How gases present in the environment affect OBA mirror surfaces at indoor swimming pool facilities.

Stina Odelros 2011-12-20

Revised version: 2012-01-05

Abstract

Corrosive environments could be problematic for all different kinds of devices. At indoor swimming pool facilities there could be formation of various kinds of gases, corrosive or not, due to formation of disinfection by-products. Disinfection is essential for keeping the swimming pool water hygienic and the most common way to achieve this is by using sodium hypochlorite (NaClO). When NaClO is used for disinfection, the main gaseous by-products formed are chlorine gas, chloroform and trichloramine.

SenseAirs gas measurement devices could be affected by the corrosive environment at indoor swimming pool facilities, where foremost chlorine gas is the one expected to be the most problematic gas that could affect the mirror surfaces inside the OBA (Optical Bench Assembly) modules.

OBA modules were exposed to chlorine gas and analyzed by SEM (scanning electron microscopy) and IR (infrared spectroscopy) measurements. Two out of three kinds of modules tested seemed to handle the corrosive environment god enough to still be functioning at an acceptable level.

Table of contents

Abstra	act	1
1. Intr	oduction	3
1.1	Background	3
1.2	Aim	3
2. Clea	aning and disinfection of indoor swimming pools	3
2.1	Cleaning of surfaces in and around the pool area	4
2.2	Filtration of swimming pool water	4
2.3	Disinfection of swimming pool water	1
2	2.3.1 Chlorine	4
2	2.3.2 Chlorine dioxide	5
2	2.3.3 Bromine and iodine	ŝ
2	2.3.4 Hydrogen peroxide	ŝ
2	2.3.5 Ozone and UV-light	õ
3. For	mation of gas due to chemical reactions	ŝ
3	3.1.1 Bromine compounds	ŝ
3	3.1.2 Chlorine gas	7
3	3.1.3 Trihalomethanes	7
3	3.1.4 Chloramines	7
3.2	Summary	7
4. Ехр	perimental	3
4.1	Experimental set-up	3
4	I.1.1 Material used	Э
4	I.1.2 Formation of Cl ₂ (g)	Э
5. Res	sults and discussion)
6. Cor	nclusion	3
7. Fut	ure investigations	3
8. Ack	nowledgements	3
9. Ref	erences	1

1. Introduction

This project was performed as a 5 credits part of the course Surface coatings for energy applications (10 c) in the autumn of 2011 at Uppsala University. The problem was given by SenseAir, a company that produces gas measurement devices for indoor analyses.

1.1 Background

SenseAirs gas measurement devices are used to measure the amount of gas (often carbon dioxide) and sometimes the temperature in a number of different areas. Gas measurement devices could for instance be used to monitor the carbon dioxide level indoors to regulate the ventilation needed in the facility. When sensors are used as a complement to the ventilation system this leads to significant energy savings. In the gas sensor, the crucial component is the optical module called OBA (Optical Bench Assembly). OBA modules include mirror surfaces that earlier have shown to be affected in corrosive or polluted environment. After experiencing some problems with measurement devices placed at indoor swimming pool facilities, SenseAir improved the mirror surfaces in the OBA modules. The question now, which this report will try to answer, is whether or not the improved mirrors can withstand the corrosive environment at indoor swimming pool facilities.

1.2 Aim

The aim of this project is to find out which gases are usually formed as by-products when cleaning and disinfecting public indoor swimming pools and try to estimate theoretically if they could affect the OBA mirror surfaces in the gas measurement devices. The project also includes testing of how some of these gases present at indoor pool facilities affect the mirror surfaces and OBA modules.

2. Cleaning and disinfection of indoor swimming pools

To minimize the health effects that can arise when bathing in public indoor swimming pools it is essential to have good water purifying and disinfection methods. Due to the fact that a lot of people gather in a small area, the risk of transferring bacteria, microorganisms, viruses etc. increases. If the pool maintenance is proper then there will be no risk for this transfer [1].

To maintain a good water quality, both cleaning and disinfection is essential. First you need to make sure that as little dirt and organic pollutions as possible may enter the water or pool area. This is done by keeping surfaces in and around the swimming pools as clean as possible (see section 2.1) ^[1]. To prevent bacteria, virus and other microorganisms from the opportunity to replicate and grow in the water it is essential to have a good water purification technique. This often means to combine a water filtering technique with a water disinfection technique. In Sweden, as well as in the rest of Europe and in the US, it seems like the most common combination is a sand or perlite filter for water filtration and sodium or calcium hypochlorite as antiseptic agent ^{[2] [3] [4]}.

