.kemi.se/templates/PRIOpage.aspx?id=4562 [Accessed 25 November 2009]

Kemikontoret, 2001. *Riskhantering 3 – Tekniska Riskanalysmetoder*. Stockholm: Kemikontoret.

Khan, F. I. & Abbasi, S. A., 1998. *Risk assessment in chemical process industries*, [e-books] Available at: http://books.google.com/books?id=_dO3SERngTsC&lpg=PP1&pg=PP8#v=onepage&q=&f=false [Accessed 10 September 2009].

Khan, F. I., 2003. *Risk Assessment Methods according to Dow Chemical Exposure Index*. [ppt] Available at: www.engr.mun.ca/~fkhan/EN-8671/DOW%20CEI_1.ppt [Accessed 3 September 2009].

Kirchsteiger, C., 1999. On the use of probabilistic and deterministic methods in risk analysis. *Journal of loss prevention in the process industry.* Volume 12, pp 399-419.

Kirk, R. E., Othmer, D. F., Kroschwitz, J. I. & Howe-Grant, M., 1993. *Encyclopedia of chemical technology*. New York: Wiley

Lewis, R. J., 2000. *Sax's dangerous properties of industrial materials.* New York: Wiley

Lubbers, J. R. et al., 1984. The effect of chronic administration of chlorine dioxide, chlorite and chlorate to normal health adult male volunteers. *Journal of Environmental Pathology, Toxicology and Oncology*. Volume 6, pp 229-238.

Masschelein, W. J., 1979. *Chlorine dioxide: chemistry and environmental impact of oxychlorine compounds.* Ann Arbor: Ann Arbor Science

Meggs, W. J., Elsheik, T. & Metzger W. J., 1996. Nasal pathology and ultrastructure in patients with chronic airway inflammation (RADS and RUDS) following an irritant exposure. *Journal of Toxicology- Clinical Toxicology*. Volume 34(4), pp 383-396.

Miljösamverkan Västra Götaland, 2000. *Handledning för kemikalietillsyn på industrier och hos andra användare av kemiska produkter*. [pdf] Available at: http://cf.vgregion.se/miljo/miljosamverkan/dokument/kemtillsynshandledning_nov00_def.pdf [Accessed 24 November 2009]

Ministry of Environment in British Columbia, 2009a. *Mackenzie Pulp Mill (Worthington Pulp Mill) – Chlorine Dioxide Release*. [webpage] Available at: http://www.env.gov.bc.ca/eemp/incidents/mackenzie-mill-chlor-diox-feb09.htm [Accessed: 11 October 2009]

Ministry of Environment in British Columbia, 2009b. *Prince George Pulp Mill - Chlorine Dioxide Spill*. [webpage] Available at: http://www.env.gov.bc.ca/eemp/incidents/pg-chem-spill-feb09.htm [Accessed: 11 October 2009]

Miyamoto, J., 1996. Environmental and health issues. *Pure and applied chemistry*, Volume 69(9), pp 1737-1748.

National Institute of Standards and Technology, 2005. *Oxidative Stress/DNA Damage and DNA Repair*. [webpage] Available at: http://www.cstl.nist.gov/div831/DNATechologies/DNA_Damage_Repair.htm [Accessed 28 September 2009]

National Library of Medicine, 2009. *Methemoglobinemia*. [webpage] Available at: http://www.nlm.nih.gov/medlineplus/ency/article/000562.htm [Accessed 28 September 2009]

National Research Council, Committee on Acute Exposure Guideline Levels and Committee on Toxicology, 2007. *Acute Exposure Guideline Levels for Selected Airborne Chemicals: Volume 5*. [pdf] Available at: http://www.nap.edu/catalog.php?record_id=11774 [Accessed 28 September 2009]

Nationalencyclopedin, 2009. *Surte*. [webpage] Available at: http://www.ne.se/lang/surte [Accessed 17 November 2009]

New York Times, 1988. *Maine Monitors Chlorine Leak at Paper Mill*. [webpage] Available at: http://www.nytimes.com/1988/02/07/us/maine-monitors-chlorine-leak-at-paper-mill.html [Accessed 9 October 2009]

Nilsson, J., 2003. *Introduktion till riskanalysmetoder*. [pdf] Available at: http://130.235.7.155/publikationsdb/docs/3124.pdf [Accessed 2 September 2009].

North Carolina Morning Star, 1993. *Gas leak evacuates pulp mill*. [webpage] Available at: http://news.google.com/newspapers?nid=1385&dat=19930624&id=pREWAAAAIBAJ&sjid=6BQEAAAAIBAJ&pg=1316,3063991 [Accessed 9 October 2009]

Nystedt, F., 2000. *Riskanalysmetoder.* [pdf] Available at: http://130.235.7.155/publikationsdb/docs/7011.pdf [Accessed 6 September 2009].

Oak Ridge Institute for Science and Education, 2009. *ERPG Definitions and Background Information*. [webpage] Available at: http://orise.orau.gov/emi/scapa/erpg-defn.htm [Accessed 19 November 2009]

OxyChem, 2009. *Treatment of drinking water with chlorine dioxide (ClO_2).* [pdf] Available at: http://www.oxy.com/Our_Businesses/chemicals/Documents/sodium_chlorite/technicalData/Treatment%20of%20Drinking%20Water%20with%20Chlorine%20Dioxide.pdf [Accessed 29 Sep 2009]

Pappersnytt, 2009. *Slarv orsakade explosion på Stora Enso Skoghall*. [webpage] Available at: http://pappersnytt.se/index.php/nyheter/1-nyheter/285-slarv-orsakade-explosion-pa-stora-enso-skoghall- [Accessed 9 October 2009]

Paulet, G., et Desbroussess, S., 1970. On the action of chloride dioxide (ClO2) at low concentrations on laboratory animals. *Archives des Maladies Professionnelles: Medecine du Travail et de Securite Sociale*. Volume 31(3), pp 97-106.

Paulet, G., et Desbroussess, S., 1972. Sur la toxicologie du ClO_2. *Archives des Maladies Professionnelles et de l'Environnement*. Volume 33(1-2), pp 59-66.

Paulet, G., et Desbroussess, S., 1974. Action du bioxyde de chlore sur le rat en exposition discontinue. *Archives des Maladies Professionnelles et de l'Environnement*. Volume 35(9), pp 797-804.

Pelin, K., (kalle.pelin@akzonobel.com), 2009. Re: *En snabb fråga*. [e-mail] Message to C., Käck (bt05ck9@student.lth.se). Sent Friday 14 November 2009, 13:06. [Accessed 10 December 2009]

Prevent, 2008. *Kemiska ämnen*. [online database] (Updated December 2008) Available at: http://elin.lub.lu.se/elin?func=citrix&application=ASN_chemical_substances&resid=140 [Accessed 29 Sep 2009]

Prince George Fire Rescue Service, 2009. *News Release - Chemical Spill at Canfor Sites on PG Pulp Mill Road*. [pdf] Available at: http://www.env.gov.bc.ca/eemp/incidents/pdf/09-02-01-pg-chemspill-news.pdf [Accessed 11 October 2009]

Rausand, M., 2005. *Preliminary Hazard Analysis*. [pdf] Available at: http://www.ntnu.no/ross/srt/slides/pha.pdf [Accessed 18 January 2010]

Renn, O., 1998. The role of risk perception for risk management, *Reliability Engineering and System Safety*, Volume 59(1), pp 49-62.

Richardson, S.D., Plewa, M. J., Wagner, E. D., Schoeny, R. & DeMarini, D. M., 2007. Occurrence, genotoxicity, and carcinogenicity of regulated and emerging disinfection by-products in drinking water: A review and roadmap for research, *Mutation research*, Volume 636, pp 178-242.

Schorsch, F., 1995. *Study of acute toxicity of chlorine dioxide administered to rats by vapor inhalation*. Verneuil-en-Halatte: Institut National de l'Environnement Industriel et des Risques (INERIS).

Simpson, G. D., 2005. Practical Chlorine Dioxide. Houston: NACE International

Sinnott, R. K. et al., 2005. *Chemical Engineering Volume 6: Chemical Engineering Design*. [e-book] Oxford: Butterworth-Heinemann. Available at: http://books.google.se/books?id=DJaxUL3numgC&pg=RA1-PA378&lpg=RA1-PA378&dq=The+Mond+Fire,+Explosion+and+Toxicity+Index&source=bl&ots=2b-8qzcX2s&sig=oM10dpqXNJckycmiz0Y8eLNe58c&hl=sv&ei=lK2fSp-rOo_a-Qav9PjkDw&sa=X&oi=book_result&ct=result&resnum=2#v=onepage&q=The%20Mond%20Fire%2C%20Explosion%20and%20Toxicity%20Index&f=false [Accessed 3 September 2009].

Slater, R., 1998. *Safety Critical Systems Analysis.* [webpage] Available at: http://www.ece.cmu.edu/~koopman/des_s99/safety_critical/ [Accessed 8 Oct 2009]

Slovic, P., 1999. Trust, Emotion, Sex, Politics, and Science: Surveying the Risk-Assessment Battlefield, *Risk Analysis*, Volume 19(4), pp 689-701.

Statens Haverikommission, 2008. *Rapport RO 2008:02: Olycka med utsläpp av svavelsyra vid Kemira Kemi AB i Helsingborg*. [pdf] Available at: http://www.helsingborg.se/upload/Trygghet%20sakerhet%20och%20beredskap/Haverikommissionens_rapport_RO_2008_08.pdf [Accessed 17 November 2009]

Tyler, B. J. et al., 1996. *A toxicity hazard index*. [pdf] Available at: http://membership.acs.org/c/chas/jchas_archives/1996/3(1)/1996-3-1tylertoxicityhazardindex.pdf [Accessed 10 December 2009]

World Health Organization, 2002. *Concise International Chemical Assessment Document 37*. [pdf] Available at: http://www.who.int/ipcs/publications/cicad/en/cicad37.pdf

[Accessed 28 September 2009]

Värmlands Folkblad, 2000. *300 liter klordioxid läckte ut i Skoghall*. [webpage] Available at: http://www2.vf.se/vf/docs/visa.asp?nyhetsID=ea57f2f7fc5d8a6cae5284bea67b2d8b [Accessed 9 October 2009]

Värmlands Folkblad, 2002. *Stort pådrag vid Gruvön vid utsläpp av klordioxid i går kväll*. [webpage] Available at: http://www2.vf.se/vf/docs/visa.asp?nyhetsID=363ae46591578fd4ec581261492e3974 [Accessed: 9 October 2009]

Värmlands Folkblad, 2003. *Litet koldioxidsläpp från Gruvön*. [webpage] Available at: http://www2.vf.se/vf/docs/visa.asp?nyhetsID=3c69f9659c9709e6fa4289d8a61fcf68 [Accessed 9 October 2009]

WorkSafeBC, 2009. *Young Worker Accidents*. [webpage] Available at: http://www2.worksafebc.com/Topics/YoungWorker/WCBInitiatives-YWAccidents.asp?reportid=33957 [Accessed 9 October 2009]

Appendix A – Different methods for assessing risk

Table of Contents

1. Qualitative methods for risk assessment

1.1 Hazard and Operability Analysis (HazOp)

This method has been especially developed within the chemical process industry to meet the requirements of this type of business. The method itself is thorough and systematic, based on a number of “guide words” (Davidsson et al., 2003). There are seven “guide words”, for example “none”, “opposite”, “more” and “less” (Karlsson, 1993). Systematically, these words are being applied throughout the system, following the blueprints and diagrams. A simple pipe could be analyzed with those “guide words” as well as the reactor. What happens if there are “more” flow in the pipe? What happens if the flow goes the “opposite” way? What happens if there is “none” flow (Kemikontoret, 2001)?

The “guide words” are being used to challenge the normal functions of different components, for example pumps or valves, as well as parameters, for example temperature or pressure, within the system. Some of those challenges will reveal dangerous conditions and risks. Besides those, the method will also reveal lots of aggravating conditions, maybe not dangerous, but definitely affecting the capacity and production of the industry (Kemikontoret, 2001).

Since the method is very thorough, it requires experience and knowledge as well as a lot of technical background material to be conducted sufficient (Kemikontoret 2001).

1.2 What if?-analysis

What if? This question is the centre of the method with the same name. From this simple question, the user evaluates and investigates the possible effects from technical malfunctions or wrong handling from employees as well as lapse from the normal circumstances and routines. The method has great resemblance with simple brainstorming. What if pump A breaks down? What if the operator misses the warning signal? What if substance A instead of substance B is filled into the storage tank and later admitted into the process? There are a never-ending number of possible questions (Kemikontoret, 2001 & Nilsson, 2003).

Of course, not all of these different scenarios will result in an accident or divergence. Sometimes the answer to the question is simply that nothing happens. Other times the answer to the question ascertains that there will be some kind of consequence (Kemikontoret, 2001). Sometimes this method also includes the grading of this consequence, for example small or large, as well as grading the probability or frequency (Karlsson, 1993).

The method is very adoptive and can be used almost anytime and anywhere (Kemikontoret, 2001). However, to be conducted properly the method requires that the user, or the users, have extended knowledge and experience about the system and the properties within (Karlsson, 1993). Since there is no guidelines on how to conduct this method there is always a risk of the evaluation to be inconclusive, missing out important elements, because of lack of knowledge. However, since the method being used frequently within the industry for a long time, there is some praxis. One of the more helpful praxis are the advice to let the questions be asked in sequences that follows the actual process, blueprints and handling (Kemikontoret, 2001).

Since this paper focuses on risk assessment there is an amplification of this part of the method. However, the method in large also consist of suggestions for preventive measurements, investigations of the possible reasons behind the event as well as other features (Davidsson et al., 2003).

1.3 Checklists

Checklists are a wide method with range from simple checklists to more complex checklists (Kemikontoret, 2001). The most basic checklist for risk assessment is the one used when filling out the chemicals used at the industry. The information could consist of flammability, reactivity and toxicity. These types of checklists require minimal knowledge and experience (Karlsson, 1993). Normally, the degree of complexity of the checklist is somewhat higher and more experience and knowledge about the industry in question is required (Kemikontoret, 2001).

Commonly for all checklists is the fact that they are based on earlier experience. The dangers and risks of the industry are already known, and what the user is doing is simple to systematically look for these risks within the industry (Kemikontoret, 2001). The checklist also has the function of assuring the user that all necessary precautions and routines are in order with the praxis (Davidsson et al., 2003).

The checklists can be used almost anytime, during the early planning of the process, during the start of the process or during the ongoing running of the process. However, in order to conduct a proper risk assessment, the method needs to be adapted to the object, with accessible and distinct questions. What is even more important is the fact that these questions are up to date and asked according to the most recent legislations and information (Kemikontoret, 2001).

The type of checklist dealt with here should not be confused with the general checklists being used within almost every method for risk assessment to ensure that the proper steps of the method are being conducted and in the right order (Davidsson et al., 2003).

1.4 Preliminary Hazard Analysis (PHA)

This method is very straightforward, following the general description of a qualitative method for risk assessment. Simply review the defined system of your industry and identify all risks and possible accidents (Davidson et al., 2003). There are several different ways to identify hazards in a PHA. Rausand (2005) suggests, amongst other ways, to examine similar systems, review previous hazard analysis for similar systems and brainstorming in teams. The next step is to find the consequences of these and the cause of them (Karlsson, 1993). This method does not focus on the details, but the overall picture. The result from the PHA might be used as a guide for what areas of the analyzed object that should be more thoroughly examined (Nilsson, 2003).

The number of different variations for his method is huge, differing between different literatures (Kemikontoret, 2001). Some of them choose to grade the consequence and the possibility of the event, while others try to find suggestions for countermeasures (Karlsson, 1993).

The greatest problem with this method is the straightforwardness and the lack of systematic in the method. There is no certainty that the user have covered all of the possible accidents or risks, since there is no real working process for this method. The user has to rely on his experience and intuition (Karlsson, 1993).

1.5 Failure Modes and Effects Analysis (FMEA)

This method conducts a review and listing of the possible failure modes and failure functions among the parts and components of a system, in this case a chemical plant (Kemikontoret, 2001). Furthermore, it proposes different causes of these failures as well as possible countermeasures (Davidsson et al., 2003).

Failure modes, or failure functions, is the variation from the normal function, for example “open”, “closed”, “stop”, “on-stream” or “leakage”. Of course, some of these failures directly imply a risk to the industry. In other cases, they indirect imply this risk through sequences of effects or other relations (Kemikontoret, 2001). One of the greater disadvantages of this method is the inability to foresee much of these sequences, combinations of failures and events leading to an accident. The method best detect the linear relations (Kemikontoret, 2001).

Failure Mode, Effect and Critically Analysis (FMECA) is often mentioned in the same breath as Failure Modes and Effect Analysis and muddled with that method. However, there are some additional features in the first method not included into the Failure Modes and Effect Analysis (FMEA), more exactly the estimation and grading of consequences (Nystedt, 2000).

1.6 Human Reliability Analysis (HRA)

Many disturbances or direct accidents in the technological systems are caused by the wrong decisions or actions among the operators, maintenance personal or other personal. Other times random disturbances require the personal to make swift and uncertain decisions, which will affect the process and the industry. Therefore, the analysis of human reliability is an important component alongside the more technological risk assessment (Kemikontoret, 2001).

In order to find situations causing trouble for the personal, a broad understanding of the different parameters affecting the personal in the moment of the decision is needed. There is no question about the personal always doing what they think is the best or the most right. However, different parameters affecting the personal can cause misunderstanding or mishandling (Kemikontoret, 2001). These parameters consist of technological, educational as well as organizational aspects (Nystedt, 2000). The list of possible affecting parameters is very long. Various things as a stressful working environment, insufficient education, ambiguous alarm or unclear routines can be mentioned (Kemikontoret, 2001).

2. Semi-quantitative methods for risk assessment

2.1 Dow Fire and Explosion Index (Dow F&EI)

The Dow Fire and Explosion Index was created in 1964 by the Dow Chemical Company (American Institute of Chemical Engineers, 1994a). This first document was based on something called the Factory Mutual’s Chemical Occupancy Classification Guide, which in turn was based mainly on experiences over the past years in the United States (Gupta, et al., 1997). Since then, the Dow Fire and Explosion Index has continuously evolved within the Dow Chemical Company and furthermore been published and popularized by the American Institute of Chemical Engineers. Today, the Dow Fire and Explosion Index are spread all over the world and frequently used (American Institute of Chemical Engineers, 1994a).

The Dow Fire and Explosion Index is used to evaluate the risk of fire and explosions in chemical industries. Preferentially, the method is used during the early planning and construction of the industry to evaluate and possibly help find alternative, better, constructions. Primary is the breakdown of the industry into separate units, for examples storages, pumps, reactors or absorbers. Each one of those units will be looked upon with the same methods, estimating their contribution to the total risk. The first step is to obtain the material factor (MF). The material factor is a measure of the energy that could be released from the material, more exactly the chemical, based on reactivity and flammability. Next, the product unit hazards factor (PUHF). To calculate this factor you have to take into account different penalty factors, generated from properties of the process. The product of the MF (the danger with the chemicals) and the PUHF (the danger with the process) is multiplied and becomes the index. This index can be compared with an existing and pre-determined table for the indexes. This table consists of five different degrees, from light through moderate, intermediate and heavy to severe (American Institute of Chemical Engineers, 1994a).

In summary, you can ascertain that the more dangerous chemicals you put into the system the higher the index will be. The same reasoning complies with the dangerous process equipment, risk of spilling, careless handling of chemicals and so on. On the other hand, working with improvements of the safety by installing monitoring instruments, reduplicate critical equipment or arranging for handling an accident will lower the index (Kemikontoret, 2001).

As mentioned earlier, concerning the limitations of the semi-quantitative methods, the Dow Fire and Explosion Index cannot give a measurement of the risk associated with the different units of the industry. What it can do, is giving relative measurements of the risk, providing the management of the industry the opportunity to look more closely at those units and evaluate the risks with another method (Kemikontoret, 2001).

Besides providing the index, which is the main function of this method, the Dow Fire and Explosion Index also can provide information about the maximum probable property damage (MPPD) as well as other features (American Institute of Chemical Engineers, 1994a).

2.2 Mond Fire, Explosion and Toxicity Index (FETI)

The Mond Fire, Explosion and Toxicity Index was created in the middle of the 1970s by the Imperial Chemical Industries (Tyler, et al., 1996), because of the Flixborough accident (Andreasen & Rasmussen, 1990). Since then, the method has repeatedly gone through reform and improvements (Sinnott, et al., 2005).

Being founded on the Dow Fire and Explosion Index, and with the same objective, there is great resemblance in the methods. The working process of the methods is much similar, starting with the breakdown of the industry into minor units, the material factor (MF) and later different factors linked to the design of the process and the equipment. However, there are several discrepancies, not surprisingly, since the method was meant as a further development and improvement of the predecessor. One of the more significant differences during the calculation is the including of toxicity into the assessment. Other discrepancies worth mentioning during the calculation is the wider range of chemicals, processes and storage installations and the inclusion of offsetting factors for good design as well as control instruments and safety devices (Khan & Abbassi, 1998 and Tyler, et al., 1996).

There are also some differences concerning the final product, the indexes. The Mond Fire, Explosion and Toxicity Index present four indexes instead of one. These are fire, internal explosion, aerial explosion and overall risk. Like the Dow Fire and Explosion Index these calculated indexes can easily be compared with a pre-determinate scale. The scale consists of the degrees: light, low, moderate, high (two different groups), very high and intensive (Andreasen & Rasmussen, 1990). The gradation of the scale is relative, based on experience and judgment of analysts, giving a relative measurement of the risk, like the Dow Fire and Explosion Index (Tyler, et al., 1996).

Compared with the Dow Fire and Explosion Index, this method is by many considered as a more functional and better method, due to the fact that it is more elaborated and take into account a greater wide of parameters. Nevertheless, the method is not used in the same extent as the predecessor. Perhaps the explanation could be found in the fact that this method require more effort and knowledge from the user as well as the special features of the method still is not although known among professionals (Gupta, et al., 2003)

2.3 Dow Chemical Exposure Index (Dow CEI)

The Dow Chemical Exposure Index was created in 1986 by the Dow Chemical Company following several petrochemical accidents and especially the severe accident at the chemical plant in Bhopal, India (American Institute of Chemical Engineers, 1994b). The Dow Fire and Explosion Index focuses at hazards from fire and explosion, while the Mond Fire, Explosion and Toxicity Index to some account include toxicity, but mainly focused on the same hazards. Because of this, there was not really any method taking into account the possible hazards connected to the toxicity of the chemicals (Tyler, et al., 1996). The Dow Chemical Exposure Index was created to fill this void, functioning as a complement to the existing Dow Fire and Explosion Index. Since then the Dow Chemical Exposure Index has slowly evolved and undergone several improvements (American Institute of Chemical Engineers, 1994b).

The Chemical Exposure Index is used to evaluate the risk from possible unwanted chemical releases affecting the acute health of people within the industry or the neighboring communities and industries. The approach of this method has great resemblance with the Dow Fire and Explosion Index. Every possible source of chemical release is looked upon, much like the breakdown of the industry into smaller units. The working process for these sources is then based on the evaluation of five different factors: acute toxicity, quantity, molecular weight, distance from area of concern and different process variables. From assigning those different factors with a grade and multiply those, you gain the index. As was the case with the predecessor, the Dow Chemical Exposure Index does not present an absolute statement, but a relative. With the index one can compare the results with different possible risk sources as well as other operations where there are more information and experience (American Institute of Chemical Engineers, 1994b). The comparison might be the decision basis for where to strengthen the safety or conduct a more thorough evaluation (Khan, 2003).

Besides providing the index, the Dow Chemical Exposure Index has also evolved taking within features like calculating the dispersion (American Institute of Chemical Engineers, 1994b).

3. Quantitative methods for risk assessment

3.1 Deterministic risk assessment

When performing a deterministic risk assessment, the goal is to answer the question, what are the consequences? Since the deterministic approach assumes that the accident will or already has occurred, the probability can be neglected and the risk assessment focuses completely on the consequences (Kirchsteiger, 1999). Therefore, it is sometimes called just consequence analysis.

