

Safe, reliable and cost-effective materials for handling chlorine-containing chemicals in the industry

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1.1 Summary

Many of our most commonly used commodity chemicals contain chlorine in some form. These chemicals are often hazardous and corrosive which makes proper material selection a key issue. Finding a safe, reliable and at the same time cost-effective solution is a priority for industries such as chemical plants, pulp and paper mills and water treatment plants. In the presented project, some common, industrial chlorine-containing chemicals have been studied from a corrosion point of view. These chlorine environments are extremely difficult for most metallic materials and common material choices are instead the polymeric materials PVC or CPVC. However, the deeper understanding of the corrosion process is lacking and due to environmental adaptation of the materials' formulations previously collected corrosion data may be out of date.

The goal for this project is therefore to better understand the corrosion process of PVC and CPVC materials in chlorine environments. The results will support users and suppliers of process equipment with a better fundamental understanding about the behaviour of these materials in chlorine environments. Since the welds often are the weakest point of any piping system, the project has also studied the effect of different welding techniques (e.g., treatment of the materials by heat or solvents with the purpose of joining pipes together) on the corrosion resistance of PVC and CPVC materials in chlorine service.

The findings are aimed to be of help for users at e.g., chemical plants, pulp and paper mills and within water treatment to make better material choices, better service life predictions and to a safer working environment.

1.2 Background

Many of our most commonly used commodity chemicals contain chlorine in some form. Examples are chlorine, chlorine dioxide and sodium hypochlorite, which are used in as diverse applications as pulp bleaching at pulp and paper mills, disinfection of water, bio-fouling prevention or manufacture of plastics such as polyvinyl chloride (PVC). Due to the chlorine

content, these environments are extremely difficult for most metallic materials and a better material choice is instead a polymeric material.

Chlorine dioxide is used within pulp and paper industry for pulp bleaching but also, in lower concentrations, for water disinfection. Chlorine dioxide is unstable and must therefore be produced on site, from either the reduction of chlorate or the oxidation of chlorite. In addition to chlorine dioxide, corrosive bi-products and so-called spent acid can be formed. Spent acid can vary in composition and concentration, but is in many cases highly corrosive, and material choice for spent acid handling has caused much concern, mainly for the pulp and paper industry. A number of failures have occurred in recent years, of which two examples are shown in Figures 1-2. Besides from being a risk for both environment and health, a large failure can also have huge economic effects. A forced shut-down of the bleaching process at a pulp mill can have production effects for the whole mill. The cost of taking a pulp mill out of production is approximately 10 MSEK/day, as an estimation of the production loss. To prevent catastrophic failures like these from happening in the future, a deeper understanding of the corrosion process is needed.



Figure 1 Catastrophic failure of a 60 m³ spent acid tank made of glass-fibre reinforced polyester (FRP) with a CPVC lining.

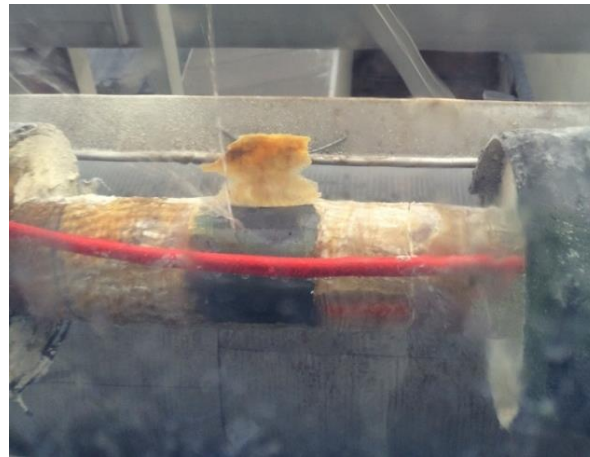


Figure 2 Leaking weld in a spent acid pipe made of FRP with a PVC lining.

Many chlorine compounds cannot be isolated in pure form but co-exist in equilibrium with other chlorine species which may have a higher reactivity towards the polymeric materials. This means that the chemical composition of a solution can vary with pH, which in turn makes pH a very important parameter for knowing the corrosiveness of the solution. One example is shown in Figure 3, which shows a diagram of the chemical composition balance of sodium hypochlorite (NaOCl), hypochlorous acid (HOCl) and chlorine (Cl₂) as a function of pH. The chlorine concentration is most often reported as the active chlorine concentration, which is the total concentration of Cl₂, HClO and ClO⁻. The fact that sodium chlorite is sold and stored in blow moulded polyethylene bottles at 125 000 ppm (at pH 12, as in the household cleaning agent “Klorin”), but at the same time causes a reduction in service life of polyethylene drinking

water pipes, where the concentration is maximum 4 ppm but at lower pH values, is confusing unless the pH is taken into account.

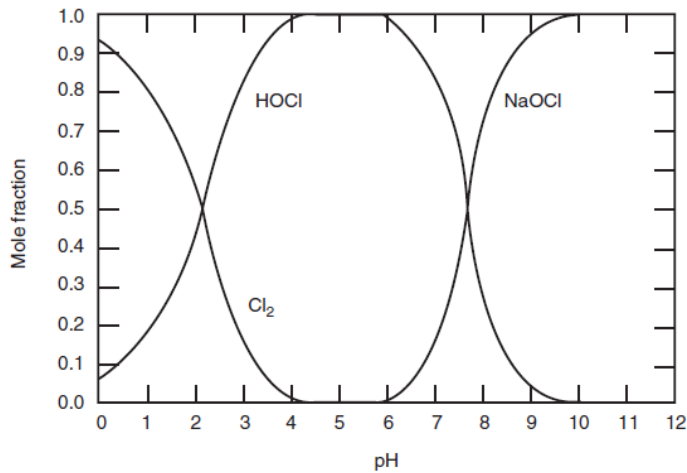


Figure 3 Example of how the relative composition of the different chlorine species in a hypochlorite solution can vary as a function of pH.

Ref: Michael G. Stevens, Paul Cohen, *Best Available Technology for Sodium Hypochlorite Storage Tanks*

Knowing all this, when it comes to choosing the right material for each chlorine environment in its specific application, many aspects must be taken into account. First of all, it must be sorted out what or which of the mentioned species the system needs to be designed for, which means that the pH is of utmost importance. Once the pH is known, other parameters for designing the chlorine handling equipment are concentration and temperature.

1.2.1 Material choice for handling chlorine-containing chemicals

When choosing the proper material, there are a number of important material aspects to consider. First of all there is the corrosion resistance, i.e. the material's ability to withstand chemical attack. The operating temperature is another important factor, since all chemical reactions are accelerated by temperature and since polymeric materials become softer with temperature. Temperature changes also lead to thermal expansion and increases stresses in the material. Another aspect is the weldability of the material and possibilities for reparations, if needed.

Some of the most corrosion-resistant and cost-effective materials for these chlorine environments are PVC and chlorinated PVC (PVC-C or CPVC). These two material groups are, however, not strictly defined materials but their properties can vary as an effect of different molecular weights, molecular weight distributions, and also the additives. The latter is particularly true for CPVC which contains impact modifiers since the extra chlorination makes the material more brittle. The degree of chlorination of CPVC can also vary and with that the properties of the material, in particular the temperature resistance and stiffness.

1.2.2 The “new” PVC materials

PVC materials need to be stabilised to prevent degradation by dehydrochlorination. The stabilisation was historically made with cadmium and later by lead compounds, but due to environmental issues, new stabilisers have been developed. It has, however, been difficult to find good replacements and the chemical resistance of the material has suffered. Due to the new stabiliser systems used today it is difficult to base new material recommendations on old experiences.

1.2.3 Joining the materials together

In practical use, the weakest link in a pipe or lining system is the welds. PVC and CPVC are difficult to weld. One possibility for joining PVC and CPVC materials is *butt fusion welding*, in which both pieces are simultaneously heated and then pressed together (Figure 4). This method usually produces welds with good quality, although the influence on corrosion resistance in the heat affected zone (HAZ) is not yet understood.

In the field, or with more complex geometries such as T-pieces, butt welding is not possible and instead *hot gas welding* with welding rods is used (Figure 5). When joining together plates or pipes with welding rods, the compatibility between the different materials is very important. Another concern in the industry is which type of welding rod to use for optimum corrosion resistance. The development of welding rods for corrosive environments is lagging behind and the lead stabilisers are just now being replaced, compared to in pipe and lining material where the stabilisers were replaced a few years ago.

A third way to join PVC pipes together is by *solvent welding*, in which a socket is glued onto the pipes' ends. The method is not considered to be as good for corrosive environments as the other two, but is sometimes preferred in the field due to practical reasons. The role of the glue, the cement, is to temporarily dissolve the polymer in the pipe and socket and allow them to fuse together (by entanglement of polymer chains) which obviously raises the question of what detrimental effects, in a similar way as for the heat treatment in butt welding, this has on the material. As in the case with new stabilizers, the cements are being replaced by new, less hazardous ones which make old experiences and data difficult to rely on. Another issue with solvent welding is the sockets themselves, which may be of a lower quality than the pipe materials. The effect may be lower corrosion and crack resistance, which is clearly illustrated by the example in Figure 6.