The filtration of pool water seems to be very friendly and does probably not contribute to any corrosive gases (see section 2.2) [3]. The disinfection of the water will on the other hand contribute a lot to formation of different corrosive gases (see section 2.3) [1]. The amount of gas in the air at indoor swimming pool facilities depends on the activity in the pool. More movement in the water leads to a larger contact area between air and water and the disinfection by-products can more easily evaporate to the surrounding atmosphere (see also section 3) [5].

2.1 Cleaning of surfaces in and around the pool area

To minimize the risk for cleaning detergent or dirt to enter and contaminate the pool water it is important to clean all surfaces regularly as well as to separate dirty shower water from the pool water. When using cleaning detergents one has to consider what detergent to use. If the used detergent is strongly basic or acidic with organic solvents there is a major wear on the material surfaces cleaned. If the detergent includes tensides, phenols, phosphates or ammonia it could affect the effect of the filters, generate foam and high amounts of bound active chlorine. Detergents containing carbon-based compounds could generate chlorinated carbon compounds or thrihalomethanes and nitrogen compounds like ammonia could generate chloramines. To use antiseptic agents when cleaning surfaces is not necessary and only applicable under certain circumstances, like when bad pool water quality is experienced [1].

2.2 Filtration of swimming pool water

To remove solid impurities from swimming pool water, a filtration system is used, often constructed and located in the basement of the facility. Elderly facilities often have open filter systems which could contribute to some gases released in the basement during filtration. In modern facilities the most common filter system is based on closed sand filters and the only gas formation would be in the pool area. When water is filtrated, some additives are used to trap organisms in the water before filtering but the additives should not react and form any gases ^[3]. Gas could be formed during filtration due to earlier addition of antiseptic agents to the water but that will be discussed below under section 2.3 "Disinfection of swimming pool water".

2.3 Disinfection of swimming pool water

To keep the pool water clean from microorganisms that could cause health issues for humans, antiseptic agents should be used continually. An antiseptic agent should be quick-acting against bacteria and virus and have a long lifetime so that an efficient amount of antiseptic agent is maintained in the water. There is two different ways of using antiseptic agents in swimming pool water: first one is to prevent microorganisms from growing and the second one is acute treatment and only applied when problems with the water quality are experienced. There are several different disinfectants and methods for pool water cleaning. The most effective agent is chlorine and chlorinating is the most abundant method for disinfection of pool water [1]. When a disinfectant, like sodium hypochlorite is added to the pool water, the pH value will change. To stabilize the pH and maintain a pH between 7.2 and 7.6 you usually add sulfuric acid (H₂SO₄) or hydrochloric acid (HCl) [3].

2.3.1 Chlorine

The most common method for swimming pool water disinfection is to add a salt containing chlorine, for example sodium hypochlorite (NaClO) or calcium hypochlorite (Ca(ClO)₂). Most often NaClO is used as antiseptic agent, when the salt is added to the water, NaClO forms hypochlorite ions (ClŌ) and hypochlorous acid (HClO) in a pH dependent equilibrium (see equations 1 and 2) [1].

$$NaClO \leftrightarrow Na^+ + ClO^-$$
 [eq. 1]
 $ClO^- + H_2O \leftrightarrow HOCl + OH^-$ [eq. 2]

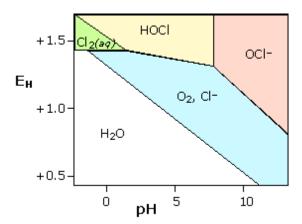


Figure 1: Pourbaix diagram of chlorine in water [6].

From the Pourbaix diagram for chlorine in water (figure 1), it can be seen that Cl_2 (aq) decomposes to HOCl and ClO $^{\circ}$. At the potential (E_H) approximately E_H = 1.5 and pH between 2.5 and 7.5 HOCl will be the dominant species and at pH > 7.5 ClO $^{\circ}$ will be dominating in the system $^{[6]}$. HClO is better at killing bacteria than ClO $^{\circ}$ so the higher pH in the water, the more chlorine has to be added to maintain a good disinfection. When adding NaClO to the pool water there is also formation of chloramines and others disinfection by-products (see section 3 "Formation of gas due to chemical reactions"). If sodium hypochlorite is mixed with acid a reaction will start and chlorine gas (Cl_2) will be formed as a disinfection by-product. Cl_2 is a toxic and corrosive gas that could give trouble with breathing for people in the facility $^{[1]}$.