In risk assessments of chemicals and chemical processes, the consequences are for example expressed in concentrations or heat radiance at different distances from the source. These values are calculated using simulations or advanced models describing such things as the spreading of chemicals or explosion radius. These models take in account all affecting parameters, everything from wind speed to the density of the chemical, humidity and so on. The uptake, distribution and effects of the chemical in plants, animals or humans, must also be modeled and considered (FOA, 1998). The calculated values can then be compared to threshold values giving a hint of the severity of the consequences.

3.2 Probabilistic risk assessments

This class of methods consists of quantitative risk assessment (QRA) and the tree-methods.

3.2.1 QRA

To perform a QRA is essentially to answer three questions. First, what can go wrong? Second, what is the probability of this happening? Third and final, what are the consequences if this happens? In order to answer these questions, the possible scenarios must be identified and the probabilities and consequences of these scenarios must be given numerical values (Apostolakis, 2004). The difference from the deterministic methods for risk assessment is, as stated above, the inclusion of a numerical estimation of the probability.

The answer to the first question is important for answering the two other questions in a correct manner. Therefore, scenarios have to be created to model the course of events. Every scenario consists of events that lead to an undesired end state, for example an explosion or release of a toxic gas (Apostolakis, 2004). Criticism has been raised that it is impossible to take every possible scenario in account, and that a quantitative risk assessment therefore cannot give a value of the total risk. To silence the critics, Kaplan and Garrick (1981) suggest the use of experts and experiences to create a list of plausible scenario categories and then create a category that contains "*all scenarios not otherwise included in the list*". These are then given an approximated value by experienced professionals. By doing this, "every" scenario possible can be accounted for in the QRA (Kaplan & Garrick, 1981).

The probabilities of the different scenarios are often derived from empirical data, logical systems or expert opinions. Empirical data are statistics from experiments or historical data that gives the probability of a scenario. Logical systems are for example fault trees, where the probability for the scenario is calculated from the probabilities for every event leading to the end state. This is explained more thoroughly later. Expert opinions are subjective assumptions and can be used to esteem the probabilities of an event (Davidsson, et al., 2003).

The result from this method is, as mentioned before, a numerical value. There are several methods to present this value visually, thus making it easier for those who read to overlook and comprehend. The most common way of presentation is by drawing the individual risk as contours on a map. An example of this is presented in figure A.1. One can also plot the societal risk in a FN-curve. The FN-curve is a plot of the cumulative frequencies of different scenarios and the expected consequence of these scenarios expressed as number of fatalities. An example of this is presented in figure A.2. The individual risk measure are often given as the risk of dying per year for a person who spends the entire year close to the risk source (Davidsson, et al., 2003). The societal risk, often referred to as the group risk, represents the potential loss of life or number of deaths per year (Health and safety executive, 2009). Unlike the societal risk, the individual risk does not depend on how many persons that inhibits or stay in the area (Nystedt, 2000).

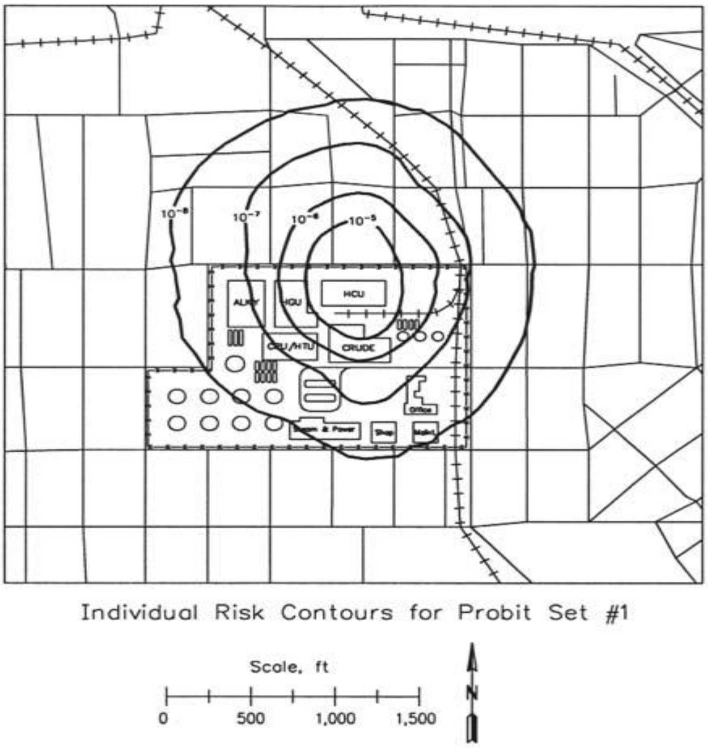

Figure A.1, An example of risk contours representing the individual risk close to a risk source (Cornwell & Marx, 2009).

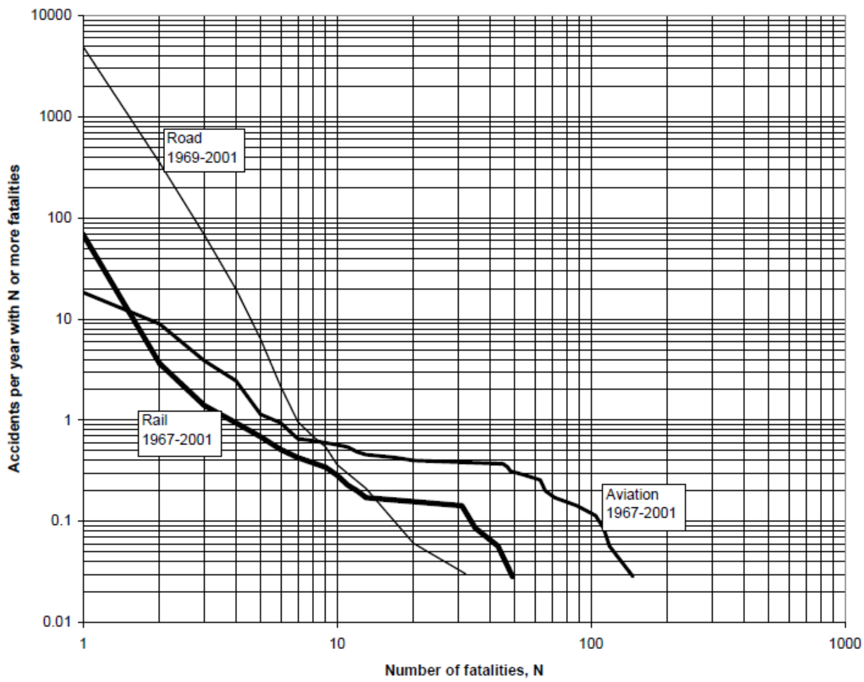

Figure A.2, An example of a FN-curve used for presenting the societal risk (Health and safety executive, 2003).

3.2.2 Event and fault trees

Event trees are used to identify and quantify possible outcomes from a specific triggering event. Starting with the event, one looks at the sequence of actions of the operator and equipment, creating branches that form different scenarios with different consequences. By introducing probabilities into the branches, the probability for each consequence might be calculated. This method is often referred to as a bottom-up-method, meaning that it starts with one triggering event branching out to a set of consequences (Davidsson, et al., 2003). An example of this is presented in figure A.3.

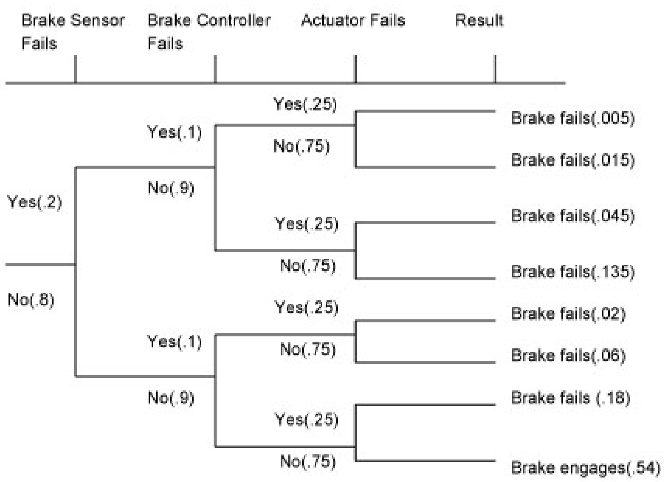

Figure A.3, An example of an event tree. The triggering event is that the brake sensor fails. The system then branches out to the different consequences (Slater, 1998).

In contrast to event trees, fault trees are a top-down-method. This means that the method starts with one consequence or outcome, then trying to identify what different triggering events that may lead up to the consequence. The tree consists of the logical expressions “and” and “or”, describing the course of events leading to the specified consequence. The logical expression “and” means that two or more events have to occur at the same time for the examined consequence to happen. The logical expression “or” means that only one of a number of possible events has to occur for the examined consequence to rise. Probabilities might also be incorporated in this method (Davidsson, et al., 2003). An example of this is presented in figure A.4.

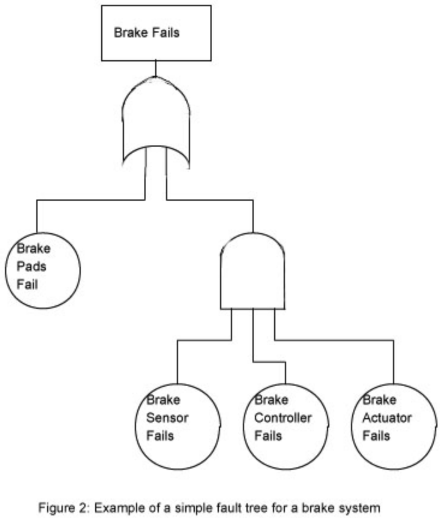

Figure A.4, The fault tree identifies events leading to a consequence. “And” and “or” gates are used to logically model the system investigated (Slater, 1998).

Both these methods are often used as integrated parts of a QRA.

Appendix B - Representative ClO_2 storage facility

The representative ClO_2 storage facility is not a model in the traditional sense, but more of a summary and context of the impressions and information from the different study visits. Several conditions and properties were common for these visited ClO_2 storage facilities. These common denominators are the base for the representative ClO_2 storage facility.

The quantity of ClO_2 stored varied between the ClO_2 storage facilities. The largest storage had a capacity of 1500 m^3 while the smallest had a capacity of 600 m^3. In some of the ClO_2 storage facilities the storage capacity were divided between equally large storage tanks, operated parallel and connected with each other as communicating vessels. The storage tanks were not completely filled. The filling degree varied within 70% to 80 %. In case of overfilling of the storage tanks, some of them had overleap. All of the different ClO_2 storage facilities had level measure units to avoid overfilling in the first place.

All the visited ClO_2 storage facilities were located close to waters. In two cases, the storage tanks were located in instant proximity to the water, probably not more than 70 meters from the water. All of the pulp mills were located in the outskirts of villages or minor towns, close to residential areas. The distance between the ClO_2 storage facility and the closest residential areas varied between 400 meters and 800 meters. There were however, several larger buildings sited inside the pulp mill, some of them situated between the storage area and residential areas. Perhaps these buildings could somewhat embower and narrow a possible leakage of gaseous ClO_2.

Around the ClO_2 storage facility there were mainly areas of pebble or asphalt, scattered building and random junkyard. In the asphalt around the storage tanks there could be found wells to the drainage system, numbers varying between the ClO_2 storage facilities. There were uncertainties whether those were incorporated in a closed system or open to the regular drainage and purification plant. In one case there were instruments monitoring the drainage, able to enclose an unwanted leakage. At others, the drainage went directly to the nearby waters or the purification plant. At all of the ClO_2 storage facilities this drainage system as well as other piping systems runs right under the storage tanks. In case of an extended leaking, this could undermine the storage tanks causing a rupture. Since the most of the ClO_2 storage facilities were old facilities with a long history of industry, there are great chances of even more piping systems than the known ones located in the ground. However, it is unlikely that these are still being used.

One of the ClO_2 storage facilities had their storage tanks out in the open while the others had their storage tanks partly inside buildings.

None of the visited ClO_2 storage facilities had a sufficient dike built around the tanks. In fact, there was only one having a dike at all. However, this dike was only able to contain about 30% to 50% of the maximum volume stored.

The location of the inbound and outbound pipes as well as the pumps varied between the ClO_2 storage facilities. It was hard to find any general design. In some cases, these inbound and outbound pipes were placed in pipe bridges. In general, they were unprotected, but located away from traffic.

In most of the cases, the storage tanks at the ClO_2 storage facilities were situated close to the deliverance area of chemicals. This means that there are heavy traffic, tanker trucks and freight trucks, passing in the immediate vicinity of the tanks. On top of that, there is constantly traffic all over the pulp mill with smaller vehicles, forklifts, trucks and so on. The standard of the protection against collisions varied between the different ClO_2 storage facilities. One mill had what seemed to be sufficient protection. One had some protection, but not sufficient, while the last one had no protection at all.

All of the ClO_2 storage facilities were located in close to or at small distance from other large storage tanks containing chemicals. At some of the visited ClO_2 storage facilities, there was no distance between them, while in others the storage tanks were located at different ends of the building or around a corner. Examples of chemicals stored nearby are sodium chlorate ($NaClO_3$), sulfur dioxide (SO_2), sulfuric acid (H_2SO_4), hydrogen peroxide (H_2O_2) and methanol (CH_3OH).

The ClO_2 storage facilities and the pulp mills had generally short distances to the nearest fire station. In one case, the fire station was located just outside the front gate, while another have had their own fire station at the actual pulp mill until some years ago. None of the visited stated that they had sprinklers in the immediate vicinity to the ClO_2 storage facility.

The storage tanks and pipes were made of FRP lined with a layer resistant to corrosion. An external organization or company inspects the tanks. The inspections look at the corrosive damages as well as signs of cracks or other weaknesses in the material. At some ClO_2 storage facilities, inspections are carried out every sixth year. At others, the experts give their opinion on when to conduct the next inspection. Some questions about the inspection companies and their knowledge were raised. No one was questioning the expert organization however. The inbound and outbound pipes of the storage tanks are inspected with the same routines and frequency. The workers stated that there is almost never any leakage from the actual pipes. In the event of a leakage, the cause is often old seals rather than damaged pipes. Freezing could be an issue, but it seemed like the workers at most of the ClO_2 storage facilities are aware of this problem and take countermeasures.

Since generation of gaseous ClO_2 inside the storage tanks is unwanted due to the risks of explosion, the storage tanks were ventilated. The ventilation strips the gas from above the solution, keeping the concentration of the gas low. This ventilation system is driven by fans in atmospheric processes or by the main process vacuum in vacuum processes. The ClO_2 storage facilities all had another ventilation system in standby in case of malfunction of the regular system. Furthermore, the water used for absorbing the ClO_2 is kept at a low temperature, if necessary by the use of chillers.

There have been occasional thermal decompositions in the reactors of all ClO_2 production facilities looking back in time. Nowadays this phenomenon is quite rare. However, there are still a possibility of this occurring in both reactor and storage tanks. For this matter, all the storage tanks were equipped with explosion lids to release the raised pressure from inside the tank. The storage tanks also had vacuum release to counteract sudden pressure decreases.

There was a pump moving the solution from the manufacturing to the storage tanks and then another pump distributing the solution from the storage tanks. Both these pumps had a reserve pump standing in standby. Some of the ClO_2 storage facilities had several distribution lines from the storage tanks and therefore several pairs of pumps. It is common that within the pair of pumps, the work is divided, the pumps taking turns performing. It is rare that these pumps malfunction. One of the workers stated that they have not replaced their pumps since 1989, while another stated a technical lifetime of 10 years to 15 years. In both cases, the representatives talked about the pump itself. Seals, filling and other exchangeable equipment are replaced frequently to prevent smaller leakages, approximately once every 3 years. These smaller leakages are more common than the pumps malfunctioning.

Malfunction among the different valves is also unusual. With proper maintenance and “exercise”, they have a technical lifetime similar to the pumps. Of course, the ClO_2 storage facilities stated this lifetime somewhat different, probably on the cause of the usage of different types and brands. If the function of the valves is decreased, they are replaced.

All of the ClO_2 storage facilities had special prohibitions for lifting equipment over the storage tanks, in order to avoid equipment from falling onto the storage tanks and possibly damage them. In one of them there was also a prohibition against placing or storing equipment or goods close to the storage tanks.

Two out of the three ClO_2 storage facilities had automatic gas detectors placed in the surroundings of the storage tanks. However, the number of detectors varied as well as the location. Foremost, the detectors were located inside buildings, mainly close to the reactor and similar equipment. None of them had automatic detectors outside at the storage tank area. The detection level of the instruments differed between the ClO_2 storage facilities, between 0.1 ppm and 0.3 ppm. The detectors immediately send a signal to the operator in case of high concentrations as well as automatically sound signals and lights. The operator could take measures, sounding the alarm and initiating an evacuation of the part of the pulp mill including the ClO_2 storage facilities. With a telephone call, the operator could alert personal conducting a more extent evacuation and alarm procedure. Of course, the routines for this procedure varied some between the different visited locations. Some of the ClO_2 storage facilities also had a manual button for sounding the alarm. There were no systems for preventing the degassing of ClO_2 from a leakage or preventing the spreading of gaseous ClO_2 as well as the solution of ClO_2.

Workers at the different ClO_2 storage facilities stated that it is common that one can smell ClO_2 while close to the facility. Some stated this to be more frequent than others did. The smell of ClO_2 indicates that the concentration in the air is above the recommended Swedish “Takgränsvärde”. However, it is unclear whether the contamination of the air could come from leakage of the storage tanks, the pipes, the reactor equipment or other equipment.

The study visits gave the impression that the safety awareness in general had shortcomings. Of course, there were differences in the safety awareness between the visited ClO_2 storage facilities. The most distinct observation was the fact that workers seldom made use of the breathing mask, even if they could smell ClO_2 in the air. Like mentioned above, this smell was a clear indicant that the concentrations had reached the “Takgränsvärde”. The workers negligent established that the smell was there frequently and they know they should make use of their breathing masks. One of the pulps mills had had a compulsion on the usage of breathing mask. However, this compulsion had been withdrawn. The workers themselves also stated that the respect for the gas alarm were somewhat low, possibly on the course of the alarm sounding too often. To gain a deeper understanding for the safety culture and other aspects of the safety awareness was difficult considering the short amount of time spent at the different ClO_2 storage facilities. The ClO_2 storage facilities had regular meetings with management, experts and workers concerning among other things the safety aspects. The frequency of these meetings varied between several per year up to once per three years.

The ClO_2 storage facilities in general had made good preparations considering safety clothes and breathing masks in the surroundings of the storage tanks and other areas where chemicals were handled.

Risk analysis was performed almost solely in the case of a reconstruction or new construction. Although the employees found the methods rather complex and hardscrabble, there was a belief that their purpose and result is useful.

Appendix C – Motivations for the assessed probabilities and consequences in the risk analysis

Table of Contents

1. Probability

Under this heading, the causes used in the risk assessment of the representative storage facility will be discussed. Their assessed probabilities will also be motivated.

1.1 Sabotage

Sabotages are a plausible threat towards companies and industries. A recent example of this is the sabotage of equipment at SSAB (Dalarnas Tidning, 2009). The sabotages can be of two different categories, either personal or organizational. Personal sabotages are executed by single persons and might arise from grudge against the company. This grudge might be caused by notice to quit, demotion or similar. Organizational sabotages are executed by rival companies or by organizations with a political agenda.

Sabotages due to personal reasons are assumed to have low probability. These types of sabotages do appear in media from time to time. However, a person is probably more likely to sabotage some kind of machinery or equipment than storage tanks or pipes containing hazardous chemicals, most of all considering the personal safety and health.

Sabotages due to organizational reasons are also stated with low probability. The chemical industry, in this aspect not including the oil industry, is not that controversial. The meat industry or the fur industry is more in the focus. Of course, environmental groups might have an interest in interfering with the chemical industry. However, interfering probably not include causing severe leakages endangering the environment and people.

When talking about organizations and sabotages, one could of course not exclude terrorist organizations. In Sweden, this is not probable. Worldwide the situation might very much differ between different regions and countries.

1.2 Undermining

An accident involving undermining took place at the chemical company Kemira in Helsingborg, when a storage tank containing H_2SO_4 overturned. The accident was caused by broken water pipes, running directly under the storage tank (Statens Haverikommission, 2008). This accident proves that undermining could happen. However, the probability for this is assumed to be low. Even when there is some kind of pipe under the storage tanks or the pipe bridges rupturing and causing leakages, there is no guarantee that this will lead to undermining and following damages.

Besides the undermining caused by leaking or rupturing pipes, there might be undermining due to weather conditions. In the case of heavy and enduring rain, soil might be washed away or loosened and cause undermining. There are also the possible undermining from flooding, high waves and increased water levels, eating away on shores. The undermining might not only occur directly around the storage tanks or pipe bridges, but also on slopes and areas neighboring the pulp mill. Undermining due to weather conditions or happened in Surte in 1950 (Nationalencyclopedin, 2009).

Extreme weather conditions are uncommon in Sweden. The probability for undermining due to weather conditions are there for assumed to be low.

When talking about the weather conditions it is also important to remember the climate changes that are currently taking place. The consequences of those changes are today not fully determined and understood. There might be a change that the climate will change drastically in the future. Maybe not in 5 years or 10 years, but over a longer period. To be aware of this possibility is important when planning and designing the ClO_2 storage facility.

Undermining of the storage tanks or pipe bridges could not only happen because of events concerning the stability of the ground. There is also a chance of damages to the foundation of these. The effects could consist of damages caused by short-term or long-term leakages. ClO_2 has harsh corrosive properties. Small leakages on a daily bases might cause damage to the foundation, weakening of this and in the long run affect the stability of the foundation. This sequence of events could be seen as similar to undermining. The probability for this event is assumed to be low.

1.3 Thermal decomposition - "Puff"

"Puff" is the commonly used name for a rapid decomposition of ClO_2. The event is similar to an explosion, requiring a certain concentration of ClO_2 to start. There are several different causes for this event to occur.

A nearby fire could cause a sufficient temperature rise in the storage tanks, leading forward to increased degassing. The concentration of gaseous ClO_2 might reach critical levels. It is assumed that the probability and consequence of fire in nearby buildings, or in the actual building holding the storage tanks, is greater than the event of fire in nearby vehicles. The buildings at the pulp mill are full of equipment possible to catch fire. At the same time, this fire will be much more extended, than the one in a vehicle. Since the pulp mills are known as hazardous and dangerous among the local rescue services, the probability for a severe fire to happen is probably very low. Rescue services will be coming to help quickly after the alarm and highly prioritize the pulp mill. Therefore, the probability is assessed low.

To prevent degassing, the storage tanks are equipped with ventilation to reduce the amount of gaseous ClO_2. This system might malfunction. In most of the cases, the system is redundant, with systems able to continue the ventilation. Nevertheless, all of these might malfunction and the whole function might go down. There could be problems with power outages or the reserve power and so on. According to Center for Chemical Process Safety (1989), the probability for this type of equipment to malfunction is low. This seems reasonable and on the base of this, the probability is assumed to be low.

Degassing might also increase on the cause of errors in the process. There might be too high temperature on the outgoing solution, contaminations or perhaps too high concentration. The causes for these malfunctions might be technical, but also origin from mistakes among the operators. It is important to realize this fact. Nevertheless, since much focus is on the reaction and the reaction is highly monitored, the probability for this is assumed to be low.

1.4 Overfilling

Overfilling does probably not require any closer explanation. The event could happen because of different reasons. In general, these could be described as either too much ClO_2 solution entering the storage tanks or too little ClO_2 solution leaving the storage tanks. To prevent overfilling of the storage tanks there are several different technological and physical systems cooperating. These systems consist of pumps, valves and different monitoring equipments, for example level measuring units inside the storage tanks. Most of the equipment in this system is redundant. In order to cause overfilling several of those systems need to malfunction simultaneously. The probability for all of these different components to malfunction at the same time is low. Numbers given by Center for Chemical Process Safety (1989) supports this view.

Overfilling might, beside the technological causes, also come from errors among the operators. These errors could for example consist of missing alarm signals or taking the wrong actions upon the alarm signals. There is an endless list of things that might go wrong or be wrong handled. Still, the probability is assessed low.

1.5 Freezing

Freezing in the inbound and outbound pipes causes plugs to form. These plugs could in the worst-case make the pipes rupture. In order to cause freezing in the pipes, two separate conditions must be met. First, the ambient temperature must be below the freezing point of the ClO_2 solution. Second, the pipes transporting this solution must be exposed to this cold. In Sweden, the temperatures will drop below the freezing point large parts of the year. Thereby, the first condition is met. In order to be exposed to the cold, the insulation or heating of the pipes must be insufficient. Although the problem of freezing is well known among the pulp mills, there is always a slight risk that the maintenance or technical fault gives the chance of exposure. Nevertheless, probability for this is assumed to be low.