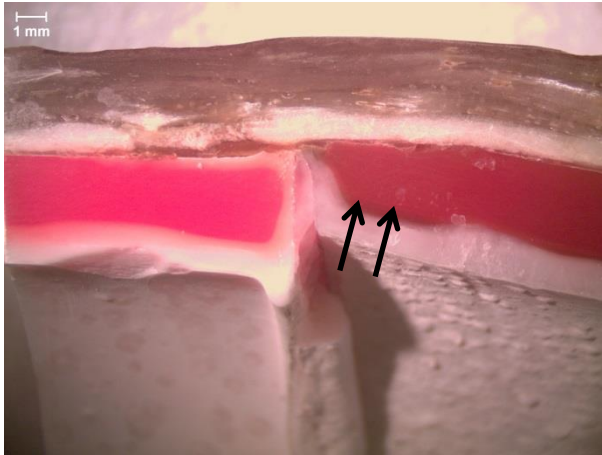


Figure 4 Cross section of a butt weld in a PVC material with full penetration of chlorine dioxide, which has not only coloured the material white, but also dark (indicated by black arrows). The reasons for the dark colouration are not yet understood.

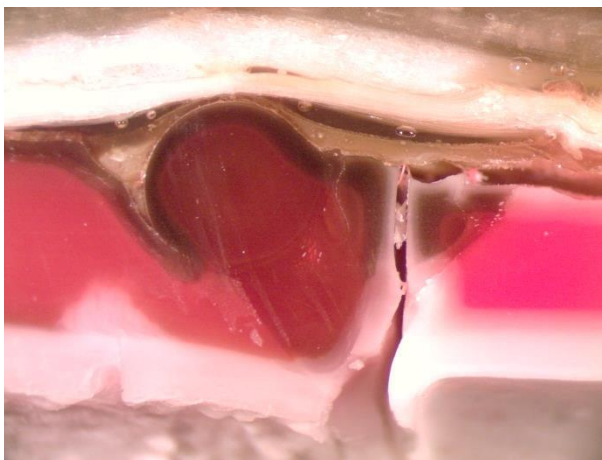


Figure 5 Cross section of a hot gas weld in PVC (cross section of welding rods in the middle of the picture). Exposure to chlorine dioxide has resulted in a crack all the way through the weld and in both white and dark discolouration.

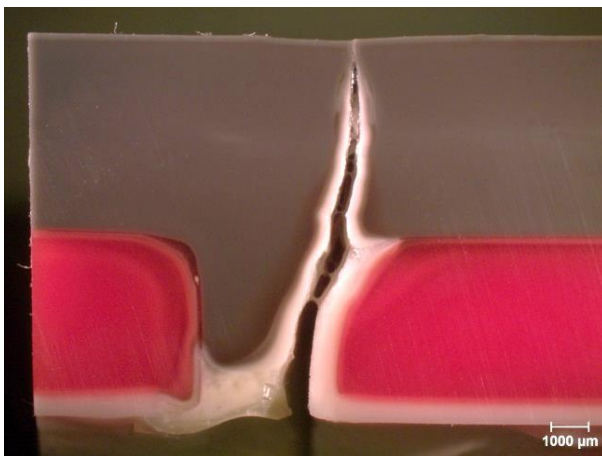


Figure 6 Cross section of two PVC pipes (red) glued together using a socket (grey) for use in a chlorine dioxide-containing environment. Note how the chlorine has affected the socket material to much larger extent than the pipe material and even induced a crack

Need for knowledge to predict service life

All in all, there is a great need for more fundamental understanding of PVC and CPVC corrosion in chlorine-containing environments, in order to predict service life and to develop better and safer materials. Today, there is little or no documented experience of using the new materials,

and updated material recommendations for use in corrosive chlorine environments as well as recommendations on joining technologies are needed.

Better knowledge of this topic would be of great significance for diverse industrial areas such as chlorine production, pulp and paper mills, and water treatment, only to mention a few.

2 Chlorine dioxide generation

In the pulp and paper industry chlorine dioxide is used for bleaching the pulp. Chlorine dioxide is not stable and must be produced on site. The residue after formation of the gaseous chlorine dioxide is called spent acid if the salt is in solution, i.e. in liquid form. There are also a number of chlorine dioxide production methods where the salt is in crystal form, i.e. as a solid.

Chlorine dioxide can be produced from either the reduction of chlorate (reaction I) or the oxidation of chlorite (reaction II). For large scale production, like for producing chlorine dioxide for bleaching in the pulp and paper industry, chlorate reduction is used almost exclusively. Small scale production, like chlorine dioxide generators for water disinfection, on the other hand, is often based on chlorite chemistry. The cost of chlorite is several times that of chlorate.



For both chlorate and chlorite based chlorine dioxide generation a number of different chemistries exists and the purity of the end product and the composition of the spent acid will depend on the chemistry used.

For chlorate reduction NaCl, HCl, SO₂, Cl₂, H₂O₂, CH₃OH and Na₂SO₃ can all be used as reducing agents and H₂SO₄ is most often used as the acidic media. Table 1 shows a summary of the most common chlorate reduction chemistries for ClO₂ production including the reducing agent used and the form of the salt (liquid or crystalline).

Table 1. A summary of the most common chlorate reduction chemistries for ClO₂ production including the reducing agent used and the form of the salt (liquid or crystalline).

Name	Reducing agent	Salt form
SVP-Conventional	NaCl	Crystal
R3	NaCl	Crystal
R2	NaCl	Solution
SVP-Lite	CH ₃ OH	Crystal
SVP-SCW	CH ₃ OH	Crystal
R8	CH ₃ OH	Crystal
Solvay	CH ₃ OH	Solution
R10	CH ₃ OH	Crystal
SVP-HP	H ₂ O ₂	Crystal
HP-A	H ₂ O ₂	Solution
Mathieson	SO ₂	Solution

Historically the Mathieson process, which uses SO₂ as the reducing agent, has been the most popular process for ClO₂ production in Sweden. Figure 7 shows a simplified scheme of chlorine dioxide production with the Mathieson process.

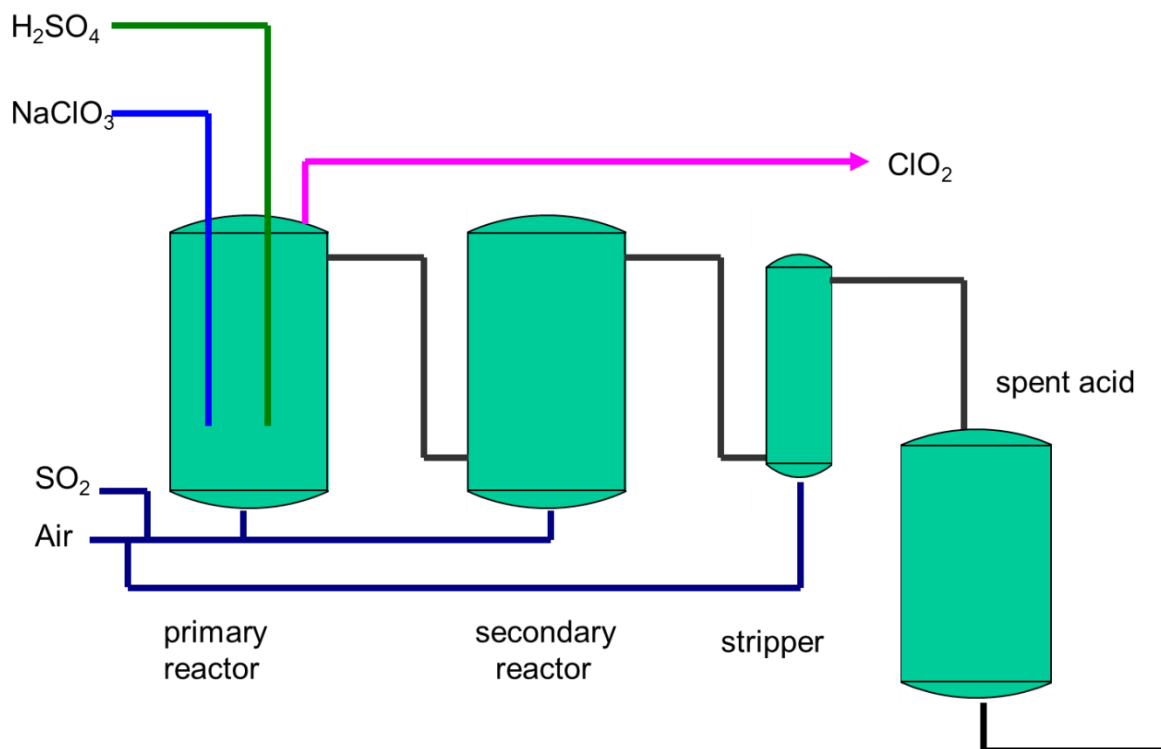


Figure 7. Simplified scheme of chlorine dioxide production with the Mathieson process

There is also a modified Mathieson process called “salted Mathieson” in which sodium chloride (NaCl) is added in small amounts to the reactants in the primary generator. The addition of NaCl improves the reduction efficiency of the chlorate and also increases the generator capacity.