The amount of chlorine in swimming pool water is often measured in concentration of free available chlorine which is the sum of hypochlorous acid, hypochlorite ions and aquatic chlorine present in the water. The amount of bound chlorine in the swimming pool water is the sum of all chlorine containing by-products formed due to chemical reactions between free available chlorine and pollutants or microorganisms in the water. Once the free available chlorine have reacted and formed some kind of by-product, the chlorine looses much of its disinfectant effect and will be referred to as bound chlorine [4]. The Swedish Government agency Socialstyrelsen has provided guideline values to follow to maintain a sufficient disinfection effect in the water. Dependent on the water temperature and pH, the minimum guideline value for free active chlorine (the same as free available chlorine) in the swimming pool water range between 0.4-1.0 mg Cl₂/L. The guideline for bound chlorine and the total amount of chlorine at all temperatures, with pH between 7.2 and 7.6, are maximum 0.4 mg Cl₂/L or 2.0 mg Cl₂/L respectively^[7]. The US guideline limits of free active chlorine in swimming pool water range between 1 and 5 mg Cl₂/L. Preferred pH is between 7.4 and 7.6 both for Sweden and US [4] [7]. When pH in the water is around 7.5, which is almost the same as the pK_a value for hypochlorous acid, the amount of free available chlorine in the swimming pool water will be even distributed between HClO and ClO^{-[4]}.

2.3.2 Chlorine dioxide

Chlorine dioxide (CIO_2) is a gas that can be used for disinfection of pool water. Due to the high efficiency against microorganisms it is foremost used for acute treatment like chock chlorinating treatment. The gas is often produced on site when mixing a chlorate or chlorite compound with an acid. Chlorine dioxide is a strongly oxidizing compound and its efficiency is not depending on the pH value [1].

2.3.3 Bromine and iodine

Other halogens that are used for disinfection are bromine and iodine. Bromine is only used in smaller facilities today and iodine is rarely used [1].

2.3.4 Hydrogen peroxide

Hydrogen peroxide (H_2O_2) can also be used for water disinfection. Small amounts of silver compounds are used as stabilizers in that case. The amount H_2O_2 used in pool water is between 2 and 5 volume%. At high temperatures, hydrogen peroxide could decompose and form oxygen gas $(O_2)^{[1]}$.

2.3.5 Ozone and UV-light

Ozone (O_3) or UV-light is sometimes used as alternatives to chock chlorinating. Ozone is a very reactive gas and therefore a very efficient disinfection agent against bacteria and other microorganisms. Due to the fact that ozone is very reactive it decomposes rather quickly into oxygen gas and it can therefore only be used for a local treatment of the pool water. Ozone used in combination with disinfection agents can reduce the amount of disinfection agent used at the same time as the disinfecting effect is maintained in the water $^{[1]}$.

UV-light is a very energy rich light that can be used for disinfection. It has the ability to change or destroy cells by photolysis. Because of the waters ability to protect against UV-light, the treatment is only local due to limited penetration depth. UV-light is therefore often used in combination with hydrogen peroxide because it enhances the disinfection effect of H₂O₂ against microorganisms ^[1].

3. Formation of gas due to chemical reactions

All disinfectants contain very reactive substances that react not only with microorganisms but also with other pollutants in the water. People visiting swimming pools contribute to adding dirt, skin cells, hair, urine, sweat, skin lotion, makeup etc. to the pool water. This kind of contaminations leads to chemical reactions in the water together with the often high temperature and highly reactive disinfectants. When using chlorine as disinfecting agent the formation of chlorine gas, trihalomethanes and chloramines is the largest issue ^[1]. The temperature in the water is often around 25-29 °C and in the surrounding air the temperature should be 1-2 °C higher. The water temperature in a bubble pool is often around 37 °C, which means that a much higher chlorine concentration is needed for disinfection (almost the double from ordinary swimming pools) ^[3].

3.1.1 Bromine compounds

Bromine can often be present, in very small amounts, in the groundwater used for filling swimming pools. These small amounts of bromine could form bromine disinfection by-products when reacting with chlorine. Chlorine will oxidize bromine and HOBr will be formed. HOBr could then continue to react with hypochlorous acid (HClO) and produce bromoform (CHBr₃), or dibromochloromethane (CHBr₂Cl) ^[4]. The amount of each bromine compound formed should not exceed 0.2 μ g/m³ for bromoform, and less for other bromine compounds. That would mean less than 0.2 ppb (at 30°C and 1 atm) of each bromine compound present in the air at indoor pool facilities, and this small amount should not alone give any negative influence on the OBA module.