1.6 Collision (tank)

Collisions with the storage tanks can happen due to many reasons, for example slipperiness and loose of control. Fundamental for avoiding these kinds of accidents are the presence of sufficient collision protection. This protection will prevent damages in the case of an accident. Sufficient collision protection will be able to stop trucks or cars from colliding with the storage tanks and inflicting damages. Most of the visited ClO_2 storage facilities had insufficient collision protection. The concrete fundaments were placed to widely apart or too close to the storage tanks. This allows the vehicles to hit the storage tank in between the fundaments. Besides preventing damages when the accidents have occurred, there are also the aspects of preventing the accident to happen in the first place. The traffic density in the area around the ClO_2 storage facility as well as the allowed speed is important features. Overall, the probability for some kind of vehicle to collide with the storage tanks, and inflict damage, is assumed to be low.

1.7 Collision (pipe)

Collisions with the inbound and outbound pipes follow much of the reasoning above. The aspects of preventing damages in case of an accident as well as preventing the accident from happen are both important here as well. Every ClO_2 storage facility has its own unique design and the location of the storage tanks inbound and outbound pipes differ. Some of them are placed on pipe bridges running high up in the air on concrete fundaments and metal frames. In other cases, the pipes are placed on the ground level or inside a building, relatively unprotected and vulnerable. This gives difficulties when stating the probability for collisions between vehicles and these pipes. Since some of the pipes seem to be properly protected, the probability for this is assumed to be medium.

1.8 Falling object (large)

Falling objects can origin from many different situations. One of these situations could be the lifting of heavy equipment over the storage tanks or for that matter the inbound and outbound pipes. Even though strictly prohibited by the pulp mills, it still happens in order to save time and money. Nevertheless, the chance of something going wrong and these objects to actually land on the storage tanks or the pipes is small. Therefore, the probability for this cause is assumed to be low.

Falling objects might also come in the form of debris from an explosion in another location at the pulp mill. This happened not so long ago at the pulp mill in Skoghall, Sweden, where a hydrogen peroxide (H_2O_2) storage tank exploded (Dagens Nyheter, 2009). Nevertheless, the probability for this is assumed to be very low. First, the chance of an actual explosion is low. Second, the chance of the debris from the explosion to land and damage the storage tanks or the pipes is low.

Another situation that might cause falling objects is weather conditions, foremost hard winds or heavy snowfall. The weather in Sweden might not be the most extreme. Sweden does not have hurricanes or anything like that. However, rough weather might occur though and recent storms like Gudrun in 2005 caused a lot of damage. However, the probability is assumed to be low.

1.9 Falling object (small)

The difference between the cause of falling object (large) and falling objects (small) is, as the name implies, the size of them. To make exact definitions is of course hard, but the reader hopefully understands the general idea.

The origin of these falling objects (small) is similar to the situations mentioned above. In addition to these, working with construction or reparation could be added. There is risk of tools, toolboxes or building material to slip out of hands, blow away or fall to the ground. An example of this is an accident in British Columbia in 2005, when two workers dropped a severed pipe section on a valve, causing ClO_2 solution to flow out from a storage tank (WorkSafeBC, 2009).

Smaller object are less probable to cause damages when falling, but more probable to appear. In other words, small object fall more often but do not cause the same damages. Many times, the insulation of the pipes prevent damages. Based on this thought, the probability is assumed low.

1.10 Corrosion

Corrosion is inevitable in the storage tanks and the pipes, because of the corrosive properties of the solution. An external organization or company controls both storage tanks and pipes at set intervals, determining if re-lining or replacing of equipment is required. Nevertheless, corrosion might lead to accidents if certain conditions are not met. One of these conditions is that an error in the process increases the corrosion speed by causing the temperature or concentration to rise. By increasing the corrosion speed, the predictions as when the next control is necessary might be wrong. However, the probability for this to happen is assumed to be low.

Another important aspect is the fact that the storage tanks should be made out of material that is suitable for the media it is built to contain, in this case ClO_2 and its corrosive properties. The wrong choice of material might cause the process of corrosion to quickly weaken the storage tanks, leading to collapse or leakage. Most storage tanks that are designed to contain ClO_2 are made out of FRP. However, FRP are an overall term that covers many different resins and fiber types (American

Composites Manufacturers Association, 2007). Therefore, it is not sure that the most suitable variant of FRP are used. The probability for this wrong choice is assumed to be low.

Another condition that might lead to corrosion is that the company controlling the corrosion is neglectful or unqualified for the task. This might cause an overestimation of the condition of the storage tanks or and underestimation the corrosion speed. This probability is assessed as medium.

Furthermore, the results from the inspections might not be taken seriously by the pulp mill or ignored. The necessary maintenance might not be performed due to neglectfulness or saving demands. Since the pulp mills obviously want this kind of service and they furthermore are aware of the corrosive properties, the probability for this event is considered low.

Last, the risk of external corrosion will be brought up. This is a factor of importance as well as the internal corrosion. There could be several reasons for this to happen. Leakages of chemicals are the foremost reason. The pulp mill handles several other chemicals besides ClO_2 with corrosive properties. Spreading of these chemicals due to spill, rupture or leakages could affect the outside of the storage tanks and weaken the structure. At the same time, leakages of ClO_2, overfilling or spills could cause the same effects. Of course, one should also mention weather conditions or defects in the material. The assumed probability for this is low, since effects on the outside of the storage tanks or the pipes are more easily noticed.

1.11 Leaking process equipment

Frequent maintenance will always fight against the harsh environment that the process equipment needs to face. High temperature, corrosive properties and high pressure will lead to wear and tear. Since there is no chance of controlling and replacing packing and valves and all other kinds of equipment at the storage tanks, pumps or pipes, there will be minor leakages all the time. This is also evident on the ClO_2 storage facilities that have been visited, where the employees stated that the smell of ClO_2 were noticeable on a daily basis. On the base of this, the probability of leaking process equipment is assumed to be high.

1.12 Earthquake

Earthquakes might potentially cause huge damages to both storage tanks and pipes. The probability for them to occur is however dependent on the seismic activity in the area. In Sweden, the probability for a serious earthquake is small, but in other countries and regions, like for example western USA or Japan, small earthquakes are common and large earthquakes are probable. For an earthquake to cause damage, the strength of the structures must be under dimensioned in respect to the force of the earthquake. The probability that an earthquake will occur is estimated to be very low.

1.13 Vibrations

Vibrations could damage the storage tanks and the pipes in both the short- and long perspective. Frequent vibrations in the presence of the equipment can lead forward to weakening of the structures and the material of these. Extreme vibrations could in worst-case result in the direct rupture of the storage tanks or the pipes. These vibrations might origin from many different areas. Construction works are one of these. Earthmoving, drilling, rock blasting or demolitions are action that might cause severe vibrations. Furthermore, dense traffic in the area and process equipment might cause vibrations and should be thought off. Nevertheless, the probability for this is assumed to be low.

1.14 Explosion

The fact that debris from explosions inside the pulp mill might have consequences to the ClO_2 storage facilities have been brought up earlier in this master thesis. However, one should not disregard the fact that the actual force from the explosion itself also might cause damage to property as well as humans. Since the pulp mill have storages of many different chemicals and maintain different reactions, there are many possible risks of explosions. Errors in the process might cause the different reactions to take alternative roads. One should neither forget the storages with chemicals. Some of the chemicals stored at the pulp mill could cause large damages. An accident with a storage tank of H_2O_2 exploding and damaging pipes with ClO_2 solution has been mentioned earlier. When considering storage it is important to include gas bottles sometimes present at the pulp mill. Altogether, the probability for this is very low.

2. Consequences

Under this heading, the different possible scenarios identified in the risk analysis of the representative storage facility will be discussed and their assessed consequences will be motivated.

2.1 Pipe leakage

The leakages can range from a very small hole or damage to very large holes and damages, almost as pipe ruptures. Among the scenarios mentioned in this risk assessment these extremities is already included, the pipe rupture as well as the spill. Pipe leakages should be seen as something in between. Included into the term of pipe leakages are also leakages at the equipment around the pipes, for example valves and pumps.

Since the pipe leakage is not all too large, the consequences might be small, especially if the flow in the pipe could be sealed off. The leakage would probably be detected rather quickly by operators at the control room, operators out in the ClO_2 storage facility the monitoring system or perhaps the gas detectors. Giving this, the amount of ClO_2 leaking would be limited and therefore also the consequences. The consequence to the life and health of humans is assumed to be low. Of course, there could be some minor exposure with following effects if workers happen to be present in the area at the time of the leakage. The assessment of the effects on the environment and the property follows the same reasoning. The extent of the leakage is limited and the small amounts would not be able to affect the environment since there are great chances the leakage would not even spread from the area. The costs for replacing or repairing the pipe are quite low and an event of this magnitude probably would not be noticed, although not exaggerated.

2.2 Pipe rupture

The pipe rupture gives a more severe leakage than the pipe leakage. Therefore, there is no question about the consequences being larger. Even if the leakage is detected and fixed, the leakage would most likely spread on the ground and gaseous ClO_2 would leave the solution. The concentration of ClO_2 in the air would most likely not reach the level for risking an explosion. Due to the concentration in the air, there might be a need for evacuation. Of course, this situation and the degassing are determined by the weather conditions at the time. Since there is a spreading of ClO_2

there are risks that operators would be exposed and therefore the consequences are assessed as light. Since the solution of ClO_2 will spread on the ground there could be local effects to the environment. However, these effects should be quite small and temporary. The incident or accident would probably be noticed in the newspapers, because of the evacuation, and perhaps even noticed by residences in the nearby community, because of the smell. However, since the material costs for this accident is small, the consequences to the property are assessed as small.

2.3 Tank collapse

The event of a storage tank collapsing is one of the more grave accidents in this risk assessment. A collapse would release a large amount of ClO_2 solution, spreading widely. The solution would instantaneous as well as slowly create clouds of gaseous ClO_2. Gaseous ClO_2 would possibly also emerge from the surrounding drainage and the solution of ClO_2 would possibly spread to the treatment plant or perhaps even out to the surroundings based on the design of this system. There is no question about the consequences being severe.

The storage tank collapse would be noticed immediately and set off a chain of evacuations and alarms. Never the less, there would be a great risk that workers would be exposed. There would also be some risk of the gaseous ClO_2 to spread to nearby residences and there might be a small risk for the high concentrations in the air to explode. Should this happen, there could be even more effects on the human health and life. With lack of sufficient dikes large amount of ClO_2 solution released would spread on the ground, the leakage could affect nearby waters directly or by the drainage indirectly. The consequences to the property would also be severe. The material costs for the storage tank as well as the decontamination and the loss of production at the pulp mill would be substantial. Should an explosion occur, maybe the losses would be even catastrophically large.

At the same time, the impact on the company image needs to be considered. The event would be noticed in newspapers and media. One such example is the accident at Kemira in Helsingborg, Sweden, some years ago and the coverage of this event (Statens Haverikommission, 2008). The nearby community would be affected of this event, possibly forced to evacuate or at least take safety measures. In the future their opinions concerning the pulp mill in average and the ClO_2 storage facilities in particular, would probably become less positive. Since there is a chance of severe, short-term, effects to the environment, it is likely that this matter would raise some critic within this area as well.

2.4 Tank leakage

There are several different magnitudes of the tank leakage. The authors will define this scenario as including a hole in the storage tank, larger than the diameter of a normal pipe. Hence, this leakage is more severe than the events involving pipes. The type of small leakages that could be the first signs of failure due to corrosion or insufficient sealing in flanges and such are treated as spills under chapter 2.5.

The tank leakage would, like most of the events described above, be noticed rather quickly. However, the possibilities to interfere and stop the leakage are limited. Some ClO_2 storage facilities have a system for emptying the storage tanks into the drainage or the dike, but far from all. At the other ClO_2 storage facilities you simply have to wait until the level of the solution is below the hole in the storage tank. Even when so, gaseous ClO_2 could spread from the hole in the storage tank. Hopefully, the hole will not be in the lower part of the storage tank.

The consequences to life and health of humans could be as severe as for the tank collapse. However, since the leakage is possibly smaller than the rupture, depending on the location of the hole, the consequences are likely to be less severe. The same reasoning goes for the consequences to the environment.

Concerning the consequences to the property, this event is placed similar to the tank collapse in the scale. The material damages are possibly very similar as well as production loss and other things. The event will gain attention in media and most certainly affect nearby residences with alarm, evacuation or distinct smell. That is the reason for the high grading.

2.5 Spill

The spill is defined as a very small leakage that is able to stay unlocalized for a long time. The leak might be too small to locate even if the smell and gas detectors can detect it. The effect to the health and life of the workers are not due to the large amounts at one occasion, but to the repeated exposure to small concentrations. Repeated exposure in combination with the fact that workers most likely scamp with breathing masks gives reason to think about the health effects.

This event was hard to place on the scale. Much of this master thesis has been dedicated to investigating the health effects from exposure to ClO_2. Since there is lack of resemblance and unambiguousness, the decision becomes even harder. However, since repeated exposure to minor concentrations of ClO_2 assumedly has a negative effect on the human health, this will direct the assessment. Stating, that this exposure has a negative effect, there is the question about the magnitude of these effects. The effects are probably not severe, but on the other hand, they are possibly permanent. To be on the safe side, the consequence to life and health of humans has been ranked in the higher level, at least for now. As previously have stated, more thorough investigations of the repeated exposure have to be done.

The consequences on the environment are considered small, since there are only minor amounts leaking and because of the decomposing properties of ClO_2.

Material damages from the spill are negligible. Neither is the event any reason for publications in the media, except for one reason. Should there be a conclusion that these repeated exposures are linked with negative health effects there is a great chance that this fact will gain media interest, especially since workers have been exposed for years and years without the pulp mill or authorities reacting.

Appendix D – Consequence calculations on the representative ClO_2 storage facility

Table of Contents

1. Introduction to the consequence calculations

To look at the consequences is an important part of the risk analysis. Therefore, consequence calculations will be conducted on a number of different scenarios/leakages. These different leakages and scenarios is the tank rupture, the tank leakage, the pipe rupture and the pipe leakage. Furthermore, different parameters and features of these leakages will be varied. This variation and sensitivity analysis will give a broad understanding for which parameters that have the greatest impact on the consequence.

Focus of the consequence calculations will be on the consequences to human health and life, and not on the consequences to the environment and property. In the case of environmental consequences, this is because information in the literature search stated that the consequences to the environment are not irreversible or long term. Because of this, the consequences to the environment are not seen as severe as the health consequences and are therefore simplified and based on the approximate amount of ClO_2 released in each scenario. This largely follows the health consequences, but because of the different scales, the environmental consequences are somewhat lower. The consequences to the property are hard to calculate and are therefore approximated in the same way.

The consequence calculation will commence with calculations of the source strength. A sensitivity analysis will then be conducted to investigate the different parameters influence on the source strength. Following that, the calculated source strengths will be used in the computer program ALOHA, from the Environmental Protection Agency, to calculate the distance from the source to different concentrations. This calculation will also undergo sensitivity analysis. The results from the two different sensitivity analyses will then be used to suggest different consequence mitigating actions.

2. Source strength

The source strength is the amount of gaseous ClO_2 released to the air per time unit. Depending on the properties of the chemical, the state under which this is stored and the type of leakage, different equations and assumptions are necessary. In this master thesis, all the different scenarios will be assumed to model the degassing from a pool. The difference between the scenarios and their leakages will be the size of the pool. The source strength in this case means the amount of gaseous ClO_2 leaving the pool per second.

The calculations start with looking at the partial pressure with the fixed concentration of 10 g/dm^3, but with different temperatures in the solution. The partial pressures are derived from figure D.1 and are listed in table D.1.

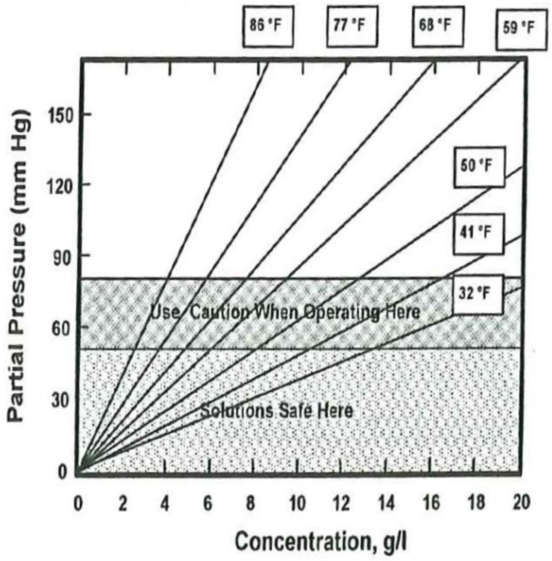

Figure D.1, The relationship between concentration, solution temperature and partial pressure for a solution of ClO_2 (Simpson, 2005).

Temperature (°C)	5	10	15
Partial pressure (Pa)	6000	7500	9500

Table D.1, Partial pressures above a solution with a concentration of 10 g/dm^3 and temperatures of 5°C, 10°C and 15°C.

When the partial pressure has been derived, the mass transfer coefficient needs to be calculated. These calculations come by the following equations (Karlsson, 1993):

$$A = \frac{V}{h} \quad \text{(Eq. 1)}$$

$$r = \sqrt{\frac{A}{\pi}} \quad \text{(Eq. 2)}$$

$$f_g = 3 * r^{-0.11} \quad \text{(If the pool is circular) (Eq. 3)}$$

$$f_g = x^{-0.11} \quad \text{(If the pool is quadratic) (Eq. 4)}$$

$$k = 8.4 * 10^{-5} * \frac{u^{0.78}}{T} * f_g \quad \text{(Eq. 5)}$$

In the equations, f_g is a geometrical factor (m^{-1}), u is the wind speed (m/s), T is the ambient temperature (K), r is the radius (m) of a circular puddle, x are the side (m) of a quadratic puddle, V are the volume (m^3) released and h are the depth (m) of the pool.

To obtain the source strength, N_A (mole/m^2*s), the mass transfer coefficient and the partial pressure are multiplied by the following equation (Karlsson, 1993):

$$N_A = k * Pa \text{ (mole/m}^2\text{*s)} \quad \text{(Eq. 6)}$$

2.1 Tank collapse

From the data of the representative ClO_2 storage facility, it is assumed that approximately 900 m^3 of ClO_2 could be released in the worst-case tank collapse. Assuming that the formed pool is 0.01 m deep, the total area covered with the solution, would be 90 000 m^2 according to the first equation. Most certainly, the leakage will not be able to cover the whole 90 000 m^2 which would equal more than 11 soccer fields. There are several reasons for the area not reaching this extreme size. The ClO_2 storage facility is located close to waters and some of the volume will end up there. Furthermore, drainages as well as cavities and roughness in the ground will contain some of the released volume. One must also consider the fact that the ground never is completely plain, leading to “rivers” more than round “pools”. Giving this, the whole volume will not be in contact with the air and degassing. Therefore, it is assumed that the area of the pool is equal to the size of one soccer field, 7480 m^2. This area could be compared with a circular pool with the radius of 48.8 m, according to equation 2.

In order to investigate how different parameters affect the source strength, a sensitivity analysis where the area, the wind speed and the ambient temperature are executed. The area are increased and decreased by 50%, this corresponding to radiuses of 34.5 m and 59.8 m. The wind speed above the solution is set to 2 m/s and 5 m/s. The ambient temperature is set to 5 °C and 20 °C, corresponding to 278 K and 293 K.

The calculations are meant to model reality, but because of the lack of knowledge, time and information, assumptions have to be made. Assumptions and simplifications is also an inherent factor in the equations used for the calculations. First, the calculations do not consider limitations in the mass transport inside the solution. In practice, concentration gradient will emerge, limiting the degassing of ClO_2. This would however be hard to determine without access to laboratory equipment. Second, the solution is assumed to be evenly distributed on the ground in the same moment as the tank collapses. In reality, it would take some time for the solution to spread and the spreading would be somewhat violent. Third and final, it is assumed that the degassing rate is constant over time. In reality, it is not since the concentration will decrease when the gas leaves the solution. The decrease in concentration leads to a decrease in partial pressure and therefore also a decrease in source strength. These assumptions are used when calculating the source strength for all scenarios and it is essential to understand that this assumption leads to an exaggeration of the source strength.

Result and sensitivity analysis

In table D.2, the geometrical factor, calculated by using equation 3 for the different pool areas, are presented. In table D.3, D.4 and D.5 the mass transfer coefficient when the area, wind speed and ambient temperature is varied, are presented. These calculations have been made using equation 5.

Area (m^2)	3740	7480	11220
Radius (m)	34.5	48.8	59.8
Geometrical factor, f_g (m^{-1})	2.032	1.956	1.913

Table D.2, The geometrical factor, f_g, for different areas.

	u = 2 m/s	u = 5 m/s
T = 278	$1.054*10^{-6}$	$2.155*10^{-6}$
T = 293	$1.000*10^{-6}$	$2.044*10^{-6}$

Table D.3, The mass transfer coefficient, k, for a pool with a radius of 34.5 m when temperature and wind speed are varied.

	u = 2 m/s	u = 5 m/s
T = 278	$1.015*10^{-6}$	$2.074*10^{-6}$
T = 293	$9.630*10^{-7}$	$1.968*10^{-6}$

Table D.4, The mass transfer coefficient, k, for a pool with a radius of 48.8 m when temperature and wind speed are varied.

	u = 2 m/s	u = 5 m/s
T = 278	$9.926*10^{-7}$	$2.028*10^{-6}$
T = 293	$9.417*10^{-7}$	$1.925*10^{-6}$

Table D.5, The mass transfer coefficient, k, for a pool with a radius of 59.8 m when temperature and wind speed are varied.

In table D.6, the source strength is calculated for 36 different scenarios. In the left column, the scenario is described in respect to the ambient temperature, wind speed and pool radius. In the header, the partial pressure of ClO_2 is stated. The partial pressure is depending on the concentration of the solution.

	6000 Pa	7500 Pa	9500 Pa
5°C, 2 m/s, 34.5 m	0.0063 mole/m^2*s	0.0079 mole/m^2*s	0.0100 mole/m^2*s
5°C, 5 m/s, 34.5 m	0.0129 mole/m^2*s	0.0162 mole/m^2*s	0.0205 mole/m^2*s
20°C, 2 m/s, 34.5 m	0.0060 mole/m^2*s	0.0075 mole/m^2*s	0.0095 mole/m^2*s
20°C, 5 m/s, 34.5 m	0.0123 mole/m^2*s	0.0153 mole/m^2*s	0.0194 mole/m^2*s
5°C, 2 m/s, 48.8 m	0.0061 mole/m^2*s	0.0076 mole/m^2*s	0.0096 mole/m^2*s
5°C, 5 m/s, 48.8 m	0.0124 mole/m^2*s	0.0156 mole/m^2*s	0.0197 mole/m^2*s
20°C, 2 m/s, 48.8 m	0.0058 mole/m^2*s	0.0072 mole/m^2*s	0.0091 mole/m^2*s
20°C, 5 m/s, 48.8 m	0.0118 mole/m^2*s	0.0148 mole/m^2*s	0.0187 mole/m^2*s
5°C, 2 m/s, 59.8 m	0.0060 mole/m^2*s	0.0074 mole/m^2*s	0.0094 mole/m^2*s
5°C, 5 m/s, 59.8 m	0.0122 mole/m^2*s	0.0152 mole/m^2*s	0.0193 mole/m^2*s
20°C, 2 m/s, 59.8 m	0.0057 mole/m^2*s	0.0071 mole/m^2*s	0.0089 mole/m^2*s
20°C, 5 m/s, 59.8 m	0.0116 mole/m^2*s	0.0144 mole/m^2*s	0.0183 mole/m^2*s

Table D.6, The source strength (mole/m^2*s) depending on area, ambient temperature, wind speed and temperature of solution (corresponding to different partial pressures), calculated with equation 6.