Many of the Swedish mills have changed from the Mathieson to the HP-A method since by this the existing facilities could achieve significant increases in capacity with minimal capital investment. In addition the HP-A method also produces less spent acid and does not produce any significant amount of chlorine as a by-product. Therefore, organo-chlorine formation in the bleaching process is minimal. Figure 8 shows a schematic drawing of the HP-A process.

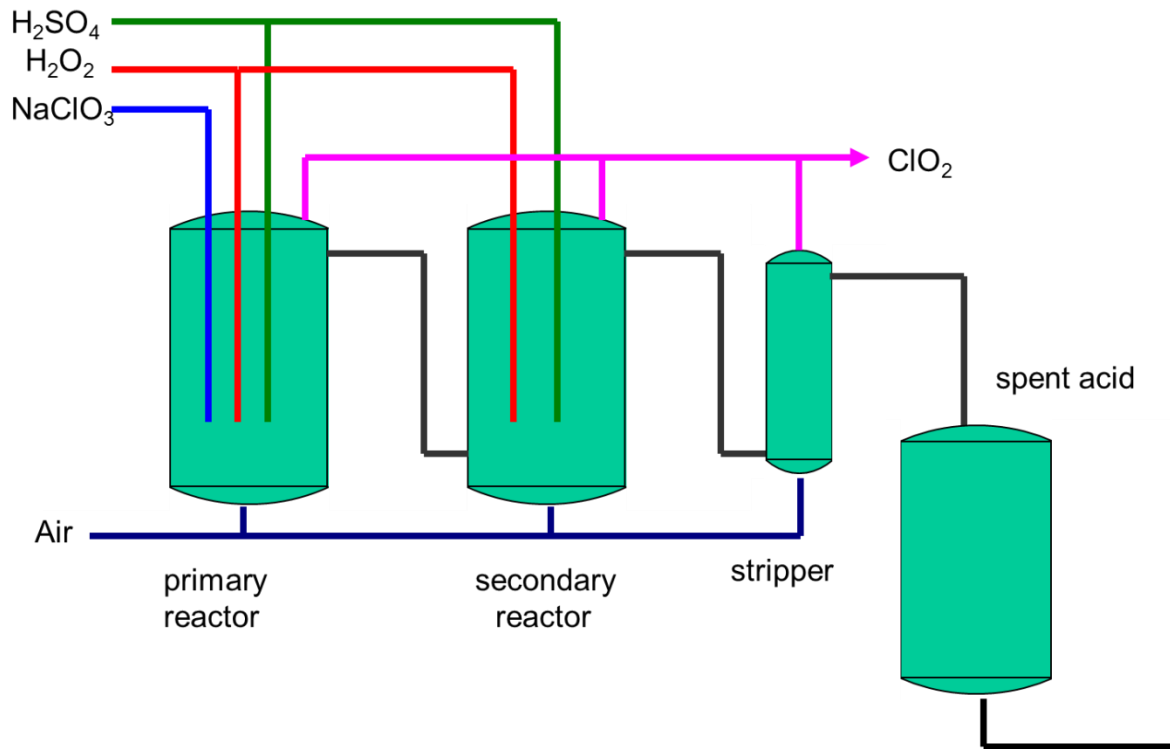


Figure 8. Simplified scheme of chlorine dioxide production with the HP-A process

In addition to the Mathieson and the HP-A processes the Solvay process, Figure 9 and the R2 process, Figure 10, also produces spent acid in liquid form. The Solvay process is essentially the same as the Mathieson system except that methanol (CH_3OH) is used in place of SO_2 as the reducing agent. In contrary to the HP-A process which produces essentially chlorine-free chlorine dioxide, the Mathieson, Solvay and R2 processes all produce chlorine as a by-product. The R2 process is based on the use of NaCl for reducing the chlorate and a mixture of NaClO_3 and NaCl is added to the generator along with H_2SO_4 . Air is used for agitation and dilution of the chlorine dioxide gas.

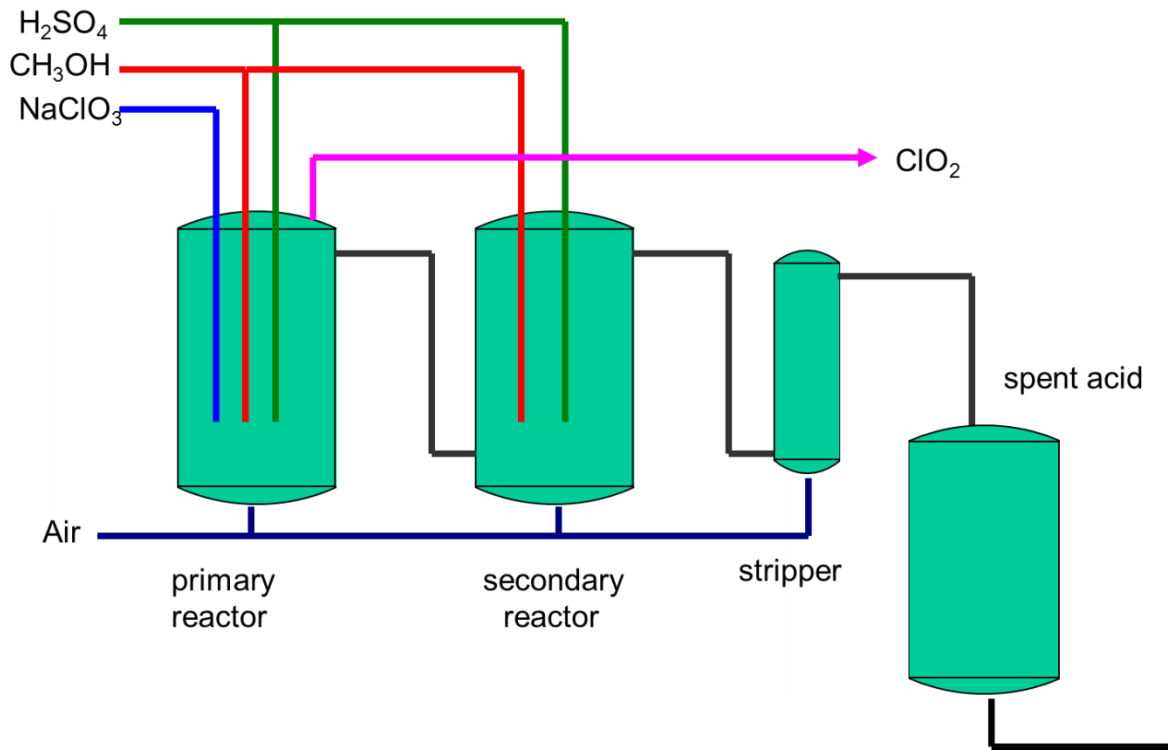


Figure 9. Simplified scheme of chlorine dioxide production with the Solvay process

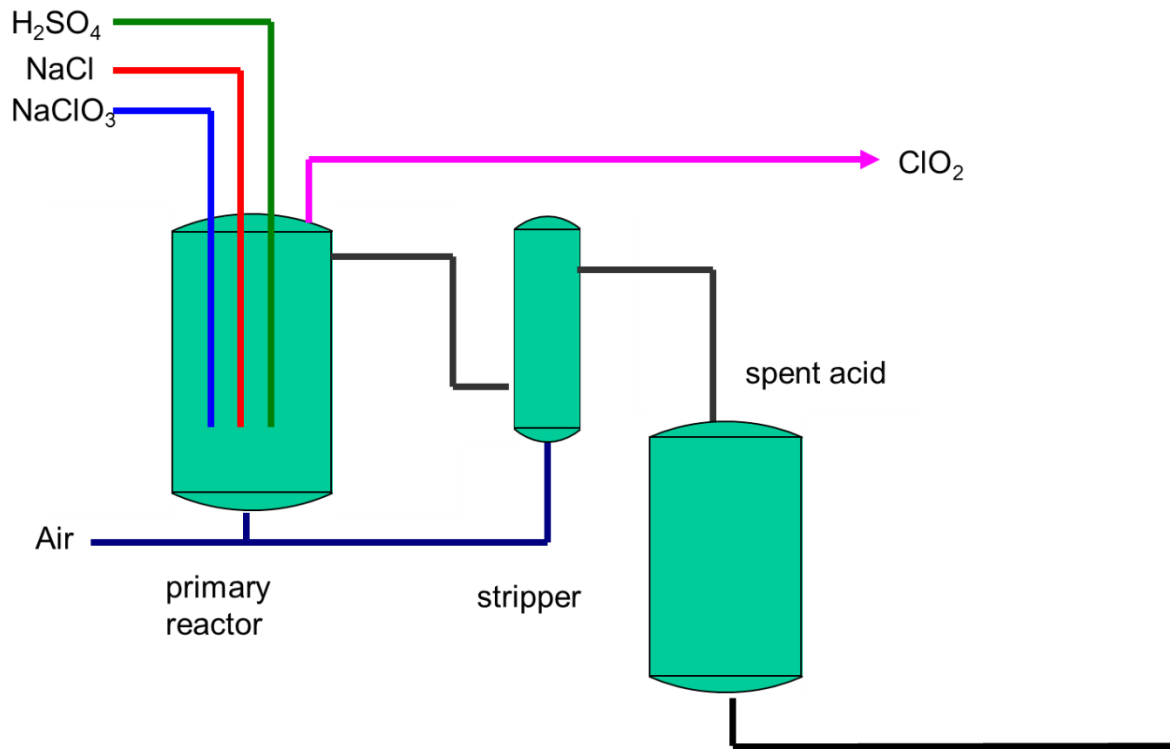


Figure 10. Simplified scheme of chlorine dioxide production with the R2 process

A more modern way to produce chlorine dioxide, and the method which is often chosen when building new plants, is the SVP (single vessel process) shown in Figure 11. This gives the salt in solid form as sodium sulphate or sodium sesquisulphate.