3.1.2 Chlorine gas

Chlorine gas will be present near the surface in the pool facility. How much Cl_2 (g) that is present is hard to estimate and reports from measurements performed at indoor pool facilities does not present any value of the amount of Cl_2 (g). The amount of Cl_2 (g) in the atmosphere of a indoor swimming pool facility is probably in the range of 0.01-0.1 mg/m^{3 [8]}. But there are some studies that show that even 10 mg/m³ could be present right above the surface ^[11]. In Sweden, the hygienic threshold value for chlorine gas in the atmosphere is 1.5 mg/m^{3 [9]}. Assuming that the amount of Cl_2 (g) is 10 mg/m³, this corresponds to 8.6 ppm (at 30°C and 1 atm).

3.1.3 Trihalomethanes

Trihalomethanes are formed when a halogen (like bromine or chlorine) reacts with an organic compound. The most common reaction products are: chloroform (CHCl₃), bromodichloromethane (CHBrCl₂), dibromochloromethane (CHBr₂Cl) and bromoform (CHBr₃). When using chlorine as disinfectant, almost 90 % of the methanes formed are chloroform. Trihalomethanes is readily dissolved in water, but can also evaporate and form gas in the building ^[1]. In a risk assessment performed by Karolinska Institute in Sweden, small amounts of chloroform in the air at a swimming pool facility was present. They estimated that the amount of chloroform in swimming pool water in Sweden is 100 μ g/L in the air near the water surface 150 μ g/m³, and in the air in the rest of the building ca 50 μ g/m^{3 [10]}. In a similar study performed in the US, the amount chloroform in the air was found to be 9-58 μ g/m^{3 [5]}. If the air right above the surface contains 150 μ g/m³ chloroform, this corresponds to 0.13 ppm (at 30°C and 1 atm), which is equal to 90 % of all trihalomethanes present.

3.1.4 Chloramines

Chloramines are formed when chlorine reacts with nitrogen containing compounds in the water. The amount of chloramines in the water increases with increasing amount of nitrogen containing compounds, water temperature, amount of active chlorine and decreasing pH. The chloramines formed in swimming pools are monochloramine (NH₂Cl), dichloramine (NHCl₂), and trichloramine (NCl₃). Trichloramine is the one responsible for the special odour that we usually call chlorine odour. Chloramines can evaporate to the surrounding atmosphere in the swimming pool facility and is easily released when there is a lot of activity in the water ^[1]. Trichloramine is the most common chloramine product in swimming pool water produced by chlorine disinfection. A Swedish study showed that the amount of NCl₃ in the air at an indoor swimming pool facility range between 0.02-0.34 mg/m³. Another study showed values ranging between 0.1-1.0 mg/m³ ^[2]. A study performed in the US showed results that indicate that the amount of trichloramine in the air range between 0.1-0.7 mg/m³ ^[5]. If the amount of trichloramin in the atmosphere at indoor pool facilities is 1.0 mg/m³, this corresponds to 0.86 ppm at 30°C and 1 atm.

3.2 Summary

The most common way to disinfect swimming pool water is to use sodium hypochlorite. The main gases present in the indoor atmosphere at pool facilities are gaseous chlorine (CI_2), chloroform ($CHCI_3$) and trichloramine (NCI_3). The amounts of these gases in the indoor atmosphere should not exceed 8.6 ppm, 0.13 ppm or 0.86 ppm for chlorine gas, chloroform or trichloramine respectively. It is therefore reasonable to expose OBA modules to gaseous chlorine, since it occurs at the highest concentration and has known high oxidation ability. The other gases could, of course, also contribute to the damage of the mirror surfaces in the sensors, but the OBA modules are not influenced by gaseous chlorine, then the probability that other gas will affect the OBA should be small.