Wind speed

The results from the sensitivity analysis, presented in table D.6, clearly show that the wind speed is an important factor affecting source strength. An increase in wind speed from 2 m/s to 5 m/s increases the source strength with over 100%. This is because the wind removes the gaseous ClO_2 from over the pool, thereby allowing more gaseous ClO_2 to leave the solution at a higher rate.

Solution temperature

Table D.6 also show that another important factor that affects the source strength is the temperature of the solution, where higher temperature leads to higher partial pressures, which give a higher rate of degassing. The relationship between the increase in solution temperature and partial pressure can be seen in figure D.1. An increase from 5°C to 10°C gives an increase of the source strength of 25% while an increase from 10°C to 15°C gives an increase of 26 %. The effect on the source strength is noticed when looking at table D.6. The different solution temperatures are correlated to the different partial pressures in that table.

Ambient temperature

An increase of the ambient temperature from 5 °C to 20 °C will increase the source strength with more than 50 %. This is if one assumes that the temperature of the leaked solution quickly will reach the ambient temperature. For more data, see table D.6.

Area

From the results presented in table D.6, one might think that the area is not an important parameter. This is however wrong. The total source strength is strongly dependent of the area. This is apparent if one look at the unit of the obtained source strength which is mole/m^2*s. This shows that the larger area, the larger amount of gaseous ClO_2 will be released. The source strength is also dependent on the area through the introduction of the geometrical factor in equation 5. However, the area does not affect the geometrical factor much, as apparent from equations 3 and 4.

To prove the effect of the area, and show the importance of installing a dike, limiting the area, the source strength from a circular pool of 250 m^2 (radius 8.9 m) will be calculated next. The calculations are the same that have been used before and will not be presented again. For data and results, see table D.7. The calculated source strengths with a dike installed is compared to total source strengths without a dike in table D.8. The differences are most likely even bigger in reality, since the concentration gradient inside the solution increases with the depth. This is a fact that has been neglected here.

Geometrical factor (m^{-1})	2.36
Temperature (K)	278
Wind speed (m/s)	5
Mass transfer coefficient	2.5*10^6
Solution temperature (°C)	5
Partial pressure (Pa)	7500

Table D.7, Parameters used and results obtained when calculating the source strength, using equations 1 to 5.

Radius (m)	34.5	48.8	59.8	8.9 (dike)
Area (m^2)	3740	7480	11220	250
Source strength (mole/m^2*s)	0.0162	0.0156	0.0152	0.0188
Source strength (mole/s)	60.6	116.7	170.5	4.7
Source strength (kg/s)	4.1	7.9	11.5	0.3

Table D.8, A comparison of source strength for different pool areas.

The difference in source strength is substantial. If a dike with the area specified above were installed, the source strength would decrease with over 1300% compared with the case in which the area is 3740 m^2. This is clear evidence that a dike is important to mitigate the consequences of a release.

Concentration

The effect from a decrease or increase in concentration on the source strength can be calculated with the same procedures as for the variation in solution temperature. From figure D.1, the partial pressures for different concentrations can be derived, while the solution temperature is held constant. These partial pressures are multiplied with mass transfer coefficients, from table D.3 to D.5, to calculate the source strengths for a selection of different pool areas and weather conditions. The result from these calculations is presented in table D.9.

Concentration (g/dm^3)	10	8	6
Partial pressure (Pa)	7500	6200	5000
Source strength (kg/s) at 5°C, 5 m/s, 34.5 m	4.1	3.4	2.7

Table D.9, The source strength depending on concentration.

The results show that concentration is an important factor in determining the source strength because of its effect on the partial pressure. A decrease in concentration from 10 g/dm^3 to 8 g/dm^3 results in a decrease in source strength of 17 %. A further decrease from 8 g/dm^3 to 6 g/dm^3 decreases the source strength with 21 %.

The change in source strength over time

The time component in the degassing rate is also worth mentioning. As stated earlier, the calculations above assume that the source strength is constant over time while in fact it decreases as the sources gets depleted no ClO_2. This exaggerates the source strength and thereby the plume length.

Eka Chemicals (1998b) do however present an equation based on empirical experiments describing the degassing rate on the base of concentration and time. The equation is exponentially decreasing and shows that a decrease in concentration from 10 g/dm^3 to 8 g/dm^3 takes approximately 20 min. A further decrease from 8 g/dm^3 to 6 g/dm^3 takes approximately 30 min. If using these rates of decreasing with the information in table D.9, one can see that an initial source strength of 4.1 kg/s after 20 minutes has decreased to 3.4 kg/s, approximately 82 % of the initial source strength. After 50 minutes, it is 2.7 kg/s, approximately 66 % of the initial strength.

2.2 Tank leakage

The scenario of the storage tank leakage is somewhat more complex than the rupture. The storage tank leakage will lead to a leakage that is extended in time. The time of the leakage is depending on the size of the hole. Therefore, the source strength will be weaker for the storage tank leakage than for the rupture, giving that the hole is not large enough so that the time component can be neglected.

According to Karlsson (1993), the time for the storage tank to empty is described by the equation:

$$t = \frac{1}{C_d * A} * \sqrt{\frac{m_0 A_t}{2\rho g}} \qquad \text{(Eq. 7)}$$

In this equation, C_d is a coefficient describing the shape of the hole, A is the hole area (m^2), m_0 is the mass in the tank when the release starts (kg), A_t is the cross-sectional area of the tank (m^2), ρ is the density of the liquid (kg/m^3) and g is the gravitational acceleration (m/s^2).

Result and sensitivity analysis

The data presented in table D.10 is used for calculating the duration of the leakage with equation 7. The density of the ClO_2 solution is assumed that of pure water, 1000 kg/m^3.

Cross-sectional area (m^2) (derived from a diameter of 4 m)	12.5
C_d	0.62
Stored mass (kg)	900000
Density (kg/m^3)	1000
Gravitational acceleration (m/s^2)	9.81

Table D.10, Data used for calculating the duration of the release.

The area of the hole will be varied to see the impact on the time for the leakage. The different areas of the hole and the following results in the duration of the leakages are presented in table D.11.

Hole area (m^2)	0.1	0.25	0.5
Time of release (s)	387	155	77

Table D.11, The different areas of the hole and the following results in duration of the leakages.

As one can see from the results presented in table D.11, the area of the hole have a great impact on the duration of the leakage. Remarkable is the fact that even small holes will have a short time of leakage. One might consider whether the source strength of a tank leakage differs in significance from the tank rupture. Probably it will not differ much, why the source strength is assumed to be approximately the same. In practice, the tank leakage will have somewhat weaker source strength.

These calculations have been conducted under the assumption that the whole volume is released from the storage tanks. In practice, the volume released is depending on the actual location of the hole. Should the hole emerge above the ground, only a fraction of the volume will be released.

2.3 Pipe leakage and pipe rupture

The scenarios of the pipe leakage and pipe rupture could be considered identical, namely the release of ClO_2 solution from pipes. What differs between them is the volume of ClO_2 solution released. In the case of a pipe leakage, a rather small volume of ClO_2 solution would be released, while a pipe rupture would lead to a larger release. In both cases, it is assumed that the degassing occurs from a pool formed by the release, like the storage tank rupture or the storage tank leakage. The pool size is dependent on the volume released.

The volume of the leakage is dependent on two parameters, the flow through the hole as well as the duration of the release. The first parameter, the flow through the hole, is the product from the size of the hole and the flow in the pipe. This parameter is depending on the needs of ClO_2 solution at the pulp mill. Typically, the storage tanks should be able to support the pulp mill with ClO_2 solution for 8 hours (Pelin, 2009). In the representative ClO_2 storage facility, with the storage of 900 m^3, this corresponds to a flow of 125 m^3 per hour or 0.0347 m^3/s. The second parameter, the duration of the release, is dependent on the time it takes to notice the leakage and shut down the flow in the pipe. One can assume that a pipe rupture will be noticed rather quickly, due to loss of flow in the pipes. However, a pipe leakage might not. Pipe leakage is something undefined and therefore can consist of anything from the tiniest hole to something that is hard to distinguish from a pipe rupture. Of course, smaller holes will not be noticed as quickly. Henceforth it is assumed that a pipe leakage will give a hole that release about 15 % of the volume flowing in the pipe.

Result and sensitivity analysis

The source strength for the pipe rupture will be calculated first. The flow through the pipe is 0.0347 m^3/s. The duration of the leakage is assumed 2 minutes. This parameter will later be varied to investigate the influence of the duration. With these parameters, the pipe rupture will release 4.2 m^3 of ClO_2 solution.

The calculations of the source strength are executed in the same way as described for the tank rupture scenario earlier. The mass transfer coefficient is calculated at a wind speed of 5 m/s. This corresponds, according to the calculation made for the tank rupture, to a worst-case scenario in respect to the rate of degassing. If the concentration and temperature of the solution is assumed to be 10 g/dm^3 and 10°C respectively, the partial pressure equals 7500 Pa. The results are presented in table D.12.

Released volume (m^3)	4.2
Area of leakage (m^2)	420
Radius of leakage (m)	11.6
Geometrical factor	2.29
Mass transfer coefficient	$2.43*10^{-6}$
Source strength ($mole/m^2*s$)	0.0182
Source strength (mole/s)	7.6
Source strength (kg/s)	0.50

Table D.12, Data used for calculating the source strength from the pipe rupture given the duration of the release to 2 minutes.

When the duration of the release is halved to 1 minute, the source strength naturally decreases with approximately 50 %, see table D.13.

Released volume (m^3)	2.1
Area of leakage (m^2)	210
Radius of leakage (m)	8.2
Geometrical factor	2.38
Mass transfer coefficient	$2.52*10^{-6}$
Source strength (mole/m^2*s)	0.0189
Source strength (mole/s)	4.0
Source strength (kg/s)	0.26

Table D.13, Data used for calculating the source strength from the pipe rupture given the duration of the release to 1 minute.

Following the calculation of the source strength for the pipe rupture is the calculation of the source strength for the pipe leakage. Given the assumption that this scenario releases 15% of the flow in the pipe, the leakage equals 0.0052 m^3/s. The duration of the release is likewise assumed to 2 minutes. This gives a total released volume of 0.6 m^3. The results are presented in table D.14.

Released volume (m^3)	0.6
Area of leakage (m^2)	60
Radius of leakage (m)	4.37
Geometrical factor	2.55
Mass transfer coefficient	$2.71*10^{-6}$
Source strength (mole/m^2*s)	0.0203
Source strength (mole/s)	1.2
Source strength (kg/s)	0.08

Table D.14, Data used for calculating the source strength from the pipe rupture given the duration of the release to 2 minutes.

From the results, it is evident that both the duration of the release and the size of the hole are important factors when calculating the source strength.

2.4 Summary of the results and sensitivity analyses

In table D.15, a summary of the sensitivity analyses concerning the source strength is presented. From the summary, one can see that the temperatures and the wind speed is not as important to the source strength as the other parameters since they do not increase/decrease the source strength in a ratio of 1:1. The other parameters largely follow this ratio. It is however hard to make a statement of how much the temperature changes the source strength in comparison with the other parameters, since the change in temperature cannot be expressed as a change in percent. One also has to think about the assumptions made during the calculations. These assumptions might have affected the numbers.

	Change of parameter	Change in source strength
Area	-50%	-48%
	+50%	+45%
Solution temperature (°C)	-5	-20%
	+5	+26%
Ambient temperature (°C)	+15	+51%
Wind speed	+150%	+105%
Concentration	-20%	-20%
	+20%	+20%
Duration of release	-50%	-48%

Table D.15, Summary of sensitivity analysis of the source strength.

3. Plume length

Based on the calculations of the different source strengths, further consequence calculations can be conducted. These calculations strive to find the exposure and concentrations at different distances from the leakage. For these calculations, the computer program ALOHA is used. ALOHA is developed by the Environmental Protection Agency, especially for such consequence calculations and is commonly used.

The focus is on the distances to the threshold limits ERPG-3 and ERPG-2, for ClO_2. These values are 3 ppm and 0.5 ppm (American Industrial Hygiene Association, 2009). More information and the exact definitions of ERPG-3 and ERPG-2 are available in the report. Furthermore, the concentrations at close range to the leakage will be examined.

Result and sensitivity analysis

Starting the calculations, some assumptions have to be stated. The source of the degassing is assumed a point source. This giving, that even if the leakage in practice has a large area for degassing, the assumption state that all gaseous ClO_2 origins from a single point. This assumption does not affect the concentration at different distances and the length of the plume over long distances. However, the assumption could have effects considering the concentrations in the immediate vicinity of the release. Another assumption made, because of limitations in ALOHA, is that no gaseous ClO_2 is decomposed by reactions or sunlight. This assumption corresponds to conditions of the night, where minimal decomposition takes place. The time of the night and the following conditions is seen as the worst-case scenario. However, this leads to an overestimation of the consequences, a view that is supported by Alp and Boughner (2005). Furthermore, it is also assumed that the source strength is constant over time. In practice, the source strength decreases as the solution is depleted of ClO_2.

Calculations will be conducted with two different weather settings. First, the wind speed is set to 2 m/s and the stability class of the atmosphere is set to E, which is stable. Second, the wind speed is set to 5 m/s and the stability class to D, which is neutral. While a low wind speed slows the spreading of a plume, it also enables to atmosphere to be stable. This leads to less dilution of the plume, which makes it longer. This should be seen as the worst-case scenario. High wind speeds on the other hand makes the plume travel fast, but the atmosphere is not as stable. Therefore, the plume is diluted faster. This configuration is often used as a dimensioning configuration when planning for example chemical industries.

The sensitivity analysis will furthermore look at different durations of the release, different source strengths and different ambient temperatures.

The source strengths that will be used are the ones calculated for a solution temperature of 10°C. Two of the source strengths have a lower concentration to model the decrease in concentration due to depletion. These values are taken from table D.9.The used source strengths are presented in table D.16.

Conditions (Ambient temp., wind speed, pool radius and concentration)	Source strength (kg/s)
5°C, 5 m/s, 4.4 m, 10 g/dm^3 (pipe leakage)	0.08
5°C, 5 m/s, 11.6 m , 10 g/dm^3 (pipe rupture)	0.50
5°C, 2 m/s, 34.5 m, 10 g/dm^3 (	1.99
5°C, 2 m/s, 48.8 m, 10 g/dm^3	3.84
5°C, 5 m/s, 34.5 m, 10 g/dm^3	4.09
5°C, 5 m/s, 34.5 m, 8 g/dm^3	3.41
5°C, 5 m/s, 34.5 m, 6 g/dm^3	2.69

Table D.16, Source strengths that will be used in the sensitivity analysis of the plume length.

Before starting the different calculations with variation in parameters, a “reference” scenario will be calculated. The parameters will then be altered systematically so that each parameters impact on the plume length can be observed. This reference scenario, a tank rupture/leakage, will have the properties stated in table D.17. The duration of the degassing is initially set to 30 minutes. In practice, the decreasing source strength gives reason to assume that the maximum distance to the selected concentrations will be decreasing as time goes. The time it takes for the gaseous ClO_2 to travel the distance also needs to be considered. Therefore, 30 minutes is assumed to represent a time when the distance is at its longest. Other parameters, for example humidity and cloud cover, are the default values set by ALOHA. These values might not be the most likely in Swedish conditions, but no consideration has been taken to this.

Source strength (kg/s)	1.99
Ambient temperature (°C)	5
Wind speed (m/s)	2
Stability class	E
Duration of release (min)	30

Table D.17, Data used for calculating the "reference" scenario concerning the plume length.

The information and results for the "reference" scenario are presented in figure D.2 and D.3.

```
SITE DATA:
  Location: SWEDEN, SWEDEN
  Building Air Exchanges Per Hour: 0.55 (unsheltered single storied)
  Time: October 29, 2009  0000 hours ST (user specified)

CHEMICAL DATA:
  Chemical Name: CHLORINE DIOXIDE        Molecular Weight: 67.45 g/mol
  AEGL-1(60 min): 0.15 ppm   AEGL-2(60 min): 1.1 ppm   AEGL-3(60 min): 2.4 ppm
  IDLH: 5 ppm
  Ambient Boiling Point: 10.9° C
  Vapor Pressure at Ambient Temperature: 0.79 atm
  Ambient Saturation Concentration: 786,960 ppm or 78.7%

ATMOSPHERIC DATA: (MANUAL INPUT OF DATA)
  Wind: 2 meters/second from E at 3 meters
  Ground Roughness: urban or forest      Cloud Cover: 5 tenths
  Air Temperature: 5° C                  Stability Class: E
  No Inversion Height                    Relative Humidity: 50%

SOURCE STRENGTH:
  Direct Source: 1.99 kilograms/sec      Source Height: 0
  Release Duration: 30 minutes
  Release Rate: 119 kilograms/min
  Total Amount Released: 3,582 kilograms

THREAT ZONE:
  Model Run: Heavy Gas
  Red   : 5.3 kilometers --- (3 ppm = ERPG-3)
  Orange: greater than 10 kilometers --- (0.5 ppm = ERPG-2)
```

Figure D.2, Information and result for the "reference" scenario.

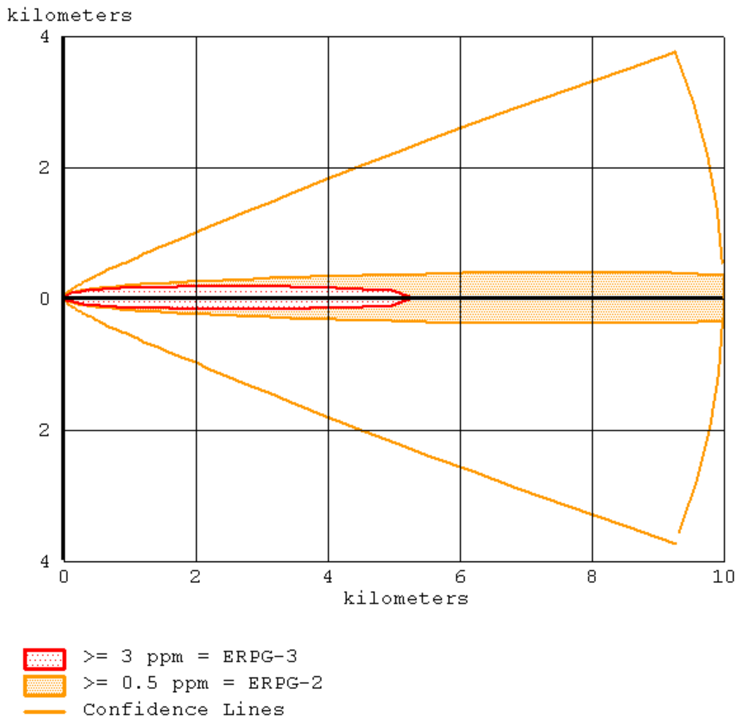

Figure D.3, Result for the “reference” scenario.

The first parameter that is varied is the ambient temperature. This temperature is increased to 20°C. The information and results for the scenario are presented in figure D.4 and D.5.

```
SITE DATA:
  Location: SWEDEN, SWEDEN
  Building Air Exchanges Per Hour: 0.39 (unsheltered single storied)
  Time: April 29, 2009  0000 hours ST (user specified)

CHEMICAL DATA:
  Chemical Name: CHLORINE DIOXIDE        Molecular Weight: 67.45 g/mol
  AEGL-1(60 min): 0.15 ppm   AEGL-2(60 min): 1.1 ppm   AEGL-3(60 min): 2.4 ppm
  IDLH: 5 ppm
  Ambient Boiling Point: 10.9° C
  Vapor Pressure at Ambient Temperature: greater than 1 atm
  Ambient Saturation Concentration: 1,000,000 ppm or 100.0%

ATMOSPHERIC DATA: (MANUAL INPUT OF DATA)
  Wind: 2 meters/second from E at 3 meters
  Ground Roughness: urban or forest      Cloud Cover: 5 tenths
  Air Temperature: 20° C                 Stability Class: E
  No Inversion Height                    Relative Humidity: 50%

SOURCE STRENGTH:
  Direct Source: 1.99 kilograms/sec      Source Height: 0
  Release Duration: 30 minutes
  Release Rate: 119 kilograms/min
  Total Amount Released: 3,582 kilograms
  Note: This chemical may flash boil and/or result in two phase flow.

THREAT ZONE:
  Model Run: Heavy Gas
  Red   : 5.4 kilometers --- (3 ppm = ERPG-3)
  Orange: greater than 10 kilometers --- (0.5 ppm = ERPG-2)
```

Figure D.4, Information and result for the scenario when the ambient temperature is set to 20°C.

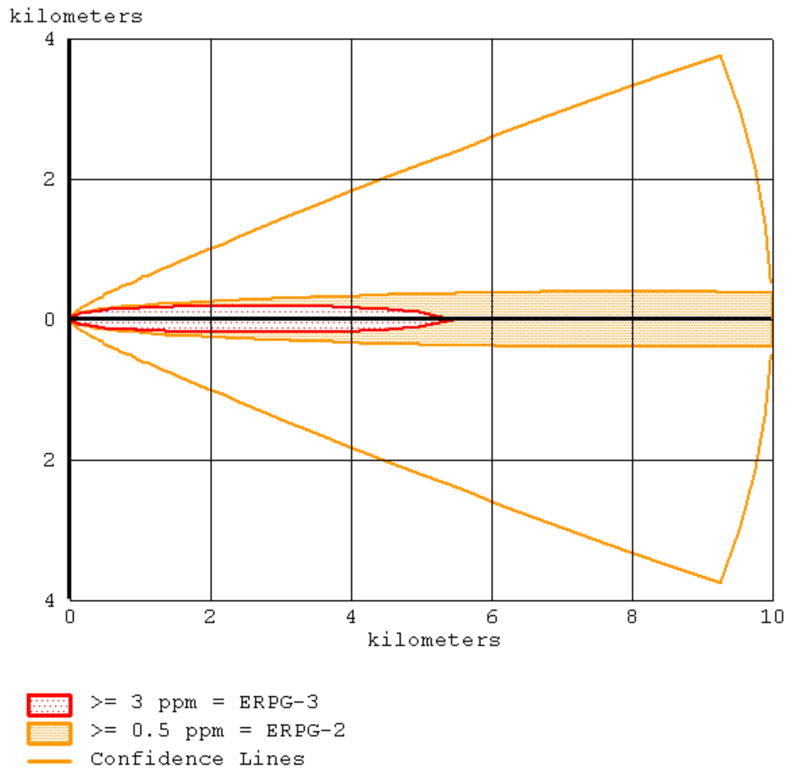

Figure D.5, Result for the scenario when the ambient temperature is set to 20°C.

As one can see when comparing figure D.5 with figure D.3, the ambient temperature does not have any apparent impact on the distance to the different ERPG. The raised temperature only increased the distance of the ERPG-3 zone with 2 %.

Second, the wind speed and atmospheric stability class is changed. The new parameters are 5 m/s and the stability class D. The information and results for the scenario are presented in figure D.6 and D.7.

```
SITE DATA:
  Location: SWEDEN, SWEDEN
  Building Air Exchanges Per Hour: 1.05 (unsheltered single storied)
  Time: October 29, 2009  0000 hours ST (user specified)

CHEMICAL DATA:
  Chemical Name: CHLORINE DIOXIDE        Molecular Weight: 67.45 g/mol
  AEGL-1(60 min): 0.15 ppm   AEGL-2(60 min): 1.1 ppm   AEGL-3(60 min): 2.4 ppm
  IDLH: 5 ppm
  Ambient Boiling Point: 10.9° C
  Vapor Pressure at Ambient Temperature: 0.79 atm
  Ambient Saturation Concentration: 786,960 ppm or 78.7%

ATMOSPHERIC DATA: (MANUAL INPUT OF DATA)
  Wind: 5 meters/second from E at 3 meters
  Ground Roughness: urban or forest      Cloud Cover: 5 tenths
  Air Temperature: 5° C                  Stability Class: D
  No Inversion Height                    Relative Humidity: 50%

SOURCE STRENGTH:
  Direct Source: 1.99 kilograms/sec      Source Height: 0
  Release Duration: 30 minutes
  Release Rate: 119 kilograms/min
  Total Amount Released: 3,582 kilograms

THREAT ZONE:
  Model Run: Heavy Gas
  Red   : 2.6 kilometers --- (3 ppm = ERPG-3)
  Orange: 6.7 kilometers --- (0.5 ppm = ERPG-2)
```

Figure D.6, Information and result for the scenario when the stability class is set to D and the wind speed 5 m/s.