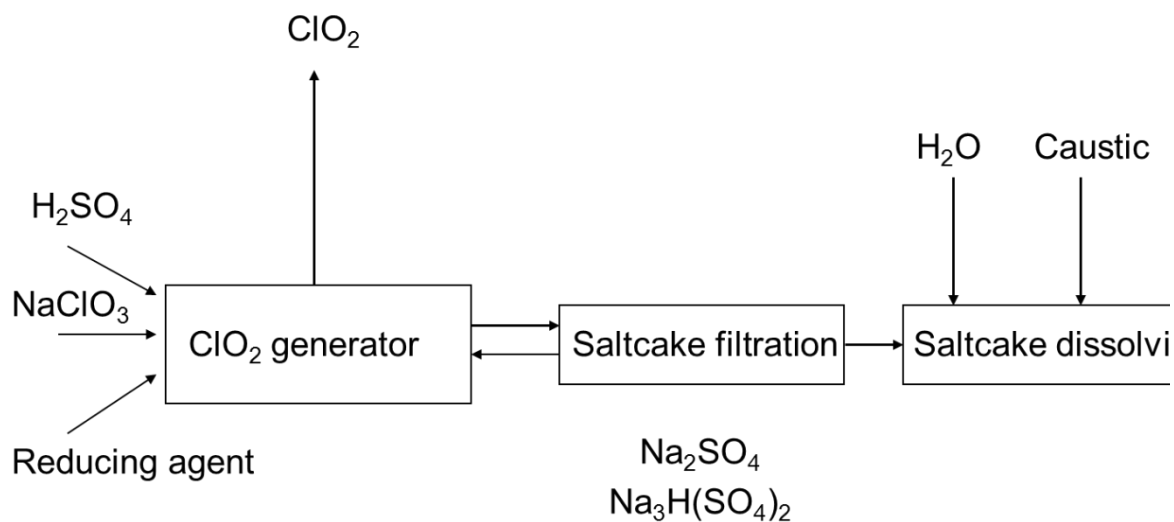


Figure 11. SVP (single vessel process)

Table 2 summarises the approximate composition of the spent acid in the different chlorine dioxide generators described above.

Table 2. The approximate composition of the spent acid in the different chlorine dioxide generators

Process	Mathieson and Solvay	R-2	HP-A
Temperature (°C)	30-40		50-55
Na ₂ SO ₄	300 g/l	280 g/l	300 g/l
H ₂ SO ₄	340-470 g/l	420 g/l	400-500 g/l
Water	560 g/l	540 g/l	
NaClO ₃	2-7 g/l	4 g/l	3-5 g/l
NaCl	1 g/l	2.5 g/l	
Cl ₂	traces	traces	
ClO ₂	traces	traces	1-2 g/l
H ₂ O ₂			Presumably traces

2.1 Test station in chlorine dioxide generators

Between 2005-2008 Swerea KIMAB had a test station in the primary and secondary chlorine dioxide generators at the Skärblacka mill (HP-A), Figure 12. A number of different plastic materials were exposed, including PVC and CPVC. The conditions in the two reactors are summarised in Table 3.



Figure 12. 2005-2008 Swerea KIMAB had a test station in the primary and secondary chlorine dioxide generators at the Skärblacka mill (HP-A)

Table 3. Conditions in the reactors at the Skärblacka mill (HP-A)

Reactor	Primary	Secondary
Temperature	57-58 °C	57-58 °C
NaClO ₃	~30 g/l	~ 5.7 g/l
H ₂ O ₂	~200-300 mg/l	~200-300 mg/l
H ₂ SO ₄	~435 g/l	~ 430 g/l
ClO ₂	2.6 g/l	1.3 g/l

It has been found that in addition to the species listed there are also other very reactive species (probably radicals) produced. These are reactive enough to oxidise the generally very stable polymers PVDF and ECTFE making them unsuitable for use in chlorine dioxide reactors.

2.2 PVC lining for chlorine dioxide reactor

There are no examples of PVC used for chlorine dioxide reactors, known to the authors, but it is often used for both ClO₂ and spent acid piping and tanks. For cold chlorine dioxide solution (0-15°C) standard PVC piping can have a service life of 15 years or more, if pressure shocks and external impact can be avoided. Examination of replaced PVC equipment shows that non load bearing material has the possibility to perform well even if ClO₂ has permeated 90% of the PVC wall thickness. However, this material is most likely very sensitive to any pressure shocks, stresses or impact. A ClO₂ absorption tower was recently investigated after 29 years of service and was found to be in excellent condition. For higher temperatures or to avoid the risk of brittle fracture in PVC equipment for ClO₂ service, an external reinforcement of FRP is recommended. PVC is limited to an upper temperature of 60-70°C due to the softening temperature of PVC. Operation temperatures can be closer to the softening or glass transition temperature when an external FRP reinforcement is used.

PVC is attacked by chlorine dioxide but normally, no reduction is found in wall thickness, i.e. it is not a radical attack causing material to corrode away. The thickness of the corroded layer increases approximately with the square root of time indicating that the corrosion process is diffusion-controlled, Figure 13. Due to reactions with the pigment the corrosion depth is often visible. Local surface cracks may form in PVC where the corrosion depth may be significantly higher than the average corrosion depth, Figure 14.

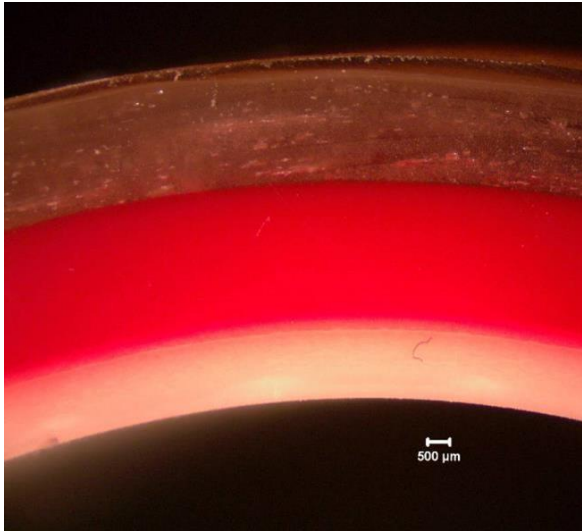


Figure 13. A case of uniform corrosion which is diffusion-controlled.

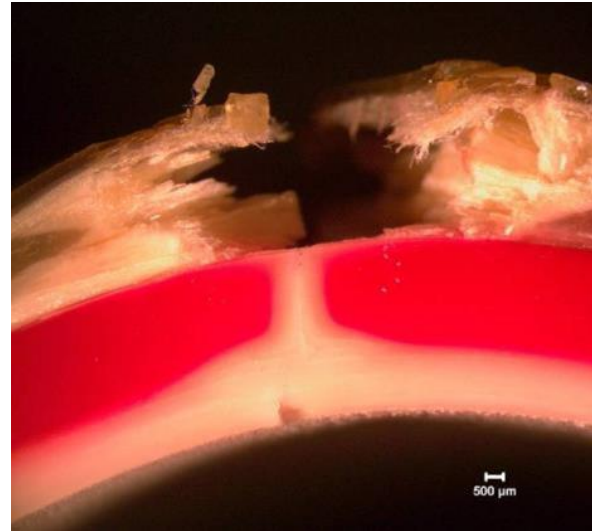


Figure 14. The corrosion causes embrittlement which can lead to surface crack formation and local corrosion

PVC-materials have been exposed in both of Swerea KIMAB's test stations. The exposure in the generator was, however, made in 2007-2008 which means that the PVC materials were most probably lead stabilised. Modern PVC-materials use different stabilisers (often Ca-based stabilisers in Europe and Sn-based in North America) and cannot be directly compared to the old materials in terms of chemical resistance. More recent exposures of modern PVC materials have been made in the spent acid test station in Karlsborg. A summary of the conditions in the two test stations is made in Table 4. As can be seen the conditions in the spent acid is quite similar to the secondary reactor, even if the temperature is about 5°C lower. It is therefore interesting comparing the performance of the new PVC material Trovidur NL with its older version exposed in the reactors, Figure 15. As can be seen the corrosion is much less severe after 2 years in the spent acid than after 1 year in the secondary reactor. This implies that the new stabiliser is performing at least as well as the old lead stabiliser.