4. Experimental

To investigate whether the OBA module mirror surfaces are affected by the atmosphere in an indoor swimming pool facility accelerated test were performed employing high concentrations of gaseous chlorine. The OBA modules were exposed at slightly elevated temperature during 72 hours in a reaction chamber, see figure 2, which was equipped with a thermostat so that the temperature could



Figure 2: Reaction chamber used for experiments.

be regulated. Three different kinds of mirror surfaces were tested in chlorine gas atmosphere, labelled X, Y and Z. To reduce the number of experiments the number of samples was set to 15. This sample series consisted of three different kinds of mirror surfaces with four samples of each type, and reference samples for each type of OBA mirror, which were not exposed to chlorine gas. For simplicity the different samples was named A-O (see table 1).

Туре			X	X		Υ			Z						
Sample	Α	Ε	G	J	M	С	F	Н	Κ	0	В	D	1	L	N
Experiment number	1	1	2	2	none	1	1	2	2	none	1	1	2	2	none
Analytical method	SEM	IR	IR	IR	SEM (Ref.)	SEM	IR	IR	IR	SEM (Ref.)	SEM	IR	IR	IR	SEM (Ref.)

Table 1: Sample and experiment number for the different samples.

4.1 Experimental set-up

Two identical experiments were performed. In both experiments 6 samples were placed in the top cover of the chamber and accelerated test were performed at 38°C during 72 hours. In the experiments the samples were mounted on the top flange of the reaction chamber using adhesive, inert tape. In the second experiment the top cover and the bottom of the chamber was covered by aluminium foil to minimize the corrosion of the reaction chamber. This did not however affect the exposure conditions. Figures 3 and 4 show the experimental set-up one and two respectively



Figure 3: Samples placed at the top cover for experiment 1.



Figure 4: Samples placed at the top cover for experiment 2.

10 ml of Klorin™ liquid were placed on a heating plate in the reaction chamber. 5 ml of acetic acid (Ättiksprit) was added before closing the chamber carefully. The temperature of the heating plate was set to 38°C.

4.1.1 Material used

"Klorin" is the trademark for a solution containing sodium hypochlorite in water with 27 g NaClO /kg solution. The amount sodium hypochlorite added is 0.004 mole, see table 2 and equations 3 and 4.

Properties of Klorin		The amount NaClO added is calculated by equa	tion 3 and 4:
Density, ρ _{Klorin}	1.06 g/ml	m - m + a - 0.296 a NaClO	[00.2]
Volume added, V _K	10 ml	$m_{NaClO} = m_K * c_K = 0,286 \ g \ NaClO$	[eq. 3]
Mass added, m _K	10.6 g	$n_{NaClO} = m_{NaClO} * M_{NaClO} = 0.004 mole$	[eq. 4]
Molar mass, M _{NaClO}	74.4 g/mole		

Table 2: Properties of Klorin used for calculations in equation 3 and 4.

"Ättiksprit" is the name of a solution containing c = 12 vol% acetic acid (CH₃COOH or HAc) in water. The density of the solution is assumed to be almost 1 g/ml, somewhere between $\rho_{(H2O)}$ =0.988 g/ml and $\rho_{(HAC)}$ =1.049 g/ml. The amount acetic acid added is 0.01 mole, see table 3 and eq. 5-6.

Properties of Attiksp	Amo		
Density, ρ _{Ättiksprit}	1 g/ml		
Volume added, V _Ä	5 ml	m_{HA}	
Mass added, m _Ä	5 g	n_{HAc}	
Molar mass, M _{HAc}	60.05 g/mole	-	

ount HAc added is calculated by equation 5 and 6:

$$m_{HAc} = m_{\ddot{A}} * c_{\ddot{A}} = 0.6 \ g \ HAc$$
 [eq. 5]
 $n_{HAc} = m_{HAc} * M_{HAc} = 0.01 \ mole$ [eq. 6]

Table 3: Properties of Ättiksprit used for calculations in equation 5 and 6.

4.1.2 Formation of Cl_2 (g)

Sodium hypochlorite decomposes into hypochlorus acid and hypochlorite ions when dissolved in water. Klorin is a basic solution so the hypochlorite ion will be the dominating species before mixing with the acid (see also eq. 1-2 and section 2.3.1 "Chlorine"). When mixing Klorin with Ättiksprit, the following reactions takes place:

$$Cl0^- + H^+ \leftrightarrow HCl0$$

 $HAc \leftrightarrow H^+ + Ac^-$
 $2HCl0 + 2H^+ + 2e^- \leftrightarrow Cl_2(g) + 2H_20$ [eq. 7]

From equations 1 and 2, assuming 100 % yield and that all NaClO are present in the solution as HClO, the amount of HCIO available for the reaction in equation 7 is 0.004 moles (equation 3 and 4). The amount of HAc in the solution will be 0.01 moles, as calculated by equations 5 and 6. The limiting species in this reaction (equation 7) will therefore be HCIO. Since the amount of acid exceeds the amount of base, the resulting solution will be acidic (pH around 4) and from the Pourbaix diagram (figure 1) we can see that an acidic solution will drive the equilibrium in equation 2 towards the right side of the reaction. Therefore the assumption that all NaClO present in the solution will be in the form of HCIO is supported.