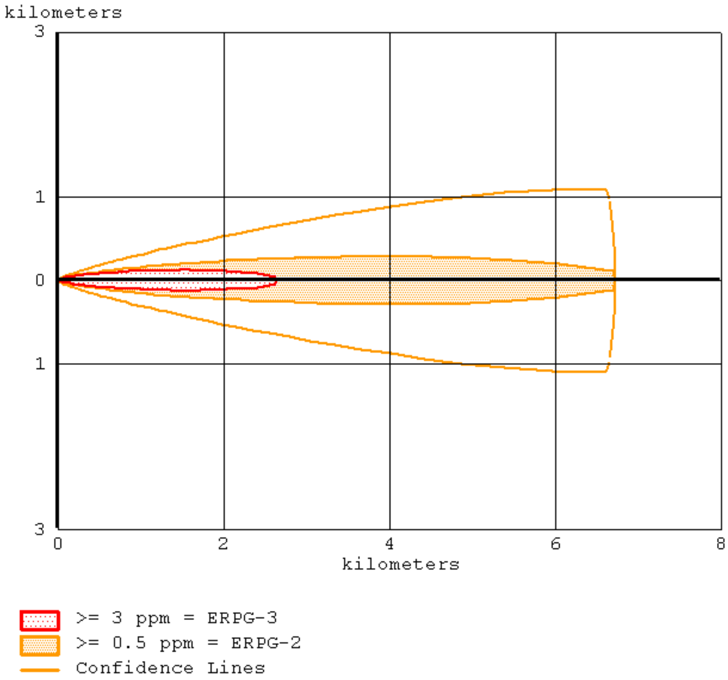

Figure D.7, Result for the scenario when the stability class is set to D and the wind speed 5 m/s.

When comparing figure D.3 and D.7, it is obvious how big of an impact the wind speed and the atmospheric stability class have on the distance of the plume. The length of this plume decreases with more than 50 % when the weather conditions change.

Important to notice with this result is that the source strength used is based on the wind speed of 2 m/s. This could have affected the results. Furthermore, it is important to remember that the presented results show the situation at the altitude of 3 meters. The winds at this altitude might not be the same as on the ground. Given these uncertainties, another calculation is performed. This time with the “correct” source strength based on the wind speed on 5 m/s. The information and results for the scenario are presented in figure D.8 and D.9.

```
SITE DATA:
  Location: SWEDEN, SWEDEN
  Building Air Exchanges Per Hour: 1.05 (unsheltered single storied)
  Time: October 29, 2009  0000 hours ST (user specified)

CHEMICAL DATA:
  Chemical Name: CHLORINE DIOXIDE        Molecular Weight: 67.45 g/mol
  ERPG-2: 0.5 ppm    ERPG-3: 3 ppm
  IDLH: 5 ppm
  Ambient Boiling Point: 10.9° C
  Vapor Pressure at Ambient Temperature: 0.79 atm
  Ambient Saturation Concentration: 786,960 ppm or 78.7%

ATMOSPHERIC DATA: (MANUAL INPUT OF DATA)
  Wind: 5 meters/second from E at 3 meters
  Ground Roughness: urban or forest      Cloud Cover: 5 tenths
  Air Temperature: 5° C                  Stability Class: D
  No Inversion Height                    Relative Humidity: 50%

SOURCE STRENGTH:
  Direct Source: 4.09 kilograms/sec      Source Height: 0
  Release Duration: 30 minutes
  Release Rate: 245 kilograms/min
  Total Amount Released: 7,362 kilograms

THREAT ZONE:
  Model Run: Heavy Gas
  Red   : 3.8 kilometers --- (3 ppm = ERPG-3)
  Orange: 9.8 kilometers --- (0.5 ppm = ERPG-2)
```

Figure D.8, Information and result for the scenario when the stability class is set to D, the wind speed 5 m/s and the source strength is based on the wind speed of 5 m/s, 4.09 kg/s.

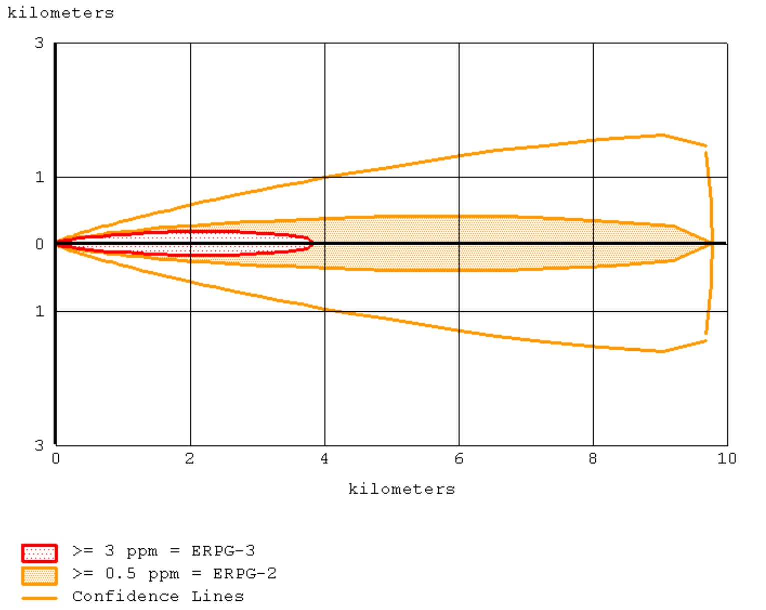

Figure D.9, Result for the scenario when the stability class is set to D, the wind speed 5 m/s and the source strength is based on the wind speed of 5 m/s, 4.09 kg/s.

The results show that the change in weather conditions and the according change in source strength still have an impact on the length of the plume. The distance was decreased with 28% compared with the “reference” scenario.

Continuing investigating the influences from the wind speed and the stability classes and the interaction with the source strength, the weather conditions were returned to the “reference” state, wind speed of 2 m/s and stability class E. Meanwhile, the source strength was however increased to 3.84 kg/s. The information and results for the scenario are presented in figure D.10 and D.11.

```
SITE DATA:
  Location: SWEDEN, SWEDEN
  Building Air Exchanges Per Hour: 0.55 (unsheltered single storied)
  Time: October 29, 2009  0000 hours ST (user specified)

CHEMICAL DATA:
  Chemical Name: CHLORINE DIOXIDE        Molecular Weight: 67.45 g/mol
  AEGL-1(60 min): 0.15 ppm   AEGL-2(60 min): 1.1 ppm   AEGL-3(60 min): 2.4 ppm
  IDLH: 5 ppm
  Ambient Boiling Point: 10.9° C
  Vapor Pressure at Ambient Temperature: 0.79 atm
  Ambient Saturation Concentration: 786,960 ppm or 78.7%

ATMOSPHERIC DATA: (MANUAL INPUT OF DATA)
  Wind: 2 meters/second from E at 3 meters
  Ground Roughness: urban or forest      Cloud Cover: 5 tenths
  Air Temperature: 5° C                  Stability Class: E
  No Inversion Height                    Relative Humidity: 50%

SOURCE STRENGTH:
  Direct Source: 3.84 kilograms/sec      Source Height: 0
  Release Duration: 30 minutes
  Release Rate: 230 kilograms/min
  Total Amount Released: 6,912 kilograms

THREAT ZONE:
  Model Run: Heavy Gas
  Red   : 7.5 kilometers --- (3 ppm = ERPG-3)
  Orange: greater than 10 kilometers --- (0.5 ppm = ERPG-2)
```

Figure D.10, Information and result for the scenario when the stability class is set to E, the wind speed 2 m/s and the source strength 3.84 kg/s.

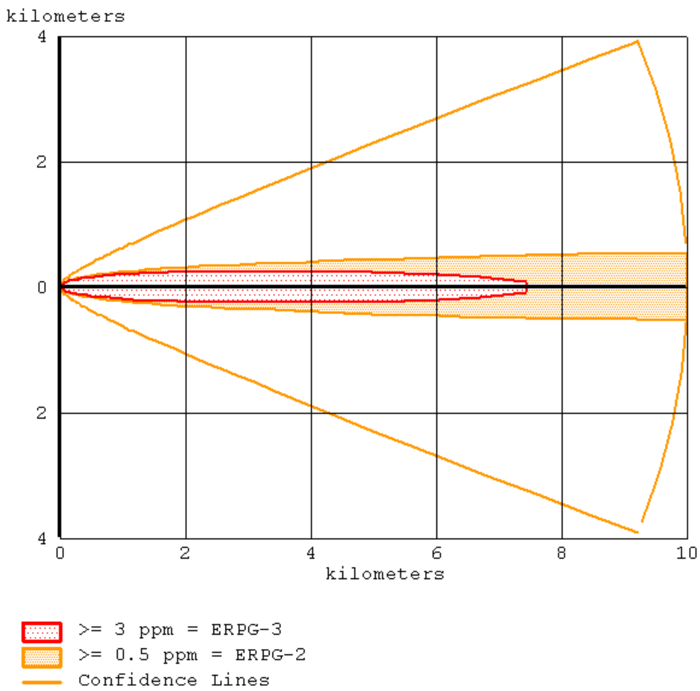

Figure D.11, Result for the scenario when the stability class is set to E, the wind speed 2 m/s and the source strength 3.84 kg/s.

The change in source strength had large impact on the distance. This is evident when comparing figure D.11 with figure D.3. When the source strength is doubled, the distance increases 39%.

In order to look at the scenarios of pipe rupture and pipe leakage, these source strengths is used. Once again, one should be aware of the fact that the used source strength is based on the wind speed of 5 m/s, while the weather conditions in ALOHA is stated as 2 m/s and stability class E. These both correspond with a worst-case scenario according to the calculations made above. The information and results for the scenarios are presented in figure D.12 to D.15.

```
SITE DATA:
  Location: SWEDEN, SWEDEN
  Building Air Exchanges Per Hour: 0.55 (unsheltered single storied)
  Time: November 20, 2009  0000 hours ST (user specified)

CHEMICAL DATA:
  Chemical Name: CHLORINE DIOXIDE        Molecular Weight: 67.45 g/mol
  AEGL-1(60 min): 0.15 ppm   AEGL-2(60 min): 1.1 ppm   AEGL-3(60 min): 2.4 ppm
  IDLH: 5 ppm
  Ambient Boiling Point: 10.9° C
  Vapor Pressure at Ambient Temperature: 0.79 atm
  Ambient Saturation Concentration: 786,960 ppm or 78.7%

ATMOSPHERIC DATA: (MANUAL INPUT OF DATA)
  Wind: 2 meters/second from E at 3 meters
  Ground Roughness: urban or forest      Cloud Cover: 5 tenths
  Air Temperature: 5° C                  Stability Class: E
  No Inversion Height                    Relative Humidity: 50%

SOURCE STRENGTH:
  Direct Source: 0.08 kilograms/sec      Source Height: 0
  Release Duration: 30 minutes
  Release Rate: 4.8 kilograms/min
  Total Amount Released: 144 kilograms

THREAT ZONE:
  Model Run: Heavy Gas
  Red   : 982 meters --- (3 ppm = ERPG-3)
  Orange: 2.6 kilometers --- (0.5 ppm = ERPG-2)
  Yellow: less than 10 meters(10.9 yards) --- (286 grams/(cu m))
  Note: Threat zone was not drawn because effects of near-field patchiness
    make dispersion predictions less reliable for short distances.
```

Figure D.12, Information and result for the pipe leakage scenario.

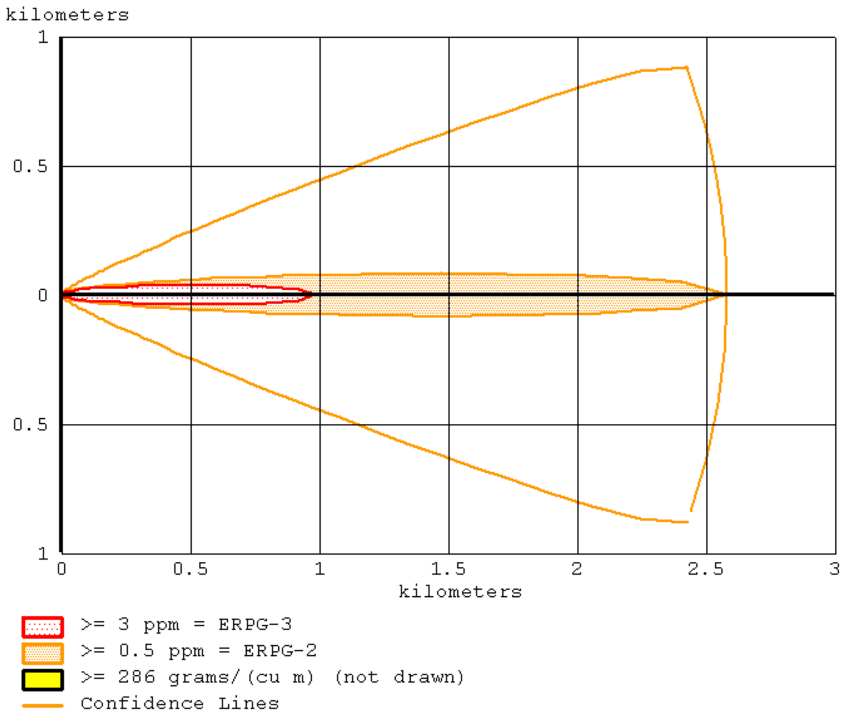

Figure D.13, Result for the pipe leakage scenario.

```
SITE DATA:
  Location: SWEDEN, SWEDEN
  Building Air Exchanges Per Hour: 0.55 (unsheltered single storied)
  Time: November 20, 2009  0000 hours ST (user specified)

CHEMICAL DATA:
  Chemical Name: CHLORINE DIOXIDE        Molecular Weight: 67.45 g/mol
  AEGL-1(60 min): 0.15 ppm   AEGL-2(60 min): 1.1 ppm   AEGL-3(60 min): 2.4 ppm
  IDLH: 5 ppm
  Ambient Boiling Point: 10.9° C
  Vapor Pressure at Ambient Temperature: 0.79 atm
  Ambient Saturation Concentration: 786,960 ppm or 78.7%

ATMOSPHERIC DATA: (MANUAL INPUT OF DATA)
  Wind: 2 meters/second from E at 3 meters
  Ground Roughness: urban or forest      Cloud Cover: 5 tenths
  Air Temperature: 5° C                  Stability Class: E
  No Inversion Height                    Relative Humidity: 50%

SOURCE STRENGTH:
  Direct Source: 0.5 kilograms/sec       Source Height: 0
  Release Duration: 30 minutes
  Release Rate: 30 kilograms/min
  Total Amount Released: 900 kilograms

THREAT ZONE:
  Model Run: Heavy Gas
  Red    : 2.6 kilometers --- (3 ppm = ERPG-3)
  Orange: 6.8 kilometers --- (0.5 ppm = ERPG-2)
  Yellow: less than 10 meters(10.9 yards) --- (286 grams/(cu m))
  Note: Threat zone was not drawn because effects of near-field patchiness
    make dispersion predictions less reliable for short distances.
```

Figure D.14, Information and result for the pipe rupture scenario.

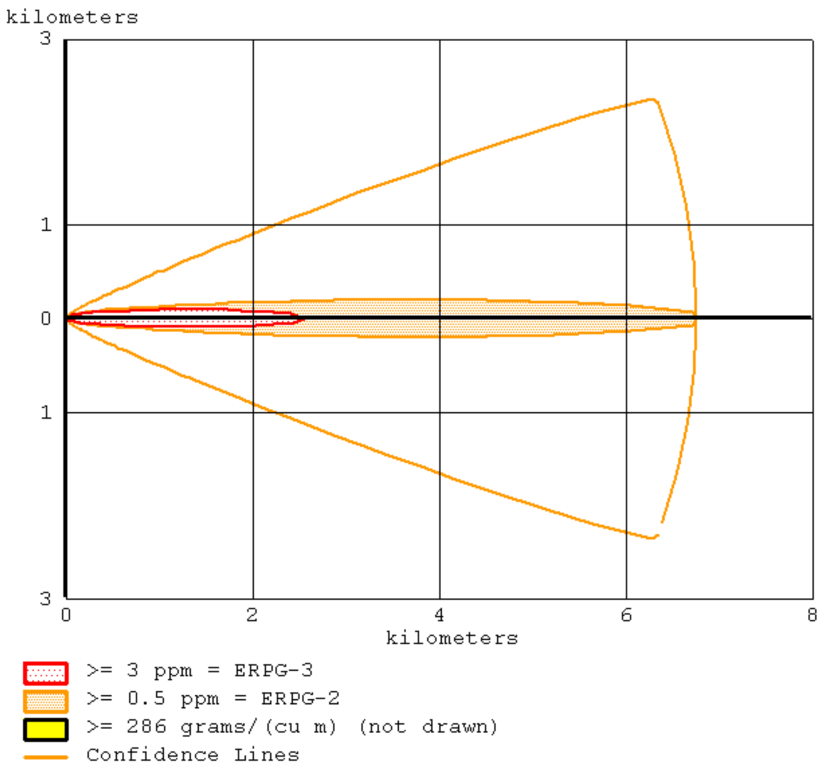

Figure D.15, Result for the pipe rupture scenario.

Although severe, it is evident from figure D.12 to D.15 that the pipe leakage and pipe ruptures are far less severe than the tank leakage and tank rupture.

The next parameter varied is the duration of the leakage and thereby the degassing. During the previous calculations, the duration of the release have been fixed at 30 minutes. The duration will now be changed to 5 minutes and 60 minutes. The information and results for the scenarios are presented in figure D.16 to D.17.

```
SITE DATA:
  Location: SWEDEN, SWEDEN
  Building Air Exchanges Per Hour: 0.55 (unsheltered single storied)
  Time: October 29, 2009  0000 hours ST (user specified)

CHEMICAL DATA:
  Chemical Name: CHLORINE DIOXIDE        Molecular Weight: 67.45 g/mol
  AEGL-1(60 min): 0.15 ppm   AEGL-2(60 min): 1.1 ppm   AEGL-3(60 min): 2.4 ppm
  IDLH: 5 ppm
  Ambient Boiling Point: 10.9° C
  Vapor Pressure at Ambient Temperature: 0.79 atm
  Ambient Saturation Concentration: 786,960 ppm or 78.7%

ATMOSPHERIC DATA: (MANUAL INPUT OF DATA)
  Wind: 2 meters/second from E at 3 meters
  Ground Roughness: urban or forest      Cloud Cover: 5 tenths
  Air Temperature: 5° C                  Stability Class: E
  No Inversion Height                    Relative Humidity: 50%

SOURCE STRENGTH:
  Direct Source: 1.99 kilograms/sec      Source Height: 0
  Release Duration: 5 minutes
  Release Rate: 119 kilograms/min
  Total Amount Released: 597 kilograms

THREAT ZONE:
  Model Run: Heavy Gas
  Red   : 4.4 kilometers --- (3 ppm = ERPG-3)
  Orange: 9.2 kilometers --- (0.5 ppm = ERPG-2)
```

Figure D.16, Information and result for the scenario when the duration of the release is set to 5 minutes.

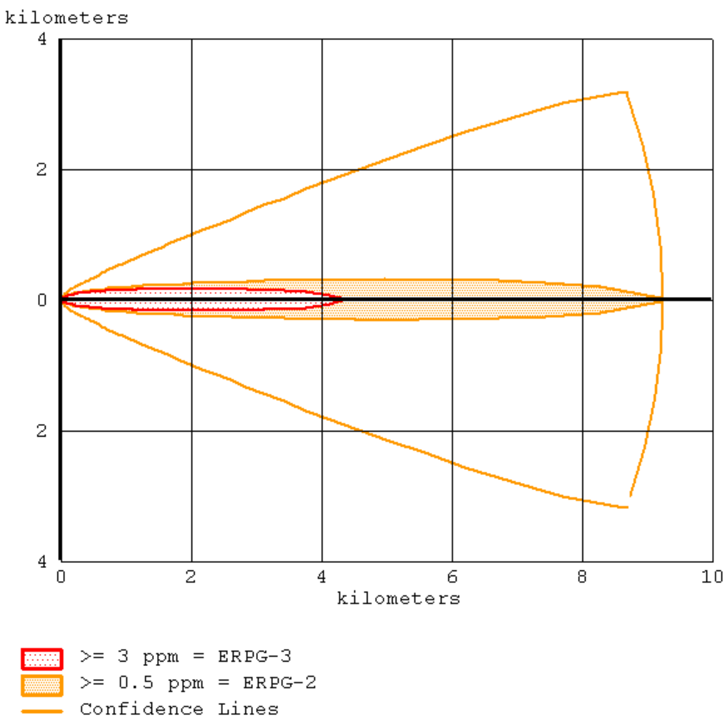

Figure D.17, Result for the scenario when the duration of the release is set to 5 minutes.

When the duration is decreased to 5 minutes, the distance of the plume has decrease 19 % from the “reference” scenario. The increase of the duration to 60 minutes does not give any change compared with the “reference” scenario, and is therefore not presented visually here. The results need to be overlooked with the fact that an earlier assumption stated that no decrease in degassing would take place, unlike the practice. Nevertheless, the results show that the duration of the release could have an impact on the length of the plume and the distance of the exposure. However, the most important reason why the duration of the release should be limited can be seen when comparing figure D.18 and D.19.

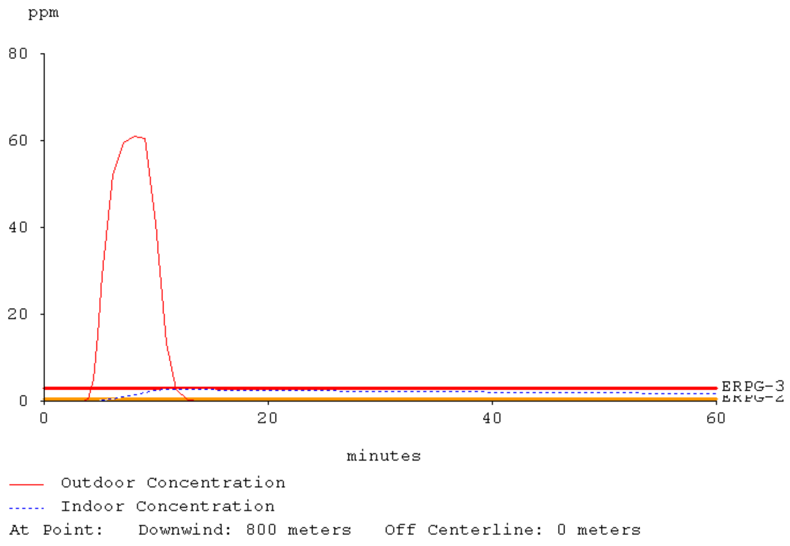

Figure D.18, A plot of the concentration at 800 meters distance from the source, depending of the time from the release. In this plot, the duration of the release is set to 5 minutes.

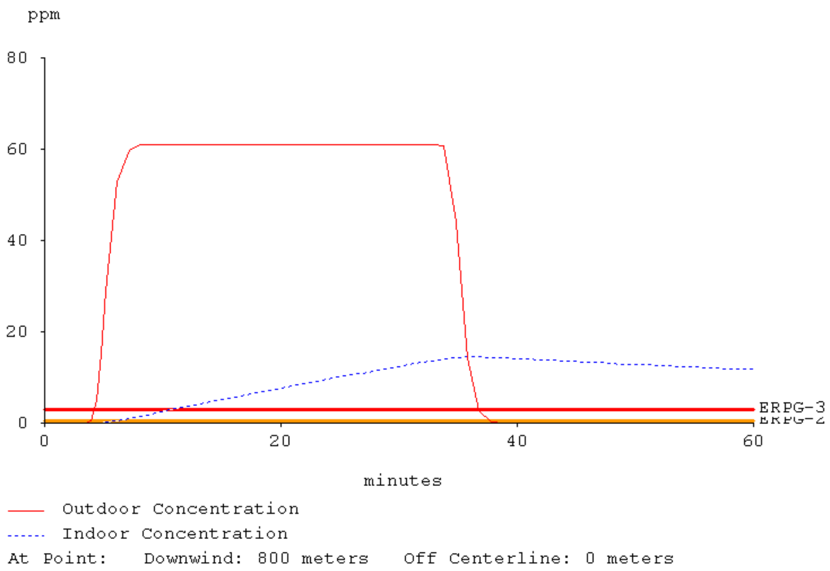

Figure D.19, A plot of the concentration at 800 meters distance from the source, depending of the time from the release. In this plot, the duration of the release is set to 30 minutes.