Samples of the same grade PVC with lead, tin and Ca/Zn stabilisers are also presently being exposed in the spent acid test-station (see below) in order to have more comparable results of different stabiliser systems. Unfortunately there has been no possibility to access the samples before finishing this report.

Table 4. Conditions in the reactors at the Skärblacka mill (HP-A) compared to the spent acid test station in Karlsborg (HP-A).

Reactor	Primary Skärblacka	Secondary Skärblacka	Spent acid Karlsborg
Temperature	57-58 °C	57-58 °C	50-55 °C
NaClO ₃	~30 g/l	~ 5.7 g/l	3-5 g/l
H ₂ O ₂	~200-300 mg/l	~200-300 mg/l	traces
H ₂ SO ₄	~435 g/l	~ 430 g/l	~490 g/l
ClO ₂	2.6 g/l	1.3 g/l	1-(2) g/l

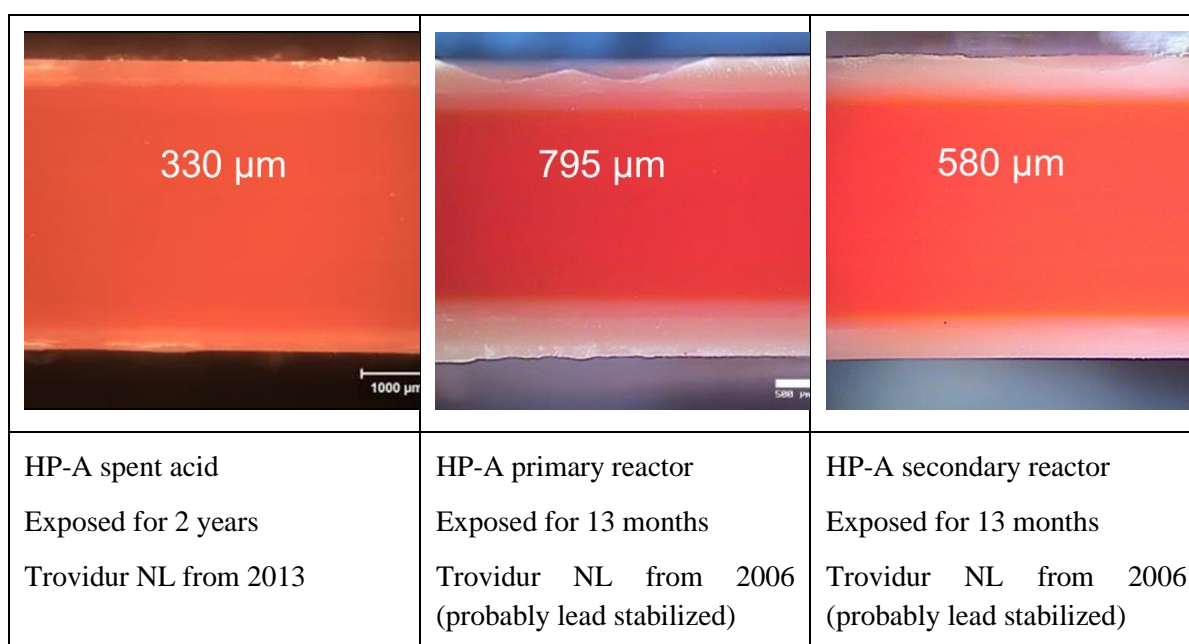


Figure 15. Trovidur NL exposed in the spent acid test station at Karlsborg mill and in the primary and secondary reactors at the Skärblacka mill.

It is important to note that different PVC grades can have very different corrosion rates in chlorine dioxide. For unknown grades the suitability of the material should be verified by experiments or practical experience before it is used.

CPVC lining

There is only one examples of CPVC used for chlorine dioxide reactors, know to the author, and this was for a small scale reactor (Purate). This reactor was investigated after around 8 months in service and was found to be in very good condition with only minor ClO₂ attack of the CPVC. CPVC is also often used for both ClO₂ and spent acid piping and tanks. For cold chlorine dioxide solution (0-15°C) standard CPVC piping can have a service life of 15 years or more, if pressure shocks and external impact can be avoided. Similar to PVC, CPVC is attacked by ClO₂. Normally, no reduction is found in wall thickness, i.e. no signs of radical attack causing material to corrode away. The thickness of the corroded layer increases approximately with the square root of time indicating that the corrosion process is diffusion-controlled. The corrosion rate strongly depends on temperature and chlorine dioxide concentration. The corroded layer leads to an increased brittleness in the CPVC material which in combination with external impact in the form of i.e. pressure shocks can lead to failures. At higher temperatures or to avoid risk of brittle fracture in CPVC equipment for ClO₂ service an external reinforcement of FRP is recommended. CPVC has a higher softening temperature compared to PVC and can be used at temperatures up to 90°C. It has also been found that the corrosion rate is lower for CPVC compared to PVC. Summarised, the material behaves similar to PVC but can withstand temperatures up to 90°C and generally has a higher corrosion resistance. Just as PVC the material is oxidised by the ClO₂ but does not seem to be affected differently in the reactor compared to in a pure ClO₂ solution.

Just as for PVC it is important to note that different CPVC grades can have very different corrosion rates in chlorine dioxide and it is important that the suitability of the material is verified by experiments or practical experience before it is used.

A number of different PVC and CPVC materials have been exposed in the primary and secondary reactors at Skärblacka. In comparison to ECTFE and PVDF that despite their normally very good corrosion resistance is degraded in a ClO₂ reactor, CPVC performs well as regards the depth of attack and the brittleness of the material. It is, however, oxidised by the diffusion chlorine dioxide as can be seen in Figure 16, which shows the oxidation as measured by FTIR linescan over the cross section of the exposed sample.

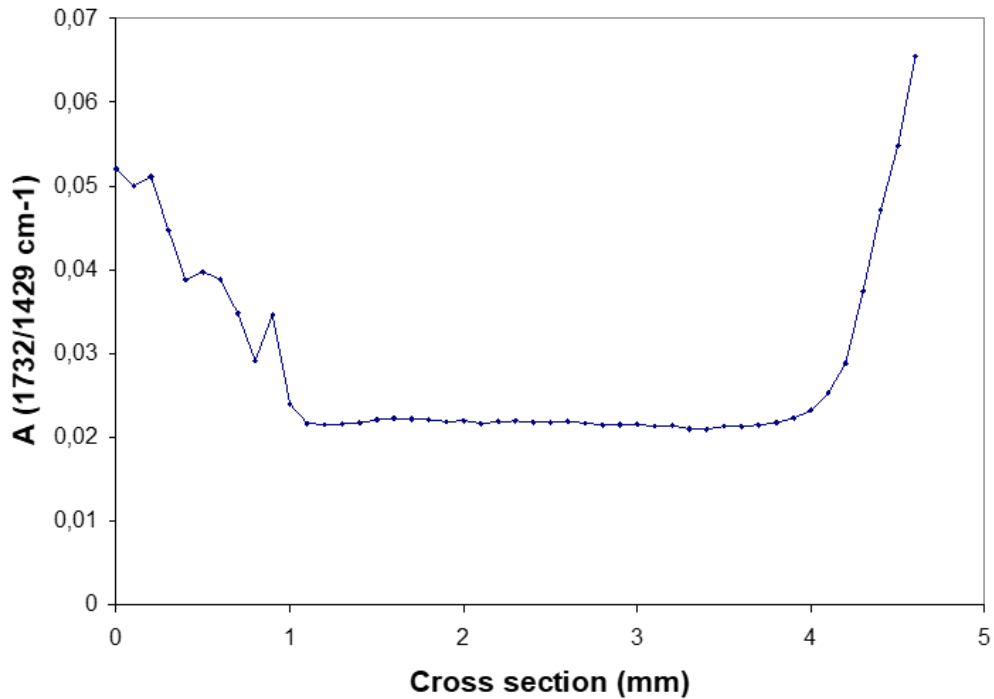


Figure 16. FTIR linescan of the oxidation over the cross section of a CPVC 3216 sample after 13 months exposure in the primary reactor.

Figure 17 shows the % unaffected core of the materials exposed in the primary and secondary reactors. It is interesting to note that the difference is not so large between the two reactors even of the concentration of ClO_2 is reported to be half as much in the secondary (1.3 vs 2.6 g/l). The CPVC materials are performing slightly better than the PVC-materials. This effect seems to be more pronounced in the primary reactor compared to the secondary.