From equation 7, with the assumption that we have 100 % yield in the reaction, 0.004 moles HClO reacts with equal amount of HAc and produce 0.002 moles of chlorine gas.

Properties of Chlorine gas					
Molar mass, M _{Cl2}	71 g/mole				
Mass produced, m _{Cl2}	0.142 g				
Amount present in chamber	57.5 g/m ³				

Table 4	4: Properties	of chlorine	gas and	d calculated	mass
produc	ed during the	reaction.			

Reaction chamber					
Radius, r	7.5 cm				
Hight, h	14 cm				
Volume, V=πr²h	2.47 dm ²				

Table 5: Measured size of the reaction chamber used and calculated volume.

If the yield is 100 % then 0.142 g Cl_2 (g) is produced in the reaction chamber, see table 4. The amount of Cl_2 (g) in the chamber, assuming that all chlorine produced in the chamber is in the gas phase, is then calculated to be 57.5 g/m^3 , or well over 50 000 ppm (assuming 38°C and 1 atm). 50 000 ppm Cl_2 (g) present in the chamber equals approximately 5800 times the amount predicted at the water surface at indoor swimming pool facilities. In the experimental set-up the amount of 50 000 ppm chlorine gas during 72 hours corresponds to almost 48 years of the 8.6 ppm (maximum amount present) chlorine gas present at indoor swimming pool facilities. Thus the tests represent an accelerated test as asserted, and OBA modules which can withstand this treatment can safely be assumed to meet a 15-20 years life span, as suggested by SenseAir to be a typical sensor life time.

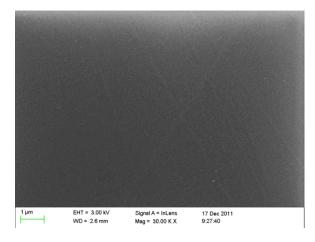
5. Results and discussion

Instantly when mixing Klorin and Ättiksprit the smell of chlorine is apparent, and after closing the reaction chamber gas formation was observed in the beaker. After 72 hours the reaction chamber was evacuated from gas and opened. Condensation was observed inside the reaction chamber as well as evidence of corrosion. On the Z modules, cracks in the top golden layer were observed after the experiment. On the other two module types no direct changes could be observed by occular inspection.

Six of the samples were analyzed with Scanning Electron Microscopy (SEM): A, B, C and M, N, O. The rest of the samples (D-L) were sent to SenseAir for Infrared Spectroscopy (IR) measurements.

The SEM analysis provides information of surface morphology. SEM pictures were obtained in the direction normal to the mirror surfaces. In SEM, the sample is bombarded with energetic electrons (typically of the order 10 keV) that interacts with the atoms in the samples and scatters. The scattered electrons produce different types of signals that give different types of information about the sample. Because the OBA modules consist of plastic modules with mirror surfaces, they are not electrically conducting and when bombarding the samples with electrons the sample will become charged. A charged sample will provide distort SEM micrographs and therefore a silver tape was placed over one end of the module attached - both to the mirror surface and to the sample holder. In figures 5-10, the SEM micrographs from modules A, B, C, M, N and O are shown.

In figure 5 and 6, SEM micrographs from module X are presented for sample M and A respectively. When looking at the two micrographs, the only significant difference between the two is the difference in contrast. From looking at these two micrographs, the surface morphology of module X appears to be unaffected by the corrosive experimental environment.



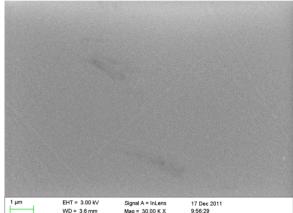
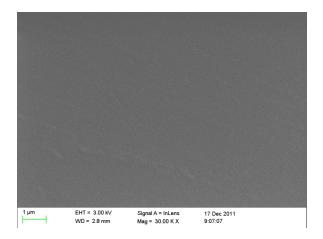


Figure 5: SEM micrograph of module X, sample M.