The duration of the release also determine the duration of exposure because of the fact that the plume will be diluted quickly as soon as the release are stopped. Since the ERPG values are given for a 60-minute exposure, the damages might be mitigated if the exposure is limited to 5 or 3 minutes.

The distance to where the concentration in the plume is 0.3 ppm is also calculated. This is because 0.3 ppm corresponds to the “Takgränsvärde” stated by the Swedish Arbetsmiljöverket. The result, presented in figure D.20 and D.21, should be compared with the results in figure D.6 and D.7. The reason for this is that ALOHA cannot calculate any exact plume lengths above 10 km. Hence, a scenario where the plume length falls below this distance has to be used.

```
SITE DATA:
  Location: SWEDEN, SWEDEN
  Building Air Exchanges Per Hour: 1.05 (unsheltered single storied)
  Time: October 29, 2009  0000 hours ST (user specified)

CHEMICAL DATA:
  Chemical Name: CHLORINE DIOXIDE        Molecular Weight: 67.45 g/mol
  ERPG-2: 0.5 ppm    ERPG-3: 3 ppm
  IDLH: 5 ppm
  Ambient Boiling Point: 10.9° C
  Vapor Pressure at Ambient Temperature: 0.79 atm
  Ambient Saturation Concentration: 788,098 ppm or 78.8%

ATMOSPHERIC DATA: (MANUAL INPUT OF DATA)
  Wind: 5 meters/second from E at 3 meters
  Ground Roughness: urban or forest      Cloud Cover: 5 tenths
  Air Temperature: 5° C                  Stability Class: D
  No Inversion Height                    Relative Humidity: 50%

SOURCE STRENGTH:
  Direct Source: 1.99 kilograms/sec      Source Height: 0
  Release Duration: 30 minutes
  Release Rate: 119 kilograms/min
  Total Amount Released: 3,582 kilograms

THREAT ZONE:
  Model Run: Heavy Gas
  Yellow: 8.8 kilometers --- (0.3 ppm)
```

Figure D.20, Information and result for the scenario when the concentration is set to 0.3 ppm.

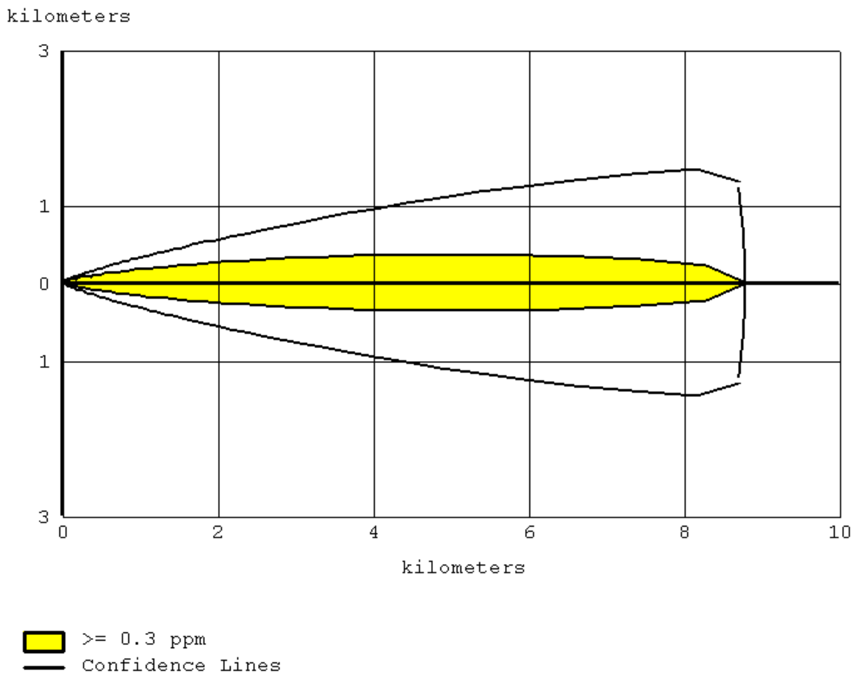

Figure D.21, The results for the scenario when the concentration is set to 0.3 ppm.

The result show that the plume length with this cut off value in ALOHA is 8.8 km. This is 31% longer than if 0.5 ppm is used as a cut off value.

A sensitivity analysis of the time component will be conducted next. This is to see how the depletion of the source affects the plume length. The source strengths that are being used are the last two in table D.15. The plume from these will be compared with the result in figure D.8 and D.9. The two source strengths in table D.16 correspond to concentrations of 8 g/dm^3 and 6 g/dm^3. From the information in the section *The change in source strength over time*, it is known that a source strength of 8 g/dm^3 will be reached after approximately 20 minutes and a concentration of 6 g/dm^3 after approximately 50 minutes. The results are presented in figure D.22 to D.25.

```
SITE DATA:
  Location: SWEDEN, SWEDEN
  Building Air Exchanges Per Hour: 1.05 (unsheltered single storied)
  Time: October 29, 2009  0000 hours ST (user specified)

CHEMICAL DATA:
  Chemical Name: CHLORINE DIOXIDE        Molecular Weight: 67.45 g/mol
  ERPG-2: 0.5 ppm    ERPG-3: 3 ppm
  IDLH: 5 ppm
  Ambient Boiling Point: 10.9° C
  Vapor Pressure at Ambient Temperature: 0.79 atm
  Ambient Saturation Concentration: 788,098 ppm or 78.8%

ATMOSPHERIC DATA: (MANUAL INPUT OF DATA)
  Wind: 5 meters/second from e at 3 meters
  Ground Roughness: urban or forest      Cloud Cover: 5 tenths
  Air Temperature: 5° C                  Stability Class: D
  No Inversion Height                    Relative Humidity: 50%

SOURCE STRENGTH:
  Direct Source: 3.4 kilograms/sec       Source Height: 0
  Release Duration: 20 minutes
  Release Rate: 204 kilograms/min
  Total Amount Released: 4,080 kilograms

THREAT ZONE:
  Model Run: Heavy Gas
  Red   : 3.5 kilometers --- (3 ppm = ERPG-3)
  Orange: 8.9 kilometers --- (0.5 ppm = ERPG-2)
  Yellow: greater than 10 kilometers --- (0.3 ppm)
```

Figure D.22, The plume lengths for a concentration of 8 g/dm^3. This concentration is reached 20 minutes after the release.

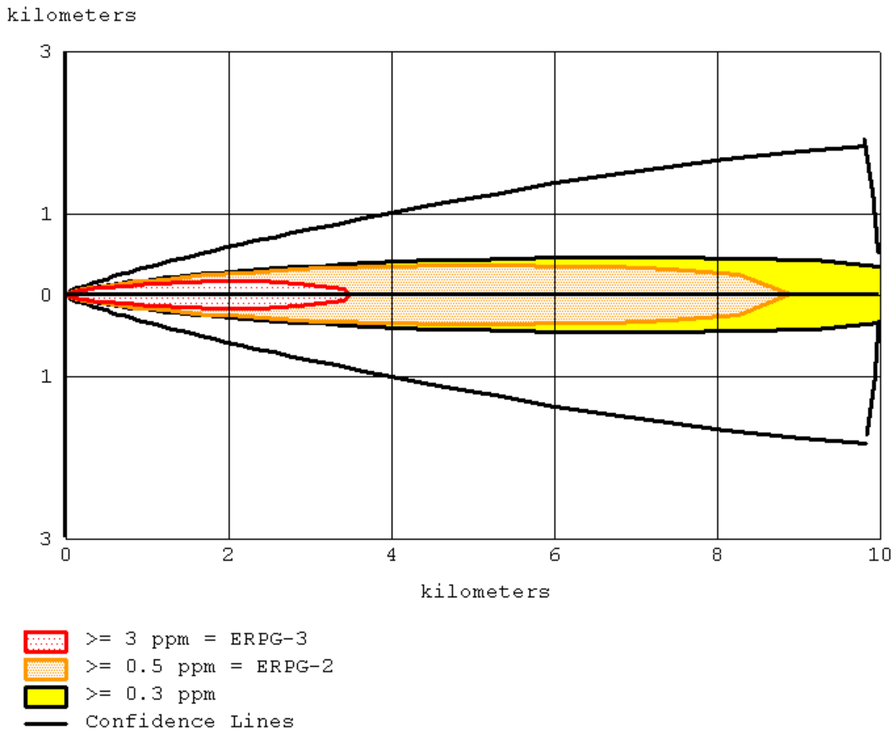

Figure D.23, The plume lengths for a concentration of 8 g/dm^3. This concentration is reached 20 minutes after the release.

```
SITE DATA:
  Location: SWEDEN, SWEDEN
  Building Air Exchanges Per Hour: 1.05 (unsheltered single storied)
  Time: October 29, 2009  0000 hours ST (user specified)

CHEMICAL DATA:
  Chemical Name: CHLORINE DIOXIDE        Molecular Weight: 67.45 g/mol
  ERPG-2: 0.5 ppm    ERPG-3: 3 ppm
  IDLH: 5 ppm
  Ambient Boiling Point: 10.9° C
  Vapor Pressure at Ambient Temperature: 0.79 atm
  Ambient Saturation Concentration: 788,098 ppm or 78.8%

ATMOSPHERIC DATA: (MANUAL INPUT OF DATA)
  Wind: 5 meters/second from e at 3 meters
  Ground Roughness: urban or forest      Cloud Cover: 5 tenths
  Air Temperature: 5° C                  Stability Class: D
  No Inversion Height                    Relative Humidity: 50%

SOURCE STRENGTH:
  Direct Source: 2.7 kilograms/sec       Source Height: 0
  Release Duration: 30 minutes
  Release Rate: 162 kilograms/min
  Total Amount Released: 4,860 kilograms

THREAT ZONE:
  Model Run: Heavy Gas
  Red   : 3.1 kilometers --- (3 ppm = ERPG-3)
  Orange: 7.9 kilometers --- (0.5 ppm = ERPG-2)
  Yellow: greater than 10 kilometers --- (0.3 ppm)
```

Figure D.24, The plume lengths for a concentration of 6 g/dm^3. This concentration is reached 50 minutes after the release.

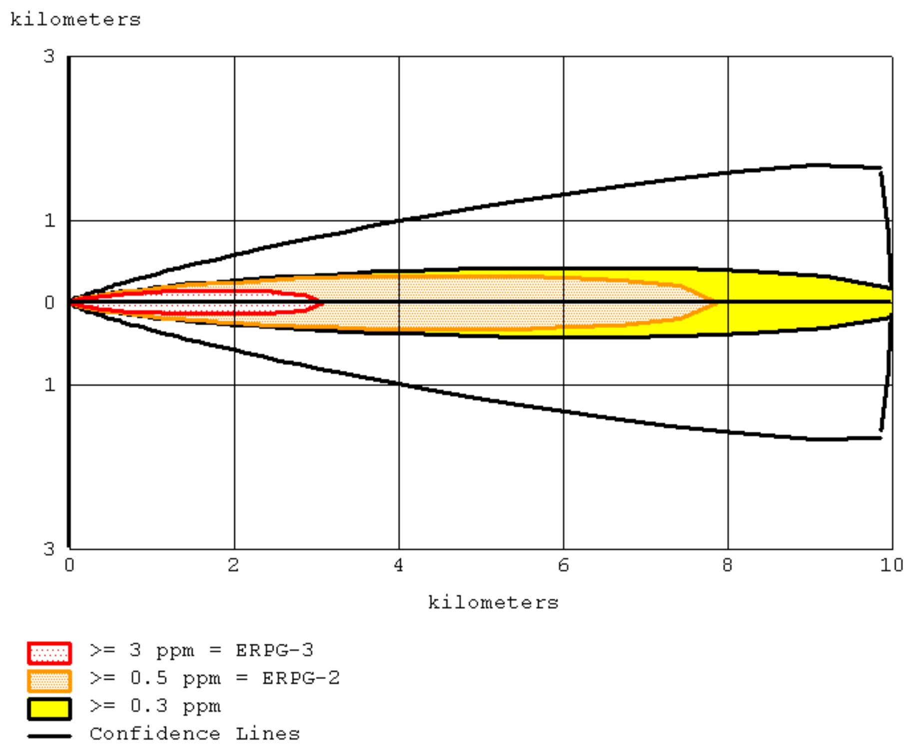

Figure D.25, The plume lengths for a concentration of 6 g/dm^3. This concentration is reached 50 minutes after the release.

When comparing the results in figure D.22 to D.25 with the one in figure D.8 and D.9, one can see that the plume length, in respect to the ERPG-3 value, decreases with 8% during the first 20 minutes. If the solution is allowed to be degassing for 50 minutes, the plume length will be decreased by 19%.

However, these results assume that the plume lengths are instantaneous. In reality, this is not the case. It will take some time before the plume will reach its full length after the initial release, as indicated by the results in figure D16 and D.17. Because of this, the source strength has decreased before the plume will reach the length calculated in figure D.8 and D.9. It is therefore important to understand that the plume lengths are exaggerated.

In table D.18, a summary of the different plume lengths are presented.

Source strength, wind speed, stability class and duration of the release	Distance to ERPG-3	Distance to ERPG-2
1.99 kg/s, 2 m/s, E, 30 min	5.3 km	>10 km
1.99 kg/s, 5 m/s, D, 30 min	2.6 km	6.7 km
4.09 kg/s, 5 m/s, D, 30 min	3.8 km	9.8 km
3.84 kg/s, 2 m/s, E, 30 min	7.5 km	>10 km
0.08 kg/s, 2 m/s, E, 30 min	982 m	2.6 km
0.50 kg/s, 2 m/s, E, 30 min	2.6 km	6.8 km
1.99 kg/s, 2 m/s, E, 5 min	4.4 km	9.2 km

Table D.48, A summary of the plume lengths calculated above,

Finally, a “reverse” calculation will be made. In the calculation the distance will be set to 20, 100, 400 and 800 meters from the source and the concentration at these distances will be calculated. These calculations will be made with the weather parameters stated in table D.19 and with source strengths of 3.84 and 0.5 kg/s.

Ambient temperature (°C)	5
Wind speed (m/s)	2
Stability class	E
Duration of release (min)	30

Table D.19, The weather conditions and duration of the release used when calculating the concentration at different distances from the source.

The concentration at the different distances, when calculated for source strength of 0.5 kg/s, is presented in table D.20.

Distance from source (m)	Concentration (ppm)
20	7340
100	481
400	63
800	23

Table D.20, The concentration at different distances when the source strength is set to 0.5 kg/s.

The concentration at the different distances, when calculated for source strength of 3.84 kg/s, is presented in table D.21.

Distance from source (m)	Concentration (ppm)
20	38900
100	2570
400	277
800	98

Table D.21, The concentration at different distances when the source strength is set to 3.84 kg/s.

4. Explosion

The partial pressure at which ClO_2 might undergo explosion-like decomposition is approximately 10 kPa. According to the ideal gas law, this corresponds to a concentration of 286 g of ClO_2/m^3. When calculating the possibility of an explosion, a worst-case scenario with source strength of 11.5 kg/s is first used. The result is presented in figure D.26. From the figure, it is apparent that an explosion is possible in proximity of 18 meters from the source. In addition, with scenarios using source strengths of 7.9 and 4.1 kg/s, explosion is possible, see figure D.27 and D.28.

```
SITE DATA:
  Location: SWEDEN, SWEDEN
  Building Air Exchanges Per Hour: 0.39 (unsheltered single storied)
  Time: November 9, 2009  0000 hours ST (user specified)

CHEMICAL DATA:
  Chemical Name: CHLORINE DIOXIDE        Molecular Weight: 67.45 g/mol
  ERPG-2: 0.5 ppm    ERPG-3: 3 ppm
  IDLH: 5 ppm
  Ambient Boiling Point: 51.6° F
  Vapor Pressure at Ambient Temperature: greater than 1 atm
  Ambient Saturation Concentration: 1,000,000 ppm or 100.0%

ATMOSPHERIC DATA: (MANUAL INPUT OF DATA)
  Wind: 2 meters/second from E at 3 meters
  Ground Roughness: urban or forest      Cloud Cover: 5 tenths
  Air Temperature: 20° C                 Stability Class: E
  No Inversion Height                    Relative Humidity: 50%

SOURCE STRENGTH:
  Direct Source: 11.5 kilograms/sec      Source Height: 0
  Release Duration: 30 minutes
  Release Rate: 1,520 pounds/min
  Total Amount Released: 45,636 pounds
  Note: This chemical may flash boil and/or result in two phase flow.

THREAT ZONE:
  Model Run: Heavy Gas
  Red   : greater than 6 miles --- (3 ppm = ERPG-3)
  Orange: greater than 6 miles --- (0.5 ppm = ERPG-2)
  Yellow: 20 yards --- (286 grams/(cu m))
  Note: Threat zone was not drawn because effects of near-field patchiness
    make dispersion predictions less reliable for short distances.
```

Figure D.26, The range within an explosion might occur, using source strength of 11.5 kg/s. The distance is presented under the headline threat zone and the threshold is set to 286 g/m^3.

```
SITE DATA:
  Location: SWEDEN, SWEDEN
  Building Air Exchanges Per Hour: 0.39 (unsheltered single storied)
  Time: November 9, 2009  0000 hours ST (user specified)

CHEMICAL DATA:
  Chemical Name: CHLORINE DIOXIDE        Molecular Weight: 67.45 g/mol
  ERPG-2: 0.5 ppm    ERPG-3: 3 ppm
  IDLH: 5 ppm
  Ambient Boiling Point: 51.6° F
  Vapor Pressure at Ambient Temperature: greater than 1 atm
  Ambient Saturation Concentration: 1,000,000 ppm or 100.0%

ATMOSPHERIC DATA: (MANUAL INPUT OF DATA)
  Wind: 2 meters/second from E at 3 meters
  Ground Roughness: urban or forest      Cloud Cover: 5 tenths
  Air Temperature: 20° C                 Stability Class: E
  No Inversion Height                    Relative Humidity: 50%

SOURCE STRENGTH:
  Direct Source: 7.9 kilograms/sec       Source Height: 0
  Release Duration: 30 minutes
  Release Rate: 1,040 pounds/min
  Total Amount Released: 31,350 pounds
  Note: This chemical may flash boil and/or result in two phase flow.

THREAT ZONE:
  Model Run: Heavy Gas
  Red   : greater than 6 miles --- (3 ppm = ERPG-3)
  Orange: greater than 6 miles --- (0.5 ppm = ERPG-2)
  Yellow: 16 yards --- (286 grams/(cu m))
  Note: Threat zone was not drawn because effects of near-field patchiness
    make dispersion predictions less reliable for short distances.
```

Figure D.27, The range within an explosion might occur, using source strength of 7.9 kg/s.

```
SITE DATA:
  Location: SWEDEN, SWEDEN
  Building Air Exchanges Per Hour: 0.39 (unsheltered single storied)
  Time: November 9, 2009  0000 hours ST (user specified)

CHEMICAL DATA:
  Chemical Name: CHLORINE DIOXIDE        Molecular Weight: 67.45 g/mol
  ERPG-2: 0.5 ppm    ERPG-3: 3 ppm
  IDLH: 5 ppm
  Ambient Boiling Point: 51.6° F
  Vapor Pressure at Ambient Temperature: greater than 1 atm
  Ambient Saturation Concentration: 1,000,000 ppm or 100.0%

ATMOSPHERIC DATA: (MANUAL INPUT OF DATA)
  Wind: 2 meters/second from E at 3 meters
  Ground Roughness: urban or forest      Cloud Cover: 5 tenths
  Air Temperature: 20° C                 Stability Class: E
  No Inversion Height                    Relative Humidity: 50%

SOURCE STRENGTH:
  Direct Source: 4.1 kilograms/sec       Source Height: 0
  Release Duration: 30 minutes
  Release Rate: 542 pounds/min
  Total Amount Released: 16,270 pounds
  Note: This chemical may flash boil and/or result in two phase flow.

THREAT ZONE:
  Model Run: Heavy Gas
  Red   : 4.9 miles --- (3 ppm = ERPG-3)
  Orange: greater than 6 miles --- (0.5 ppm = ERPG-2)
  Yellow: less than 10 meters(10.9 yards) --- (286 grams/(cu m))
  Note: Threat zone was not drawn because effects of near-field patchiness
    make dispersion predictions less reliable for short distances.

THREAT AT POINT:
  Concentration Estimates at the point:
  Downwind: 2 yards                      Off Centerline: 0 yards
  Max Concentration:
```

Figure D.28, The range within an explosion might occur, using source strength of 4.1 kg/s.

From figure D.12 and D.14, one can see that there is a probability of explosion also in the scenario of a pipe leakage and pipe rupture. However, due to limitations in ALOHA, it is not clear how far from the source this risk exists. To decrease the risk from explosion in case of a release, one should try to lower the source strength.

5. Discussion concerning the uncertainties

As mentioned before, the consequence calculations made above are based on several assumptions. These assumptions make both the calculated source strength and the calculated length of the plume very uncertain. For one thing, there are assumptions about the physical properties of the chemical. Such assumptions are for example that the mass transport inside of the solution does not limit the degassing and that no decomposition after the release takes place. This might be the largest limitations in the consequence calculations, since the decomposition is a very important limiting factor according to Alp and Boughner (2005). There are also assumptions concerning the properties of the source, being a single source from a point or degassing from several soccer fields. The result presented should be considered as worst-case scenarios in every aspect and are probably highly exaggerated.

Because of all these uncertainties and assumptions, it is reasonable to question the validity of the plume lengths calculated. Instead of posing as a real measure of the plume length for different scenarios, the calculations real value might be that it maps the impact of different parameters on the resulting plume length. Thus creating and understanding how to mitigate the consequences.

6. Actions that might mitigate the consequences

In the sensitivity analysis made above, several parameters that affect the source strength and plume length are identified. The area from which the gaseous ClO_2 can leave the solution is one of those. This parameter is readily influenced and the most obvious measure is to install dikes around the storage tanks. This will, as has been shown, reduce the source strength. On the downside, the building might be expensive and impossible to implement at older ClO_2 storage facilities due to obstructing constructions and lack of space.

The wind is also a parameter affecting the source strength. A high wind speed above the solution increases the degassing rate, which is not desirable. However, the effect of the wind is the opposite when it comes to plume length. A high wind speed decreases the plume length. Thereby, the wind speed has both negative and positive influence on the consequences. These calculations have not looked deeper into this phenomenon. To draw a conclusion whether the effect are more positive or negative requires more work and investigation within the area. Possible mitigation of the consequences could be to place the storage tanks indoor. By doing this, no wind could affect the leakage, limiting the source strength. The indoor placement would also help contain releasing ClO_2 and keep it from spreading. However, while keeping it from spreading, the building also keeps it from diluting, which could increase the probability of an explosion.

The duration of the degassing might also be limited through different actions. The pulps mills could install different systems for suppressing and stopping the degassing. Such systems could consist of neutralizing agents consuming the ClO_2 in the solution as well as foam, covering the solution and obstructing degassing. The duration of the release could also be shortened through closer monitoring and better monitoring systems and enclosing equipments, for example remotely controlled valves.

To limit the source strength, one can also try to reduce the amount of solution being released. The obvious reason for this is the relationship between the volume released and the area of the leakage. Many of the ClO_2 storage facilities have several storage tanks working as "connected vessels". These ClO_2 storage facilities should install a valve between the storage tanks that automatically, or manually, can be closed when the levels inside starts to decrease too fast. This protective installation might prevent and limit the leakage to the volume of one storage tank at maximum, thereby limiting the source strength.

Another way to reduce the amount of solution released is to limit the size of the holes. Preventive measures for limiting the size of the hole, is collision protection. Another possible action to reduce the leakage is to reinforce the lower part of the storage tank and strengthen the pipes. Since only the solution above the hole will be released this part of the storage tank is the most important to reinforce. Finally, a third way to limit the release from a tank leakage is to have a drain that enables the solution to leave the tank to a compartment that is designed specifically to be able to contain it. This drain should be located in the very bottom of the tank so that the largest volume possible can leave the tank this way, instead of the hole.

The temperature of the solution is also important affecting the source strength. Therefore, all ClO_2 production facilities should have a cooling system for the water forming the solution. To have a maximal solution temperature of 10°C should be the norm. The pulp mill should also consider the placing of the storage tanks away from the sun and the color of the storage tanks as neutral, reflecting the sun.