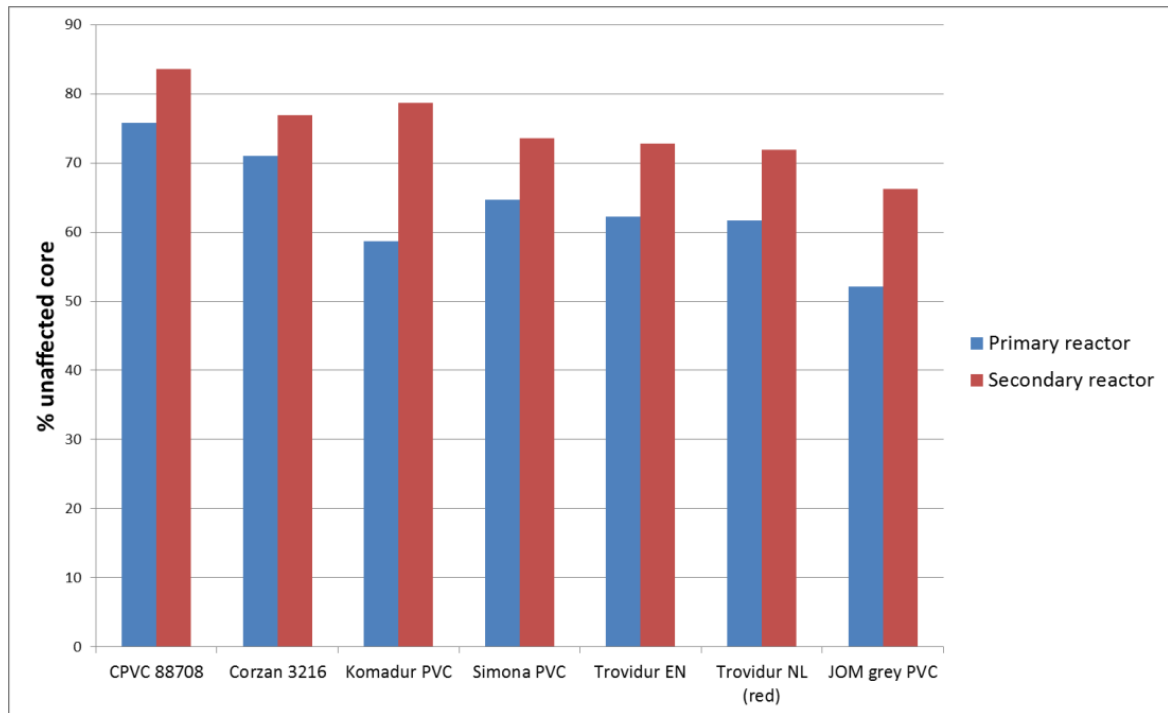


Figure 17. % unaffected core of CPVC ad PVC materials after exposure in the primary and secondary reactors at Skärblacka. Note that these materials are probably lead stabilised. The difference in corrosion (here presented as unaffected material) is not so large between the primary and secondary reactor even of the concentration of ClO₂ is half as much in the secondary, 2.6 vs 1.3 g/l.

3 Spent acid

As can be concluded from the description of chlorine dioxide generation above, spent acid does not have a single and uniform composition. In general it can, however, be concluded that the salts, sodium sulphate and sodium chloride will not normally affect plastic materials. The sodium chlorate will in itself also not affect the material, but it can be involved in post reactions producing new chlorine dioxide. It has also been found that this post reaction produces very reactive species (probably radicals) that are the same as will be produced in the chlorine dioxide reactor. The sulphuric acid has such a low concentration in the spent acid that it is fully dissociated and will thus not affect the polymeric materials except as, just as for sodium chlorate, when involved in post reactions. The same is valid for hydrogen peroxide. The older technologies, Solvay, Mathieson and R2 all produced chlorine as a bi-product. This will react with most polymeric materials.

In general, polymeric materials used in spent acid will mainly be attacked by the residual chlorine dioxide and the concentration of it will determine the performance and service life of the material. The results presented for spent acid are thus very similar to the results for exposure in chlorine dioxide. The main difference is for the fluoroplastics where it has been found that the service in spent acid resembles that in the chlorine dioxide generator where intermediate reaction products can degrade the material. It is quite probable that this would happen also for polyolefins and rubbers that can be oxidised.

3.1 Test station in spent acid

Swerea KIMAB has also a test station for materials corrosion in spent acid, which is positioned between the stripper and the spent acid tank of the chlorine dioxide production unit. This station is located at the mill in Karlsborg (HP-A® process). The test station, Figure 18, is operated under the following conditions:

- Temperature 50-55°C
- H₂SO₄ concentration 490 g/l
- Residual chlorate concentration 3-5 g/l
- Calculated ClO₂ concentration ca 1 g/l
- Presumably some residual peroxide

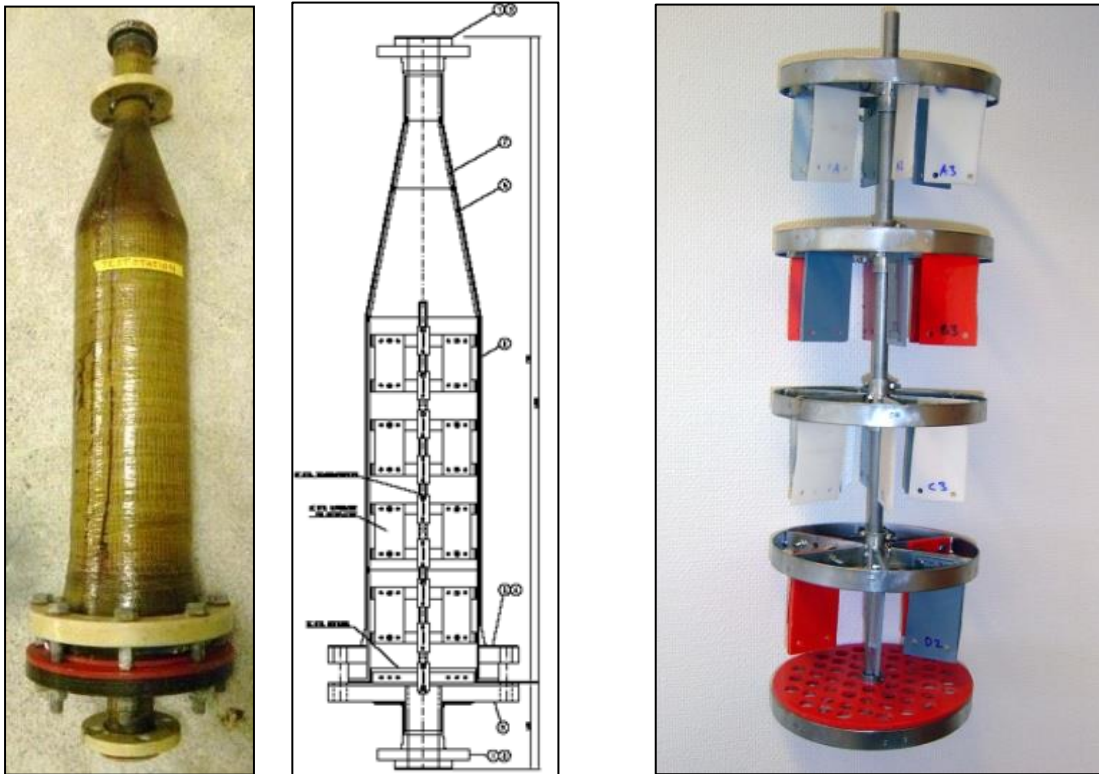


Figure 18 Test station for material corrosion testing in spent acid.

3.2 PVC for spent acid

Data from the old test station in a chlorine dioxide generator was compared with newer data from the spent acid test station to investigate how large the differences are between the two environments. Also equipment in PVC and CPVC that has been taken out of service for pure ClO₂ and in spent acid has been evaluated. The samples from the test station have been investigated in more depth than previously not to only reflect the penetration depth but to also create a bit more understanding of the degradation mechanisms in the material to better be able to predict the long term properties.

FTIR analysis shows that PVC is oxidised by the ClO_2 , Figure 19, but it does not seem to be as sensitive to the oxidising species formed by the reaction as PVDF, ETFE and ECTFE. The oxidation seems to be the same in pure ClO_2 as in the reactor. PVC often contains some CaCO_3 and this will be attacked by the ClO_2 , which can also be seen in the FTIR spectra in Figure 19.