Reference sample in 30 000 times magnification.

Figure 6: SEM micrograph of module X, sample A.
After experiment in 30 000 times magnification.

When studying the micrographs from module Y, sample O and C, in figures 7 and 8, there could possibly be a slight difference in the surface texture between the reference sample and the sample exposed to chlorine gas, at 30 000 times magnification. It appears that the reference module has a smoother surface, which could indicate changes of the mirror morphology of OBA module subjected to the accelerated chlorine gas test. With lower magnification (x 3 000 times), no difference could be visualized in the micrographs.



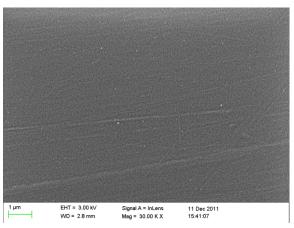


Figure 7: SEM micrograph of module Y, sample O.

Reference sample in 30 000 times magnification.

Figure 8: SEM micrograph of module Y, sample C.
After experiment in 30 000 times magnification.

Figures 9 and 10 show SEM micrographs for module Z, sample N and B, respectively. As mentioned above one could see some cracks in the top layer merely by visual inspection. In the SEM micrographs the difference is obvious. The module subjected to accelerated tests could obviously not withstand the chlorine exposure, and the top layer of the mirror surface module is severely damaged. The adhesion between the plastic substrate and the golden top layer is apparently not good enough, and when removing the silver tape from the module after the SEM analysis, much of the coating came off together with the tape. In the SEM micrograph for the reference sample, figure 9, the surface morphology of the sample appears not as smooth as samples A, M and O above. It might be an indication that the surface coating in module of type Z is not as good as the coatings in types X and Y and therefore the gas could much more easily access the surface and react with the coating. This must however be confirmed by additional experiments.

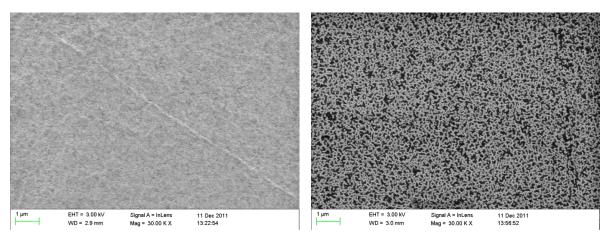


Figure 5: SEM micrograph of module Z, sample N.

Reference sample in 30 000 times magnification.

Figure 6: SEM micrograph of module Z, sample B.

After experiment in 30 000 times magnification.

The modules A-L were exposed to a 50 000 ppm chlorine gas environment for 72 hours at 38°C. This corresponds to an exposure well over 47 years of chlorine gas compared to what can be expected in a public indoor swimming pool facility. The gas measurement devices are not expected to have such a long lifetime, but if there are indications that the modules withstand this exposure, then there is a good probability that they can withstand real indoor swimming environment. The modules were only tested in chlorine gas environment. Other gases present in the indoor environment may also affect the mirror surfaces in a negative way. However if the mirror surfaces can withstand a chlorine gas environment corresponding to well over 45 years of exposure at a public indoor swimming pool facility, then the mirror surface should withstand 15 years of exposure to all different kinds of gases present at indoor swimming pool facilities discussed above.

Before making some definite conclusions about how well the mirror surfaces of the different modules can withstand the corrosive environment present in indoor swimming pool facilities one have to compare with the results from the IR measurements. The IR measurements performed by SenseAir on samples D-L show that module X and Y drop only around 3% of IR signal from before to after the exposure of chlorine gas, thus corroborating the SEM morphology analysis above. Module Z on the other hand dropped around 80% of the IR signal after the exposure, again in good agreement with what can be expected from SEM data.

6. Conclusion

Accelerated chlorine gas test of IR sensor surface modules were performed. The chlorine gas exposures corresponded to 47 years chlorine gas exposure using typical upper reported estimates of chlorine gas concentration directly above water surfaces in indoor swimming pool facilities. SEM and IR analyses show that it is difficult to see any difference between reference modules (M, O), and modules tested in Cl₂ atmosphere (A, C) for module types X and Y. It is concluded that these modules are unaffected by the accelerated tests. For module type Z the difference between reference sample and tested module is clear. The surface morphology is severely affected and the surface coating has corroded away exposing more than half of the underlying substrate. The cracks visible in the coating of module type Z after the experiment are probably due to poor adhesion of the mirror coating. It is concluded that module of type Z cannot withstand the accelerated tests, and will probably not withstand the conditions in a swimming pool facility (at least not for 45 years operation). Modules of types X and Y appears however to be good enough to withstand the accelerated test. If the corresponding IR measurements show equally promising results for the tested modules type X and Y, then there is a good chance that the modules will withstand even up to 45 years in a corrosive swimming pool environment.