The source strength is also dependent on the concentration of the solution. Most pulp mills seem to have a concentration of about 10 g ClO_2/dm^3. Higher concentrations should be avoided. One way to decrease the concentration is modifications to the process, requiring less ClO_2 per liter.

The levels of temperature and concentration above are not absolute and depend on each other. Figure D.1 shows that if the temperature is lower than 10°C, a higher concentration than 10 g/dm^3 might be tolerated. However, it is impossible to take every possible combination of solution temperature and concentration in consideration.

Appendix E – Precedent risk assessments and risk analyses

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1. Definitions

The scales for the consequences as well as definitions of the different probabilities used in the risk assessments are presented in table E.1 and table E.2.

Consequence	
Class	Magnitude
1	Small
2	Light
3	Large
4	Very Large
5	Catastrophic

Table E.1, Scale of the consequences.

Probability	
Class	Description
1 Very unlikely	Once per 1000 years or more seldom
2 Remote	Once per 100-1000 years
3 Occasional	Once per 10-100 years
4 Probable	Once per 1-10 years
5 Frequent	More than 1 per year

Table E.2, Definition of the probabilities.

2. Remarks

There have been some remarks made in the tables presented above.

*The authors have chosen to include these “scenarios” even though the actual hazardous event is not included into the defined system. However, the consequence of this event most certainly will occur inside the defined system and therefore the authors made the decision to include this event. Some of the consequences and causes for this event have been excluded since they are not relevant, due to their presence and functioning outside the system. Of course, this exclusion will result in the changing of the consequence and the probability. Therefore, the values presented for these events should be looked upon with some skepticism.

** The report did not present any values for these parameters. Whether there had been some mistake, the conducting group could not agree on these, there were no consequences at all or for what reason they were excluded was not stated.

3. Risk assessment of pulp mill ALFA from 1999

Hazard	Consequence	Cause	Probability	Consequence		
				Health	Environment	Property
Leakage of ClO_2	ClO_2 in building ClO_2 to drainage	Pipe rupture due to corrosion Leakage from packing	3	3	2	3
Water falling off absorption tower*	"Puff" in storage tank	Dirty glass in analyzer giving error display Delayed sample taking to analyzer Error signal from analyzer	3	2	2	4
Water falling off absorption tower*	"Puff" in storage tank	Stop water pump Control valve closed by signal from ClO_2 analyzer	3	3	2	4
Connection GAP-pipe breaks	Leakage of ClO_2	Falling scaffold	2	2	3	2

Rupture or leakage at storage tanks	ClO_2 to air	"Puff" due to:	3	3/4	2	3
	ClO_2 to drainage	High ClO_2 concentration				
		No ventilation				
		Solar radiation				
		Warm water and high concentration				
		Quick leveling				
Rupture or leakage at storage tanks	ClO_2 to air	Rupture of pipe connected with pump	3	3	2	2
	ClO_2 to drainage	Falling scaffold				
		Corrosion				
Rupture or leakage at storage tanks	Leakage of ClO_2	Storage tank imploding cause of vacuum	3	2	2	3
	Disorder of the production	Freezing of ventilation				
		Quick cooling of gas				

Leakage of ClO_2	ClO_2 in building ClO_2 to drainage	Pipe rupture because of freezing Leakage level analyzer because of freezing	3	3	2	3
Rupture or leakage at storage tanks	ClO_2 to air ClO_2 to drainage Disorder of the production	Collision from tractor when snow clearing	3	3/4	2	3
Leakage of ClO_2	Leakage of ClO_2	Falling scaffold Mechanical work, cutting wrong pipe	2	3	2	3
Leakage of ClO_2 at maintenance stop	Gaseous ClO_2 in building	Leaking valves ClO_2 water in tanks	?**	?**	?**	?**
Leakage of ClO2 at intercooler*	Leakage of ClO_2 in bleachery	Corrosion increasing	3	2	2	4

		Error signal from analyzer				
	"Puff" in ClO_2 pipes	"Puff" in gas cavity				
Leakage of ClO2 into acid drainage*	ClO_2 spreading to bleachery	Overflow in ClO_2 tower	3	3	2	3
	Gaseous ClO_2 in building	Leakage of valves				

Table E.3, Result of the risk assessment (Eka Chemicals, 1999).

4. Preliminary hazard analysis of pulp mill BETA from 2000

Hazard	Consequence	Cause	Probability	Consequence				
				Health	Environment	Image	Property	Production
Explosion or "puff" in the reactor*	ClO_2 in building	Contamination	4-5	3-4	1	?**	?**	?**
		Wrong dosage						
		Insufficient airflow						
		Stop						
Collapse of absorption tower*	ClO_2 in building	Explosion	3-4	2-4	1	?**	?**	?**
		Water falling off						
Power outage*	ClO_2 in building		5	2-4	?**	?**	?**	?**
Explosion or "puff" in the storage tanks	Large ClO_2 leakage	High concentration of ClO_2 in gas	2-4	2-4	2-4	1-4	?**	?**

Table E.4, Result of the preliminary hazard analysis (Eka Chemicals, 2003a).

5. Preliminary hazard analysis of pulp mill GAMMA from 2002

Hazard	Consequence	Cause	Probability	Consequence				
				Health	Environment	Image	Property	Production
Leakage of ClO_2	Large emissions	Rupture on pipes	?**	1	2	?**	1	?**
Rupture of storage tank	Leakage to courtyard	"Puff"	?**	4	4	?**	2-3	?**
		Collision						
		Corrosion						

Table E.5, Result of the preliminary hazard analysis (Eka Chemicals, 2002a).

6. Risk assessment of pulp mill GAMMA from 2008

Hazard	Consequence	Cause	Probability	Consequence		
				Health	Environment	Property
Fire in adjacent building or vehicle	Leakage from tank or pipe	Traffic accident Electric failure Arson	1	1	?**	?**
Ruptured surface water drainage	Leakage to the surface water drainage	Insufficient maintenance	?**	?**	?**	?**
Ruptured roof dewatering pipe in the ground	Undermining leading to tank collapse	To high pressure in pipe Insufficient maintenance	1	4	?**	?**
Rolls of paper overturning on to the tanks	Tank starting to leak/collapse	Paper rolls stapled to high Accident Carelessness	4	4	?**	?**

External corrosion weakening the foundation	The concrete in the fundaments are not affected	Leakage of ClO2 or other corrosive substance	?**	?**	?**	?**
Risks in connection with earthmoving	Undermining leading to tank collapse	Carelessness	?**	?**	?**	?**
		Lack of knowledge				
Rupture of cooling- and process water pipe in the ground	Undermining leading to tank collapse	Insufficient maintenance	1	4	?**	?**
		To high pressure in pipe				
		High traffic load over the pipe				
Vehicle colliding with the storage tanks	Big leakage or collapse	Sabotage	1	4	?**	?**
		Carelessness				
		Lost control				
Pipe or part of building above the tanks collapse	Leakage from tank/pipe	Insufficient maintenance	1	3	?**	?**

		Ice formation Snow load				
Corrosion inside the tank	Leakage from tank	Barrier layer worn down and not improved	3	3	?**	?**
Tanks are subject to vacuum or overpressure	Leakage from tank	Quick draining or filling of tank Shifts in temperature	1	4	?**	?**

Table E.6, Result of the risk assessment (Eka Chemicals, 2008b).

7. Preliminary hazard analysis of pulp mills DELTA from 2004 and ETA from 2003

Hazard	Consequence	Cause	Probability	Consequence		
				People	Environment	Property
Fracture in pipe to storage tank	ClO_2 solution to acid drainage	Mechanical damage	3	3	1	2
	ClO_2 solution to dike	Falling object				
	ClO_2 gas emission from leaking solution	Malfunction of mechanical seal				
		Corrosion				
Decomposition in storage tanks	Tank rupture leading to leakage of ClO_2	Too high concentration of ClO_2	4	3	3	3
	Leakage of solution to dike	No sweep air (ventilation)				
	ClO_2 gas emission from leaking solution	Too high temperature				
		Decomposition ignited by solar radiation				
Too high under pressure	Tank rupture	Malfunction or too small vacuum breaker	4	3	3	3
	ClO_2 solution to dike	Rapid cool down after decomposition				

	Heavy ClO_2 gas emission from leaking solution	Frozen vacuum seal				
Fracture in storage tank	ClO_2 solution to dike	Mechanical damage	3	2	3	3
	ClO_2 gas emission from leaking solution	Falling object on bottom flange or suction pipe				
		Corrosion				
		Damage from transport				
		Poor foundation				
ClO_2 emissions from storage tank	Smell of ClO_2	Poor ventilation	2	1	1	4
		Plugged ventilation pipe				
		Relief lid leakages				
Overfilling of storage tanks	ClO_2 solution to acid drainage	Malfunction of level transmitters	1	2	1	3
Fracture of pipe from storage tank	Uncontrolled leakage of ClO_2 solution	Bad pipe support	3	2	3	3

	ClO_2 gas emission from leaking solution Corrosion in pipe bridge	Improper installation Falling objects “Water hammering” Decomposition of ClO_2 Corrosion	

Table E.7, Result of the preliminary hazard analysis (Eka Chemicals, 2003a and Eka Chemicals, 2004).

8. Hazard identification at the Bell Bay pulp mill in Australia from 2006

Cause	Consequence	Safeguards	Action
Catastrophic ClO2 tank failure	ClO_2 leak: ClO_2 will vaporize out of the solution	Maximum concentration in solution is 10 g/L	Ensure spills from pipe bridge are contained and drained
Impact with pipe bridge		Diking around storage tanks area	Model dispersion of worst case ClO_2 release
Contact of ClO_2 with organic material		Spray leak with sodium sulfite (Na_2SO_3): converts ClO_2 to HCl	
		Piping location designed to prevent vehicle impact: piping in pipe bridges	
		Only site road underneath pipe bridge: minimizes potential for collision with pipe bridge	
		Pressure switches on piping in pipe bridge: pump will be switched off, only contents of pipe will leak	
		Rapid decomposition will be contained within the reactor only: local effects only	
		Restricted vehicle access to chemical plant areas	

Table E.8, Result of the HAZID (GHD, 2006).

Appendix F – Incidents or accidents reported in the media

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1. Maine in U.S.A., 1988

In February 1988, 424 m^3 of ClO_2 solution escaped two storage tanks at International Paper Company pulp mill in Jay. The accident occurred when two metalworkers severed a section of a steel pipe. Somehow, the workers dropped the steel pipe on a valve of one of the storage tanks causing solution to escape. The workers were replacing the regular employees that were striking at the time being. Some of the ClO_2 degassed from the escaped solution, giving two employees transverse respiratory problems. However, most of the solution flowed down into a nearby wastewater treatment lagoon (New York Times, 1988). No information was found about the consequences to the lagoon.

2. North Carolina in U.S.A., 1993

In June 1993, several workers at the Federal Board pulp mill in Riegelwood were exposed to ClO_2 when a pipe ruptured. The reason for this rupture was not identified in the article. When the leakage was detected, the pulp mill was evacuated. In total, 16 workers were exposed to gaseous ClO_2. The majority of the workers were contractors. All of the exposed workers were sent to a nearby hospital. 10 of the workers were treated and then sent home, while 6 others have to stay in the hospital for observation and further treatment (North Carolina Mornings Star, 1993).

3. British Columbia in Canada, 1994

In October 1994, the foundation of a wooden storage tank containing bleached pulp collapsed at the Macmillan Bloedel pulp mill, located at the small community of Powell River. Debris from the pulp tank hit the storage tanks containing ClO_2 solution, causing these to rupture. The storage tanks contained 600 m^3 of ClO_2 solution, all of which escaped into the surrounding dike. The sudden rupture and pressure on the dyke resulted in the breaching of this and the release of ClO_2 solution onto the ground. Gaseous ClO_2 from the solution formed a drifting cloud. To prevent further degassing, the ClO_2 solution was directed into the Malaspina Strait, a nearby stream of water. No person was harmed from the accident, mainly because the wind was blowing the cloud out to sea (Alp & Boughner, 2005). No information was found about the consequences to the stream of water.

4. Skoghall in Sweden, 2000

In August 2000, the automatic gas detection system at the Skoghall pulp mill sounded the alarm. A plastic pipe had sprung open and resulted in the immediate leakage of 0.3 m^3 of ClO_2 solution. The emergency services quickly arrived at the location and could prevent further spreading. No workers were harmed during the incident (Värmlands Folkblad, 2000).

5. Gruvön in Sweden, 2002

In October 2002, a worker at the Gruvön pulp mill noticed the distinct smell of ClO_2. The worker alarmed in order with the routines and then returned to the place for the smell, equipped with a breathing mask. ClO_2 solution was spread over the ground, arising from a nearby drainage. The leakage had approximately gone on for 10 minutes and released about 6 m^3 of ClO_2 solution. The cause for this leakage was a broken underground drainage pipe. The leakage was quickly fixed and the location was decontaminated through dilution of the solution. No workers were harmed during the incident and there were at no point any risk of further spreading possibly affecting residences within the nearby area (Värmlands Folkblad, 2002).

6. Gruvön in Sweden, 2003

In March 2003, during an outage at the Gruvön pulp mill, a smaller leakage of gaseous ClO_2 was detected. The leakage was detected both visibly and by the distinct smell. The outage was scheduled for the length of a week and the accident occurred on the final day. The storage tanks with ClO_2 solution was filled up waiting for the process to start the next day. Somehow, the pressure within the storage tank got in imbalance. This caused gaseous ClO_2 to escape through a small pipe on the roof of the storage tanks. Due to the absence of wind, the cloud was not dispersed and although it only was a small leakage, the smell was distinct over the pulp mill and the neighboring residences. The leakage was quickly fixed and the cloud slowly dispersed. The pulp mill could go back to normal the same day. However, the storage tank was put under special surveillance for the coming days (Värmlands Folkblad, 2003).

7. British Columbia in Canada, 2005

In June 2005, four contractors and two workers at a pulp mill were exposed to gaseous ClO_2 when a pipe ruptured. The rupture was caused by severe corrosion to the old piping system. All of the workers and contractors were sent to hospital with respiratory symptoms (WorkSafeBC, 2009).

8. British Columbia in Canada, 2009

In February 2009, a malfunctioning valve at the storage tank for ClO_2 at the Worthington Properties pulp mill in Mackenzie, resulted in the release of approximately 4 m^3 of ClO_2 solution. Smaller leakages from the same valve had been detected earlier during the week and temporary fixed. However, the preventive measures were not good enough and the leak sprung open again, this times more severe (Ministry of Environment in British Columbia, 2009a). Close to 30 residents from the nearby town of Mackenzie was forced to evacuate as well as 30 workers from the actual pulp mill (CBC News, 2009). There were no injuries due to the leakage and spreading of ClO_2.

9. British Columbia in Canada, 2009

In February 2009, a pipe with ClO_2 solution ruptured. The pipe was a transfer line between two pulp mills, the Prince George pulp mill and the Intercontinental pulp mill. The leakage was quickly stopped automatically and approximately 14 m^3 of ClO_2 solution was released onto the ground (Ministry of Environment in British Columbia, 2009b). There was no immediate danger for the public, since the leakage took place at an isolated location far from residences. However, workers at the location were evacuated and neighboring industrial facilities was warned. The leakage did not lead forward to any extent spreading since there were swift measures taken to reduce spreading. Personal from the local Fire Rescue Service neutralized and cleaned up the contaminated ground (Prince George Fire Rescue Service, 2009). No one was harmed during the leakage or the following work (Ministry of Environment in British Columbia, 2009b).

10. Skoghall in Sweden, 2009

In July 2009, a series of events caused the leakage on a small pipe for ClO_2 solution at the Skoghall pulp mill. The chain of events started with errors in the unloading of chemicals. The wrong chemical was unloaded into a storage tank for hydrogen peroxide (H_2O_2). This caused a quick decomposition and finally an explosion. Larger parts of the storage tank landed on the roof of the bleachery after the explosion, damaging the pipes there. One of these pipes contained ClO_2 solution, which escaped. Only about 1 m^3 escaped before the pipe was closed. No personal was harmed or injured by the explosion or the leakage (Pappersnytt, 2009).

Appendix G – Parameter identification

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1. Parameters affecting probability

In this chapter, a more extended explanation of the different parameters affecting the probability for leakages is presented.

1.1 Falling object (small)

The most important parameter for reducing the probability of falling objects is to limit the number of objects that could fall. There are several parameters affecting this probability.

Stockpiling close to the storage tanks or the inbound and outbound pipes is one. When visiting the different ClO_2 storage facilities, the storage tanks were often surrounded with minor junk yards with scattered building materials, scrap metals and plates. The weather conditions and hard winds have been mentioned as one possible cause for origin falling objects. The combination of hard winds and the scattered material is potentially dangerous.

One also has to look at the detached objects. Detached objects are here referring to old trees, parts of buildings, loose pipes and so on. The weather conditions mentioned above could possibly affect these objects as well. It will be the same dangerous consequences.

Tools, toolboxes and building materials were mentioned as possible falling objects. The less objects and the better routines for working at height, the less chance of them falling from lying around or being dropped.

Besides preventing objects from falling, the protection of the storage tanks and pipes may reduce the probability for an accident. Since most of the storage tanks are equipped with platforms and bridges on top of them, these constructions already work as a shield, even if not covering whole of the top of the storage tanks. At the same time, isolation and chequered sheet around the sides of the storage tanks work as a lighter shield and pipe bridges provide some protection for the pipes. Through enhancing these materials and constructions, one could better protect the storage tanks or the inbound and outbound pipes, reducing the probability for accidents.

Construction works and reparations should not be made when the storage tanks are being used. Such activities should be scheduled during the reoccurring full stops at the ClO_2 storage facilities, when the storage tanks are not being used. In the case of more extent construction work, the time during the stop is probably not enough and other safety measures need to be taken.

Placing the storage tanks indoor could reduce the probability for falling objects due to weather conditions. The hard winds will not affect loose material inside the building. Whether the placing reduces the probability of falling objects due to construction works or other works is more uncertain. The building could consist of several stories with bridges and platforms above the storage tanks, giving the same situation as when placing the storage tanks outdoor.

1.2 Corrosion

The more frequent controls of the corrosion one perform, the greater probability of finding corrosion damages before they become severe and dangerous.

The results and accuracy in the controls are depending on the experience and knowledge among the inspection companies.

The controls made by the external companies need to be followed up with sufficient maintenance in order to reduce the probability. Following the advices and conclusions from these controls is very important. To deviate from these conclusions will increase the risk of accidents linked to corrosion.

The prevention of errors in the process is also important. Errors in the process could lead to an increased level of corrosion inside the pipes and the storage tanks. This is a versatile problem, consisting of decontaminations, increased temperature and increased concentration among others. Close monitoring of the data from the reaction is one of the steps. Detecting abnormalities on an early stage will give the chance to take actions against them.

Placing the storage tanks indoor could somewhat reduce the probability for damages due to corrosion. The weather conditions will not affect and bring about corrosion in the same extent. However, since small leakages and spills are better contained and not as quickly dissolved in the air, the probability for corrosion due to chemical releases might somewhat increase.

1.3 Human error

The interface between human and technology is important when it comes to reducing the probability for human errors. The ClO_2 storage facilities are monitored and run by a large numbers of interfaces. These interfaces are often advanced with several different sources of information and options. To be able to sort out important data, to be able to notice variations as well as changing the right parameters are matters depending on this interface. The interface must be designed so that errors are avoided and the right actions are taken.

Another factor that might influence the probability for human errors is the fatigue and amount of stress put on the workers. If an operator has too many work tasks, the amount of stress might rise. If he is working too long or too many shifts, he might get fatigued. It is therefore important that the ClO_2 storage facilities are not understaffed and that the work time regulations as well as work task limitations are obeyed.

It is also important that the operators receive proper training and education, not only how to perform their work tasks, but also how to act if an emergency occurs. Of course, to train someone to work properly under extreme conditions and the variation within is very hard. Basic knowledge about ClO_2 and the dangers as well as preparations might lead to better decisions in an emergency.

Routines are another factor that is similar to training and education. Existence of and knowledge about routines is crucial. Even more crucial is the fact that these routines are followed. The routines are developed for a reason, to make operations and work tasks safe. Should the workers take shortcuts it might jeopardize the safety at the ClO_2 storage facility as well as the whole pulp mill. It is important that the routines are regularly reviewed and updated.

1.4 Collision

In order to reduce the probability for collision between vehicles and the storage tanks, or for that matter the inbound and outbound pipes, the pulp mills need to reduce the probability for the driver to lose control over the vehicle. The competence, experience and other qualities of the driver is something the pulp mill only occasionally can affect. The heavier vehicles is most likely transports to and from the pulp mill and driven by external companies and workers. Local workers likely drive the other smaller vehicles used within the pulp mill. These workers are probably already educated and trained by the pulp mill in order to receive their driving permission, not mistaken with their driver license. Of course, this education can be followed up and improved after some years.

Another possible parameter that can affect the probability of the driver to lose control over his vehicle is the speed limit within the pulp mill. Do speed limits even exist? If they exist, are the speed limits clearly displayed? Perhaps even more importantly, are the speed limits followed? By reducing the allowed speed limit and at the same time making sure that this limit is followed, the probability for vehicles to lose control will be reduced.

Beside the speed limit, the pulp mills can also introduce limitations in where the vehicles are allowed to drive. This could be applied in several different ways. The introducing of main roads is one of them. All vehicles are bound to follow these larger roads as long as possible. Of course, it is not possible to always make use of these roads. Especially not for the smaller vehicles, the forklifts and pickups, dropping off and picking up objects all over the pulp mill. With these roads, you could avoid the vehicles taking shortcuts that could endanger the storage tanks and the pipes.

Maintenance is another important parameter, in this case referring to the snow clearing and spreading of salt.

In order to avoid collision, the overall design of the pulp mill and the localization of the ClO_2 storage facility might be important. At the visited ClO_2 storage facilities, the storage tanks were in most cases located close to the unloading place for chemicals as well as larger roads within the pulp mill. To adjust the situation today is difficult, considering the large costs of replacing and rebuilding either the storage tanks or other facilities. Perhaps the information could be used in the future when planning and designing new ClO_2 storage facilities.

Sufficient collision protection does not affect the probability of vehicles to lose control, but the probability of these to inflict damage to the storage tanks or the pipes. A collision protection built according to the book can make it impossible for collisions to affect the storage tank. Less advanced and well-built collision protections can somewhat limit the probability. The same reasoning complies with pipe bridges and other collision protection for the pipes.

Placing the storage tanks indoor will definitely reduce the probability for collisions. Most likely, heavier trucks will not drive around indoor. The situation concerning forklifts and smaller vehicles will also be different, probably with less traffic.

1.5 Undermining

Undermining can happen due to rupture of pipes underground. Fundamental for this to happen is the existence of pipes directly under the storage tanks or close to the storage tanks. The same reasoning complies with the fundaments for the pipes or the fundaments for the pipe bridges. The underground pipes could be pipes used for drainage, surface water, chemicals or drinking water. Some of these underground pipes could be pressurized. A rupture on one of these pipes might cause a larger and quicker leakage leading forward to the undermining. The more pipes located in the presence of the storage tank, the greater the probability for one of these to rupture and possibly cause undermining.

In order to reduce probability for undermining, the pulp mills should investigate the existence of pipes in the ground around the storage tanks. There could have been industries on that location for a long time and all the piping do not necessary need to be marked on blueprints. Some of the pipes might have been there before the blueprints were drawn. Following the investigation is the inspection of the pipes. Is there corrosion, weaknesses or other damages that could lead to ruptures? If the answer is yes, the pulp mill should take measures in order to repair the damages or prevent them.

Weather conditions have been mentioned as another possible cause of undermining. To reduce the probability, the ground around the ClO_2 storage facility should have drainage to handle the possible large amounts of rain that could come from hard weathers. In most cases, the storage tanks are surrounded by asphalt. When the storage tanks are not, the pulp mill should think about covering the ground with asphalt. In addition, the storage tanks should have drainage and proper dike to deal with possible overfilling, also able to cause undermining.