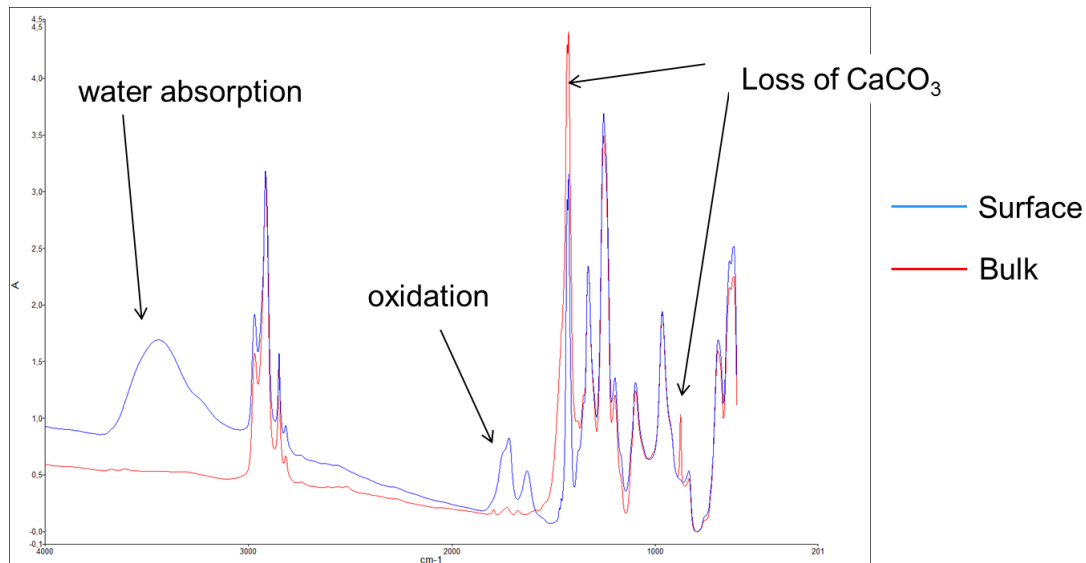


Figure 19. FTIR of Troisdorf-red near the surface and in the bulk after 2 years in the spent acid test station.

As shown in the following the Figures it is possible with FTIR linescan to detect the changes seen in the water absorption as in Figure 20, oxidation as in Figure 21, and loss of CaCO_3 as in Figure 22 over the cross section of the exposed samples. From the linescan data it can be seen that the penetration depth of the oxidation which is around 500 μm is not as deep as the water absorption and loss of CaCO_3 which is around 1000 μm . This indicates that the ClO_2 has penetrated approximately 1 mm into the material, which coincides quite well with the white discoloration seen in Figure 23. The water absorption and the loss of CaCO_3 does not necessarily affect the mechanical integrity of the PVC but the oxidation normally will. The loss of material integrity is thus probably less than the discoloration seen. Since the discoloration is easy to follow over the cross section it has often been determined as the corrosion depth and since the oxidation is proportional to this it can still be considered a valid measurement.

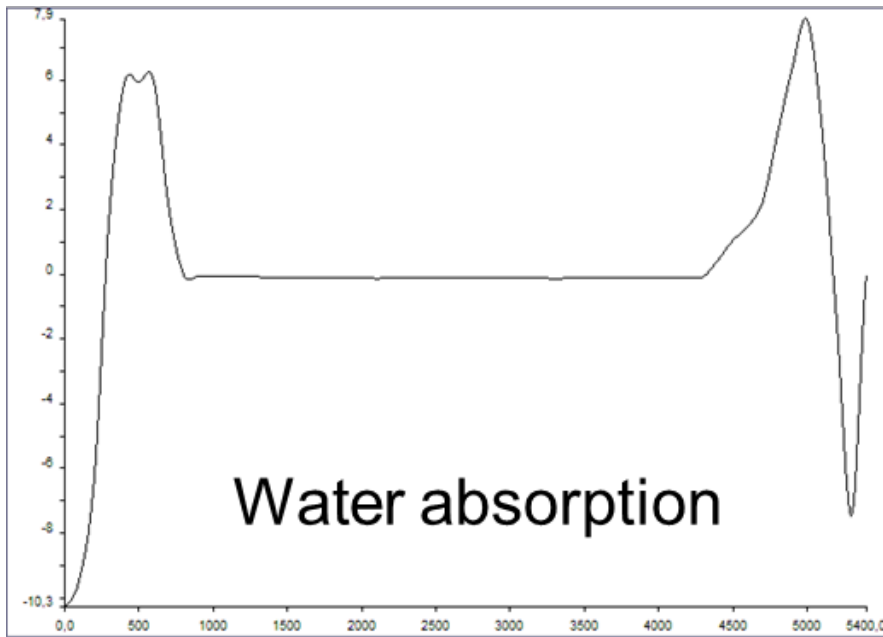


Figure 20. FTIR linescan band ratio to follow the water absorption over the cross section of a Troisdorf red sample exposed for 2 years in spent acid.

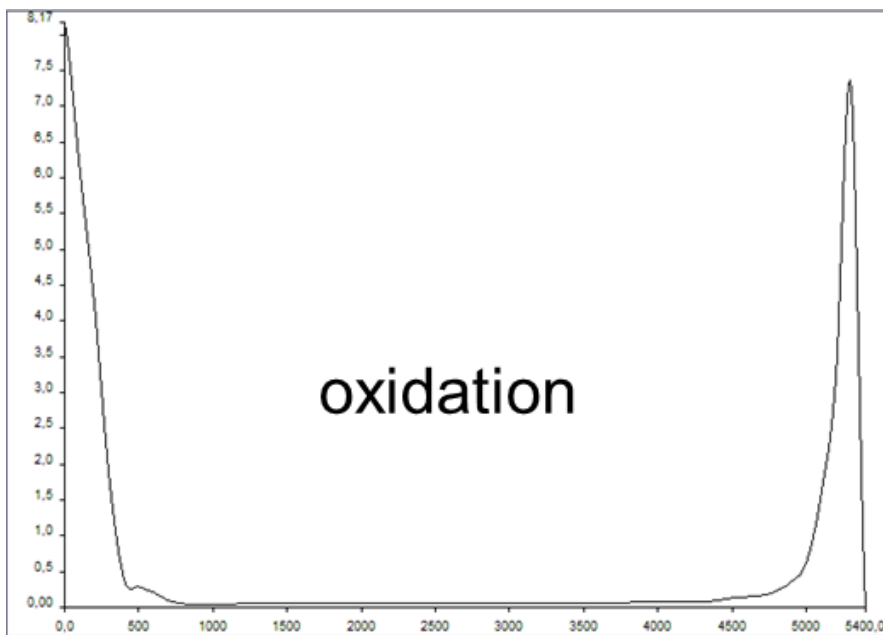


Figure 21. FTIR linescan band ratio to follow the water absorption over the cross section of a Troisdorf red sample exposed for 2 years in spent acid.

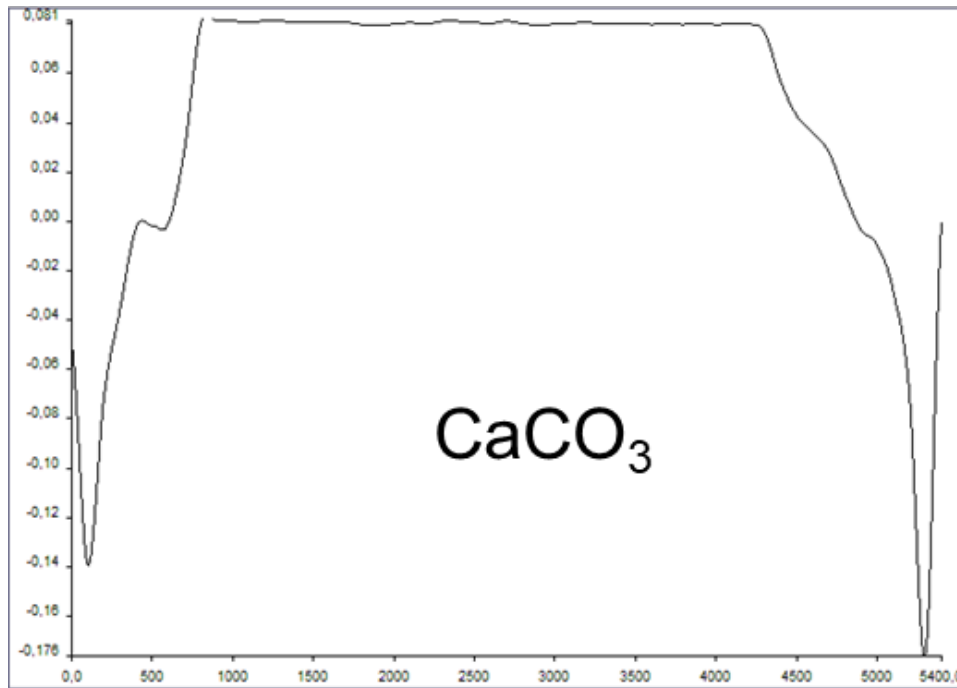


Figure 22. FTIR linescan band ratio to follow the water absorption over the cross section of a Troisdorf red sample exposed for 2 years in spent acid.

Small blisters are often found on the surface of PVC after exposure to ClO_2 and spent acid, Figure 23. They are very superficial and so far it has not been found that these have any detrimental effect on the material.