7. Future investigations

Further testing could be applicable. The Z modules did not withstand the corrosive environment corresponding to 47 years of chlorine gas at indoor pool facilities. But it might resist the corrosive environment during 20 years of time? If there would be interesting to continue to use module Z in corrosive environment, then there should be some testing on whether or not they can withstand smaller amounts of chlorine gas or during a shorter period of time.

If it would be interesting to see why the module did not resist the corrosive atmosphere, some further testing in corrosive environment and more detailed analysis in SEM could be a good idea to investigate in the coatings adhesion and porosity.

Depending on the results from the IR measurements, module X and Y might as well be tested for lower amounts of gas to see how much gas they can withstand and how long the mirror surfaces expected lifetime would be.

It could also be interesting to see if the combination of different gases affect the mirror surfaces in any other direction than predicted and assumed.

8. Acknowledgements

I would like to send my best regards to Zareh Topalian for all the help, both with experimental execution and SEM analysis. I would also like to thank Ingrid Bryntse at SenseAir for all the help with the information about the sensors and guidance in my work.

9. References

- [1] Socialstyrelsen, Bassängbad: Hälsorisker, regler och skötsel. 2006 Collected 2011-11-16 from: http://www.socialstyrelsen.se/Lists/Artikelkatalog/Attachments/9405/2006-101-1_20061012.pdf
- [2] S. Johannesson, *Mätning av trikloramin I fem simhallar I Göteborgs kommun*. 2009 Collected 2011-11-16 from: http://sahlgrenska.se/upload/SU/omrade_6/Arbets-%20och%20Milj%C3%B6medicin/VMC/Simhallar_Gbg_090526.pdf
- [3] K. Hågestad, P. Björklund, A. Jangenfeldt, *Projekt: Simhallar Badhuspersonalens hälsa*. Arbetsmiljöverket distrikt Växjö 2007 Collected 2011-11-21 from: http://www.weedo.se/pub/ProjektrapportSimhallar2007Vxj.pdf
- [4] W. A. Weaver, J.Li, Y. Wen, J. Johnston, M. R. Blatchley, E. R. Blatchley III. *Volatile disinfection by-product analysis from chlorinated indoor swimming pools*. **Water research** Volume 43, Issue 13 (2009) p. 3308-3318
- [5] S. –C. Weng, W. A. Weaver, M. Zare Afifi, T. N. Blatchley, J. S. Cramer, J. Chen, E. R. Blachley III. *Dynamics of gas-phase trichloramine (NCl3) in chlorinated, indoor swimming pool facilities.* **Indoor Air** Volume 21, Issue 5 (2011) p. 391-399
- [6] Stephen Lower, *All about electrochemistry Chlorine in water*, 2005. Simon Fraser University Collected 2011-11-28 from: http://www.chem1.com/acad/webtext/elchem/ec4.html
- [7] Socialstyrelsen, SOSFS 2004:7, *Allmänna råd: Bassängbad*. 2004 Collected 2011-11-28 from: http://www.socialstyrelsen.se/sosfs/2004-7/Documents/2004_7.pdf
- [8] Lenntech water treatment solutions, Health effects of swimming pool disinfection Collected 2011-11-16 from: http://www.lenntech.com/processes/disinfection/swimming-pool/swimming-pool-disinfection-health.htm
- [9] Arbetsmiljöverket, AFS 2005:17, *Hygieniska gränsvärden och åtgärder mot luftföroreningar.* 2005 p. 27 Collected 2011-11-27 from: http://www.av.se/dokument/afs/AFS2005_17.pdf
- [10] K. Stamyr, G. Johanson, *Hälsoriskbedömning av trihalometaner i bassängbad*. Stockholm 2006 Collected 2011-11-21 from: http://ki.se/content/1/c6/01/43/48/Trihalometaner%202-06.pdf
- [11] Unknown, Collected 2011-11-16 from: http://boffe.com/rapporter/Kemikalier%20-%20Metaller/Rapport111.pdf