Placing the storage tanks indoor might decrease the risk for undermining. Since whole of the building is standing on the foundation, the undermining needs to be extreme to be able to cause damage. When the tank is placed outdoor, the foundation is probably much smaller. Therefore less severe undermining can affect the storage tanks. The drawback from placing the storage tanks indoor is the obstructed possibility to map and control the pipes under the storage tank.

1.6 Freezing

Because of the risk of freezing, the pipes should be protected by insulation or heating systems, in order to reduce this probability. Depending on the location of the pulp mill and the climate at this location, sufficient might have different meaning. Should insulation and heating systems be installed, freezing could not happen unless these are damages or malfunctions. Crucial to decrease the probability for this to occur is therefore sufficient and frequent maintenance.

1.7 Thermal decomposition - “Puff”

Functioning ventilation is fundamental for lowering the probability of too much gas from the ClO_2 solution to accumulate and lead to a “puff”. The pulps mills seem to have sufficient ventilation and be aware of the problem with degassing. The question is instead whether they have the sufficient backup to the ventilation. Even if unlikely, there is a slight risk that the ventilation somehow will fail. The ventilation could go down on the cause of malfunctioning mechanics, power outage as well as other reasons. In this case, the important thing is to regain the ventilation quickly. There could be several methods for this, reserve power from backup generators, redundant ventilation system and so on. In the best case, all of these backups exist.

In order to decrease the probability for “puffs” it is also important to prevent errors in the process. This is a versatile problem. Errors in the process affecting the degassing could consist of decontaminations, increased temperature and increased concentration among others. Close monitoring of the data from the reaction is one of the steps. Detecting the abnormalities will give the chance to take steps against those. Working with reducing human errors causing errors in the process is another.

The location of the storage tanks is also worth thinking about. The storage tanks have a protective coating and isolation to obstruct heating. Even with this protection, the storage tanks should not be located in direct sunlight during the day to further lower the probability.

1.8 Leaking process equipment

Leakages from process equipment are almost inevitable. No matter how much effort put into designing and building to avoid leakages, the result is never perfect. Exchangeable components will get old and worn out, resulting in leakages. The equipment is strained with high pressures, temperatures and corrosive chemicals. In the process equipment definition, all of the equipment within the defined system is included. Everything from pumps, valves, joints of pipes to packings. Frequent observations and maintenance of these can reduce the probability of leaking process equipment.

2. Parameters affecting consequences

In this chapter, a more extended explanation of the different parameters affecting the consequences is presented.

Breathing masks is a fundamental parameter reducing the consequences from leakages. Nevertheless, breathing masks are not frequently used throughout the ClO_2 storage facilities, despite the fact that one occasionally can smell the ClO_2. As stated earlier, the smell of ClO_2 indicates that the level of exposure has passed the “Nivågränsvärde”. Of course, breathing masks could malfunction or being insufficient due to problems put them on. Still, they give more protection than not wearing one. All workers close to the storage tanks should have access to breathing masks and use them if necessary. Breathing masks of the full-face type is clearly superior. From time to time, people have half masks or even just a biting nozzle. As ClO_2 also effect the sight, the risk is that the gas will blind the person, who then fails to escape from the gas despite having respiratory protection. Therefore, only full-face masks should be used and available.

Frequent contact and discussion with the local emergency services is another important parameter affecting the consequences. The emergency services should be aware of the situation at the ClO_2 storage facilities, the dangers and the possible scenarios. With this knowledge, the response in case of an accident could be much better, possibly affecting the outcome and reducing the consequences. Another important feature is coordinated exercises with participants from both the pulp mill and the emergency services, exercising possible leakages and similar.

The cooperation with emergency services should also include exercises of evacuations and alarms. In the case of leakages and the detection of those, the alarm will start to sound, automatically or manually. Either way, the alarm can lead forward to evacuation of parts of the ClO_2 storage facilities reaching to the whole pulp mill. Having exercised these procedures and being aware of the procedures will probably make things go both faster and easier, thus reducing the consequences.

Another important parameter, related to the previously mentioned, is the safety culture among the workers. This aspect influences all of the mentioned parameters above. The safety culture is a wide concept. Respect for the dangers of ClO_2, the neglectfulness not wearing breathing masks, respect for the gas detection alarm and other things could be included into this. All of these aspects could possibly reduce or increase the consequences depending on the level of the safety culture. Evacuations could be stalled, unnecessary exposure could occur and leakages could be handled wrong. Proper education and knowledge is some of the ingredients needed to ensure the good safety culture.

The automatic gas detectors ensure that possible leakages are quickly detected and that that the workers attention is gained. In order to upkeep this functions, the detectors need to be frequently controlled, maintained and calibrated.

There are several different ways to suppress a leakage and milder the consequences. The first method of suppression is to spread foam or oil over the leakage. The foam will settle over the solution and stop the degassing. Spreading of different reagent is the second method. The reagent will be chosen to quickly react with ClO_2 and create less dangerous chemicals. Last, one could also consider the installation of "water screens" around the storage tanks. The water could lead the gaseous ClO_2 back into solution, somewhat stalling the degassing.

Beside the more active ways of suppressing the degassing there are also passive methods. To cover the dike with some kind of containment, for example plastics or some other material could reduce the consequences, keeping the gaseous ClO_2 from spreading further. A possible measure can be to cover the tanks with a tent.

The localization of spills from leaking process equipment is important in order to reduce the long time consequences. Visiting the different ClO_2 storage facilities and talking with workers at them lead to the impression that those smaller spills was not at all taken care of or located. The workers and the pulp mills had settled with the approach that there always would be some spills and that it is a waste of time to try finding and fixing them. The authors have another opinion, and state that the pulp mill should try to locate sources of leakage and fix those. After all, they are leakages of a dangerous chemical.

When larger leakages happen, large amounts of ClO_2 solution are released. Some of this will end up in the drainages. Since many of the pulp mills do not have knowledge over the exact design of this system, the solution might end up in many different places, leading to unnecessary exposure. Workers at the purification plant might suddenly be exposed, the solution might end up being transported directly into the waters nearby and so on. In order to prevent this, the consequences could be reduced by designing the drainage system around the storage tanks with the ability to enclose and thereby contain the leakage. There will still be some degassing from this contained solution, but the source of the gaseous ClO_2 could be better monitored and measures taken. Mapping of the drainage system is also important.

Appendix H – “Ideal” ClO_2 storage facility

Throughout the working process, several features that could enhance the safety and minimize the risks affecting the ClO_2 storage facility have been noticed. These different pieces of information have successively grown together. Together with insights and thoughts gained during the working process combined with available literature, this “ideal” has become more and more extent. To make use of this information and thoughts, an “ideal” storage facility will be presented in aspects of safety. This “ideal” ClO_2 storage facility will henceforth play an important role when developing the method for risk assessment of ClO_2 storage facilities.

The most fundamental measurement to ensure the safety is probably the construction of a sufficient dike. According to Miljösamverkan Västra Götaland (2000), all chemical storages should be surrounded with a dike. The dike should contain more than the maximum storage capacity of the storage tanks. According to Miljösamverkan Västra Götaland (2000), the basic demand for the containment is 100% of the volume in the largest storage tank and 10% of the other storage tanks volumes. The dike should be high rather than wide. The construction will then minimize the area for degassing and prevent the wind from affecting and increasing the degassing. Miljösamverkan Västra Götaland (2000) recommends the installation of a cover over the dike. Jönköpings Län (2003), state that covering of the dike is compulsory for new constructed ones. The cover will both prevent degassing and prevent rain from mass in the dike. This is also in agreement with Miljösamverkan Västra Götaland (2000) considering the building material of the dike and the foundation of this. The building material need to be resistant to the corrosive properties of the ClO_2, in order to withhold the release until decontamination and discharge could be conducted.

It is also important to build a dike around the inbound and outbound pumps as well. According to Miljösamverkan Västra Götaland (2000), which take this point even further, dikes, drip-catchers, drip plates, catchment vessels and such, should be installed at all locations risking spill or leakages. The literature mention pumps, sample-taking equipment and air bleeders.

Although the construction and formation of the dike can somewhat reduce the degassing, complementary actions need to be taken to further decrease and stop the degassing. To reduce or stop the degassing when a leakage has occurred, different vapor suppressing methods or neutralization methods can be used. An oil skim might be used to cover the solution so that ClO_2 gas cannot leave it. The used oil is required to be floating on the solution and spread quickly. Most oils can be used, but Ferweda (2004), prefers mineral oil. Another method of suppression is to spread foam over the leakage. The foam will settle over the solution and stop the degassing. The problem with foam is that it is only stable for a limited period. Therefore, foam that is stable for a relatively long time has to be used. Another problem is that rain will knock the foam down. Neither of these methods neutralizes the ClO_2 but mitigates the consequences for the time being. To neutralize the ClO_2 and stop the degassing once and for all one can use a neutralization agent that is oxidized by ClO_2. The reagent will be chosen so that it quickly reacts with ClO_2 and create less dangerous chemicals. Two examples of this are sodium thiosulfate ($Na_2S_2O_3$) and sodium bisulfate (Na_2S). More trivial agents like sawdust are also effective for neutralization (Ferweda, 2004). Systems with sprinklers could be discussed, working for suppressing the gaseous ClO_2 back into solution as well as managing to extinguish fires and importantly to dilute the surface concentration.

The advantages from constructing a dike do not stop with the prevention of leakages and the suppressing of degassing. The dike also has the capacity to work as a collision protection. According to Jönköpings Län (2003), all storages of “dangerous” chemicals that risk suffering from collisions with vehicles should be protected with sufficient collision protection. The requirements for the sufficient collision protection are not stated in the literature. According to Miljösamverkan Västra Götaland (2000), the requirements are determined from case to case. If the dike could be further strengthened to meet these requirements, there might not be need for other collision protection beside this. Should the dike not be reinforced, installation of separate collision protection is needed. This of course complies for indoor storage tanks as well. To prevent further damages from collision, the lower part of the storage tanks should be reinforced. The lower parts of the storage tanks are the most vulnerable and damages there will give the largest leakages and thereby the most severe consequences.

According to Miljösamverkan Västra Götaland (2000) as well as Jönköpings Län (2003), the presence of floor drains and street drains close to the storage tanks should be restricted. The authors do not have the same strict opinion and do not see the problem with drainages inside the dike or in the presence, given the condition that the drainage has the ability to enclose. The solution of ClO_2 should not be able to spread within the drainage and end up at different locations at the pulp mill or the surrounding environment. Should the drainage enclose leakages, there might be some difficulties with emptying this system. However, it is probably better to have this problem than the problem from workers unexpectedly exposed all over the pulp mill. If there is no drainage or cover over the dike, the pulp mill needs routines or pumps to empty the dike when necessary.

Since the analysis warned for the presence of underground pipes and the probability for these causing undermining, the advocate for the drainage might seem strange. However, the mentioned drainage would probably enhance the overall safety and should the pulp mill frequently conduct controls and maintenance, the risk of rupture or damages could be kept low. Nevertheless, in general, underground pipes in the area under or around the ClO_2 storage facility should be moved.

Continuing to look at the situation around the ClO_2 storage facility, the surrounding should not be the stockpile of building materials and objects. These objects might be driven away by hard winds or overturn and collide with storage tanks. At the same time, these stockpiles might block or obstruct emergency procedures and operations. This might cause more severe consequences than necessary considering both the size of the leakage and health of workers. Furthermore, regulations need to be improved in order to prevent falling objects and other risks derived from the activity at the pulp mill, for example, construction works.

Miljösamverkan Västra Götaland (2000) state that automatic gas detectors, or other detectors for leakages, should be placed around the ClO_2 storage facility, regardless of this being indoor or outdoor. Should the ClO_2 storage facility be placed indoor, detectors also need to be placed outside the building. The gas detectors should alarm at levels above 0.1 ppm. Likewise, manual buttons to start the alarm should be placed around the storage tank, on various distances. Placing these buttons too close to the storage tanks can make them useless in case of leakages giving clouds of gaseous ClO_2. The option to sound the alarm at the immediate sight of a leakage could save important seconds. Besides these detectors, necessary protective equipment needs to be located and available around the ClO_2 storage facility as well as in the buildings close to the ClO_2 storage facility. According to Kemikalieinspektionen (2009), such protective equipment could consist of breathing masks, protective clothing and first aid.

Most of the ClO_2 storage facilities have storage tanks and pipes made out of FRP. The resistance against corrosion might be rather high compared with other materials. Still, corrosion will exist in some extent, both internal and external. Damages from corrosion could be prevented with early detection. Controls and maintenance is necessary, but even more fundamental is the proper choice of FRP and material for the storage tanks. The inbound and outbound pipes need to be controlled in the same extent and with the same frequency as the storage tanks (Miljösamverkan Västra Götaland, 2000). According to Bergman (2009), controls should be carried out once every sixth year. The pulp mills probably do not have and will not gain the competence to conduct these controls themselves. Instead, the pulp mills must rely on external companies for these controls. According to Miljösamverkan Västra Götaland (2000), accredited companies or independent companies should perform controls. How could the pulp mills assure that the external company has the proper knowledge and experience, although accredited? The competence and result within these different companies will most differ, as will their expenses. The authors state that economics should not be the base for decisions. The most expensive external company is not necessarily the best company. Neither, should the cheapest external company be chosen on the base of them being cheapest. The results, knowledge and reliability of the companies are the important factor here. Safety should come first, which surely everyone agrees to.

Frequent controls should not only be conducted to investigate the damages from corrosion. According to Miljösamverkan Västra Götaland (2000), frequent overall supervision, control of functions and preventive maintenance should be performed. These actions should be regulated through written programs and clear instructions. Furthermore, these actions and the possible measures taken should be logged to follow up possible deviations.

Today, many of the storage facilities use separate storage tanks working as communicating vessels. One of the advantages from such system is the possibility to close one of these storage tanks down, still being able to maintain production. The “communicating vessels” need to be designed to automatically or manually, shut down the connection between the storage tanks. That shutdown could help limit leakages. Should one of the storage tanks start leaking the shutdown will prevent solution from the other storage tank to transport into the leaking one. Should the connection need to be closed manually, it is important that the valve or equipment for this is accessible. Accessible do not only mean easy to reach and operate, but also located so that it is accessible even in the case of leakages and the spreading of gaseous ClO_2. On the base of this information, several storage tanks working as connected vessel are to prefer, given that they are designed with the ability to shut down this interconnection.

According to Miljösamverkan Västra Götaland (2000), storage tanks should be equipped with overfilling protection and level measuring units. This overfilling protection, in most cases, consists of piping systems connected with the storage tanks and the ground outside the storage tanks. This system should be seen as backup for the technological systems with detectors and equipment installed inside the storage tank, monitoring flows and levels. It would be preferable that this system automatically could shut down inbound pipes in the event of overfilling. Although very low probability for simultaneous malfunction of these technological systems, the overfill protection is a backup safety measure that could be useful. The piping system should be connected with the dike and the enclosed drainage and not end up on the ground outside the storage tanks. The storage tanks should also be equipped with vacuum breakers and explosion lids to be able to handle sudden pressure changes. Fundamental is the design of these, ensuring that they are able to cope with extreme cases of pressure changes.

The storage tanks are in general better protected from falling objects than the inbound and outbound pipes. Constructions and platforms on the top of the storage tanks fill an important role protecting these, even though not their primary functions. The inbound and outbound pipes on the other hand, are often placed without protection or reinforcement. Reinforcements of these are recommended. Such reinforcements and enhancements could consist of creating pipe bridges or the installation of safety nets. These constructions might prevent damages from collisions as well as falling objects. Continuing to look at the inbound and outbound pipes there are several other actions and safety measures that need to be taken. Both active and passive measures need to be taken to prevent freezing in the pipes. Passive methods could consist of heat coils or isolation. Furthermore, the inbound and outbound pipes should have isolation valves installed to be able to deal with sudden ruptures or leakages of pipes.

The inbound and outbound pipes as well as the storage tanks should be marked with labels stating the content and the danger symbols. This is partly to inform about the dangers of the chemical and partly to avoid mistakes such as trying to repair the wrong pipe or open the wrong valve. Kemikalieinspektionen (2009), further state that information regarding the quantity and amounts of chemicals stored and their properties and risks should be accessible.

The discussion concerning the placement of the storage tanks indoor or outdoor is complicated and has been dragged up before in this master thesis. Both alternatives have their advantages and disadvantages. Placing the storage tanks indoor will certainly decrease and stall the spreading of gaseous ClO_2 after a leakage, reducing the exposure. However, the exposure within the building will be much higher, risking explosion and more severe effects on health. Could the storage tanks, and solely the storage tanks, be placed inside a building there are less danger from this high exposure, since the workers are not likely to be present in this building. There are also advantages considering weather conditions, protection of the inbound and outbound pipes and falling objects. Therefore, the recommendation is placement inside a building with the sole purpose of holding these storage tanks. This is somewhat supported by Jönköpings Län (2003). A somewhat different idea introduced during a conversation with our mentor, was the idea of large tents containing the storage tanks. This tent might not have the same strength as a building, but will in all other ways work equally well. Economically, these tents are most likely preferable.

It is recommended that the inbound and outbound pumps should be located away from the storage tanks, not inside the building. The base for this recommendation is the warm surfaces, possibly initiating an explosion and heating, leading to increased degassing.

The placement of the storage tanks and the whole ClO_2 storage facility could also be discussed in terms that are more general. The placement of the whole pulp mill should also be considered in the context of residences, environment worth to preserve and waters. The consequence calculations carried out in Appendix D showed that potential dangerous plumes of ClO_2 could travel several kilometers. This statement is supported by the consequence calculations at pulp mill GAMMA (Eka Chemicals, 2003b). Giving the large amount of solution released at storage tank ruptures, waters and nearby nature risk suffering from over wash and the following consequences. Therefore, the pulp mills need to look at those aspects. The placement is also important thinking about the risk for flooding and landslides, both short-term due to the present circumstances and long-term due to changes in the climate and environment. The pulp mills are huge consumer of fresh water, which have importance in the economics, which could affect the placing. Since the pulp mills are in fact already located where they are, there is no chance of adjust this. However, one should keep the placement in mind when constructing new pulp mills.

The placement of the storage facility inside the pulp mill also has importance considering winds, sun and traffic. Winds and sun both affect the spreading and degassing. Since they are linked with both positive and negative effects, it is hard to make a statement. The sun will increase the degassing but decrease the spreading, since the ClO_2 are decomposed due to the sun. Wind will increase the degassing but could decrease the spreading and consequences by dissolving the cloud of gaseous ClO_2. Considering the traffic, the pulp mills should direct traffic away from potential dangerous areas, like the storage tanks of both ClO_2 and other chemicals. The pulp mills should think about designing and introducing main roads in order to achieve this. Continuing on the traffic and the aspects of safety, the pulp mills need to introduce speed limits. More importantly, they must make sure that these are followed.

The placing of the ClO_2 storage facility should also be looked upon from the presence of other chemicals. According to Miljösamverkan Västra Götaland (2000), chemicals that might react with another or for other reasons are inappropriate to store near one another, should be kept apart. Kemikalieinspektionen (2009), determine that such inappropriate combinations could consist of chemicals stored near flammable materials and bottles of gas, acids and bases, strong acids and organic chemicals and strong oxidizing chemicals and oxidizable chemicals. Since ClO_2 is highly reactive, several chemicals could be considered inappropriate on the base of one of the above-mentioned reason.

The pulp mills should be enclosed with a fence and be monitoring who is entering the facility. This is to avoid sabotage and other criminal actions. One should also think about enclosing the storage tanks with a fence, given that the fence will not hinder possible actions in case of emergency and leakages. Such actions could be the closing of isolation valves or evacuations.

The introduction of redundant systems is important for enhancing the safety. The redundant systems might consist of both technological equipment as well as process equipment. Areas of importance for such redundancy can be the ventilation of the storage tanks as well as all the equipment and technology for monitoring. When talking about the redundancy, a reserve power system should be mentioned. Not all storage facilities have this backup, but must at least ensure that the most crucial systems first regain capacity when the power is back. There should also be preparations and plans for the risk that the reserve system fails or that the power does not come back as quickly.

The monitoring of the overall situation, and the processes in particular, are other important parameters to look at when it comes to safety. The system must be designed so that it automatically can take actions, or by clear information can alert an operator that can take actions. An operator need to be present at all times, visually or technologically monitoring. The interface between human and technology need to be considered. The importance of comprehending the right information to perform the right operation should be pointed out. When it comes to the automatic systems, the design of these needs to ensure that the right actions are taken based on the right signals. The monitoring of the situation is also important on the behalf of keeping the errors in the process at minimum. Increased concentrations and temperatures might cause increased degassing as well as speeding up the corrosion.

Degassing could also be prevented through a number of other actions. Miljösamverkan Västra Götaland (2000) proposes one or several of the following actions. Storage tanks should be painted with neutral colors reflecting the sun. Filling of the storage tanks should be conducted below the surface of the solution. The storage tanks should be equipped with stripping of the gas above the solution. Another action worth mentioning might be the cooling of the water in the process forming the solution. There are most certainly many other interesting aspects, but these were the most suitable.

The area of human errors is included into many of the different causes and parameters mentioned in this master thesis. At the same time, they might also be the direct cause for accidents. Human errors are hard to foresee and do not follow the standards. While probabilities for other errors can be roughly estimated, this is almost impossible for this group of actions. Reducing the probabilities for overall human errors and understanding the complexity of this area is therefore important.

There could be several reasons for human errors, for example negligence or misconceptions. Often, operators and maintenance personnel take “shortcuts” in their work to make it easier or faster. These shortcuts are often in contradiction to the manuals and safety policies of the company. An example might be that the maintenance personnel do not use all safety measures when servicing equipment or that the operators use higher than specified temperature to make the reaction go faster. These shortcuts might originate from a high workload as well as personal problems. Misconceptions are another possible reason for human errors. The number of possible misconceptions is infinite. Misconceptions might originate in the communication between humans, because of the human-machine interface or in the interpretation of manuals and rules. Stress, tiredness or similar, increases the probability for such misconceptions. Making it easier for the workers, concerning both the degree of difficulty as well as the load of work is important (Akselsson, 2008). To further strengthen the resistance to human errors, education and training could be implemented. The training should not only prepare for normal conditions, but also include preparation for unforeseen events and the ability to remain calm.

The regulations as well as the overall safety culture could be addressed through introducing management systems. The pulp mill needs to pay attention to problems with the safety culture and address these. Ignorance to the dangers of ClO_2, ignorance of the working routines and neglectfulness of the safety might cause accidents or increase the probabilities for such. Improvements of the safety culture could be made with simple methods and means. Introducing management systems could be one. Qualitative management systems, safety managements systems or perhaps even environmental management systems could be introduced. However, the introduction of such systems does not automatically bring about positive changes. The pulp mill needs to put in some effort into these systems. To achieve perfection is a long and hard road. Education, understanding and knowledge are the keys for improvement.

Improvement of the overall safety could also be achieved through encouraging workers to write incident reports and accident reports. This is many times often included into the safety management systems. The pulp mill should embrace the information in these reports and enhance the safety to avoid these events repeating themselves, a view supported by Akselsson (2008). Furthermore, risk assessments and risk analyses should be conducted frequently, and not only in the case of re-constructions or new construction.

In order to prepare the pulp mill for the event of an accident and the following spreading of ClO_2, the pulp mills should think about their preparedness. According to Kemikalieinspektionen (2009), equipment for decontamination and clearing of the leakage should be available. Emergency services and the pulp mill should conduct evacuation exercises or try the routines for alarms. The pulp mill should strive to have a far-reaching cooperation with rescue services as well as other authorities. Since many of the pulp mills only allowed the workers inside the pulp mill to actuate part of the alarm and evacuation, the cooperation with the workers at the entrance, often responsible for the larger evacuation and alarm processes, need to be tested. One can never train for the infinite variation of accidents, but one can prepare.

Observant reader has noticed that no statement has been made considering the amount of ClO_2 that should be stored. The reason is the simple fact that a pulp mill that has with taken all the safety measures mentioned above will be ready to face small storages as well as very large storages. Furthermore, the amount stored is depending on the size of the pulp mill and their production. To decrease the production due to demands of decreasing the ClO_2 storages are not practicable.

Finally, two things should be pointed out. First, this “ideal” ClO_2 storage facility is made without consideration of the economics. Second, the features presented in this “ideal” ClO_2 storage facility are a selection. Several other aspects and features then the ones mentioned here could be brought up, but since the focus is on the development of the new method, this has to do.