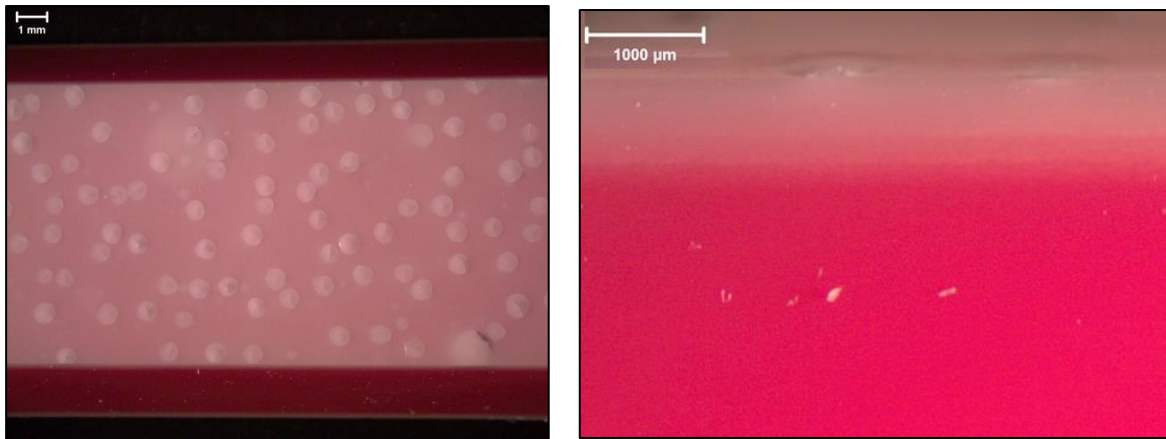


Figure 23. Small blisters on the surface of Troisdorf rot after exposure in the spent acid test station for two years.

The influence of temperature on the corrosion rate is high. For ClO_2 solutions (10-15 g ClO_2/l) a corrosion rate of $0.9 \text{ mm}/(\text{year})^{0.5}$ at $30\text{-}40^\circ\text{C}$ has been observed. At $5\text{-}10^\circ\text{C}$ the corrosion rate can be as low as $0.3 \text{ mm}/(\text{year})^{0.5}$.

In general the same recommendations given for PVC in chlorine dioxide are also valid for spent acid.

For temperatures above 40°C or to avoid the risk of brittle fracture in PVC equipment for spent acid service an external reinforcement of FRP (PN 10) is recommended. PVC is limited to an upper temperature of 60-70°C due to the softening temperature of PVC. Operation temperatures can be closer to the softening or glass transition temperature when an external FRP reinforcement is used. According to *Plastkärlnormen* (the Swedish standard for plastic containers) there should be bonding between the PVC liner and the FRP. It has, however, been found that the application of a primer to the PVC to create the adherence to the FRP can influence the impact resistance of the material in a negative way. In addition, it has been found that bonding between the PVC and the FRP can lead to fairly large internal stresses in the PVC during fabrication. These stresses will be permanent in the PVC and can increase the risk of crack formation in corroded material. Figure 24 shows the typical appearance of cracks in PVC corroded by spent acid. The thickness of the PVC liner is 3 mm and the general corrosion depth is approximately 1.2 mm. However, at the cracks the corrosion depth is up to 2.5 mm.

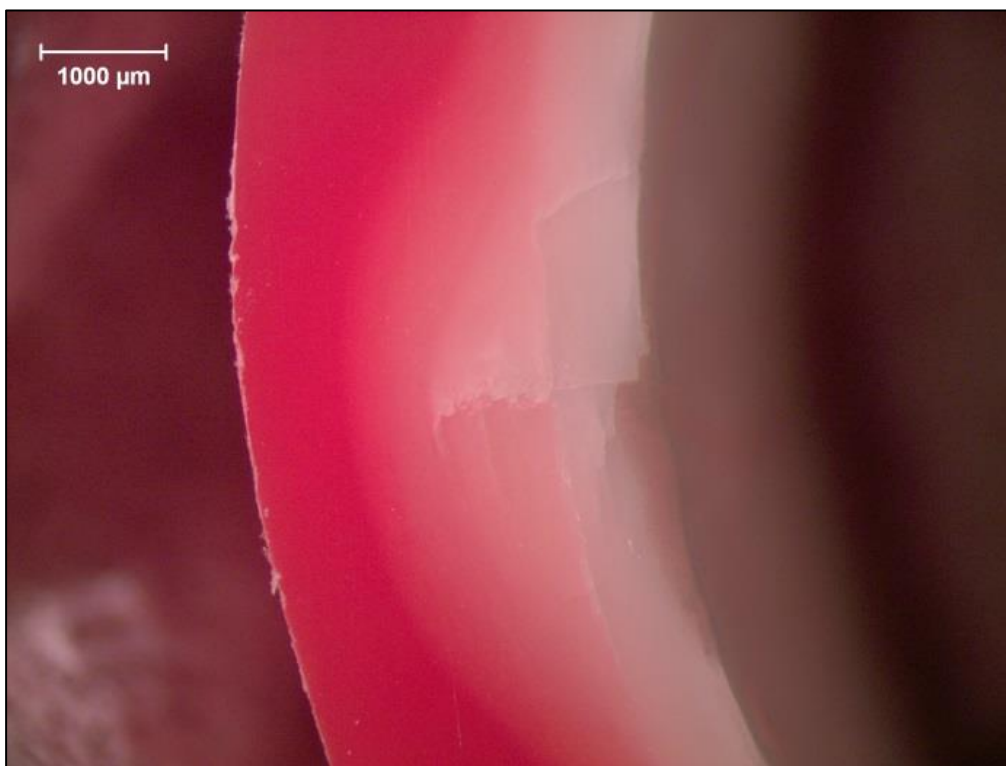


Figure 24. Polished cross section of a PVD lining used for spent acid from the HP-A process for unknown time.

It is important to note that different PVC grades can have very different corrosion rates in chlorine dioxide. For unknown grades the suitability of the material should be verified by experiments or practical experience before it is used.

In the spent acid test station at Karlsborg the corrosion rate of different PVC grades varied between 0.3 and 0.6 mm/year^{0.5}, i.e. after 10 years the depth of attack is expected to be between 0.95 and 1.9 mm.

When installing an equipment for a service life of 10 years or more, a sample should be collected after half of the planned service life, to verify that the rate of corrosion is not higher than expected. Note that

for piping it is important that the pipe thickness (pressure rating) is chosen correctly for the service pressure and temperature even for short term use.

The following factors have an influence on the service life of PVC equipment for handling spent acid solutions.

- Temperature.
- Concentration of ClO_2 .
- PVC grade
- Wall thickness of the installed PVC.
- The quality of the weld or socket joints.
- PVC can become brittle and is therefore sensitive to pressure shocks or external impact.
- Service temperature is limited to 60-70°C due to the materials softening temperature. At elevated temperatures an external FRP reinforcement should be applied, at least for long-term use.
- Surface cracking and local attack possible.

1.1.1 CPVC

Similar to PVC, CPVC is attacked by the ClO_2 in the spent acid. Normally, no reduction is found in wall thickness, i.e. no signs of radical attack causing material to corrode away. The thickness of the corroded layer increases approximately with the square root of time indicating that the corrosion process is diffusion-controlled. The corrosion rate strongly depends on temperature and chlorine dioxide concentration. The corroded layer leads to an increased brittleness in the CPVC material which in combination with external impact in the form of i.e. pressure shocks can lead to failures. At higher temperatures or to avoid risk of brittle fracture in CPVC equipment for ClO_2 service an external reinforcement of FRP is recommended. CPVC has a higher softening temperature compared to PVC and can be used at temperatures up to 90°C . It has also been found that the corrosion rate normally is lower for CPVC compared to PVC. Summarised, the material behaves similar to PVC but can withstand temperatures up to 90°C and generally has a higher corrosion resistance.

Just as for PVC it is important to note that different CPVC grades can have very different corrosion rates in chlorine dioxide and it is important that the suitability of the material is verified by experiments or practical experience before it is used. In the Karlsborg test station the corrosion rate was found to be about 0.2 to 0.4 mm/year^{0.5} for different CPVC grades, i.e. after 10 years the depth of attack is expected to be between 0.6 and 1.3 mm.

The welding of CPVC is more difficult than for PVC and it has been found that the quality of the welds is crucial to its performance. One example is a CPVC-lined FRP tank for spent acid in a chlorine dioxide plant which ruptured catastrophically after 17 years of service, that was shown in Figure 1. During the first 9 years the chlorine dioxide was produced according to the Mathieson process. After that the plant was upgraded to the HP-A process. The ultimate catastrophic rupture of the tank was initiated from a vertical crack which had developed in the lower part of the cylinder of the tank during some time. There were many factors that contributed to this crack being formed but the initiating factor to the failure was a significant misalignment in a weld, Figure 25.

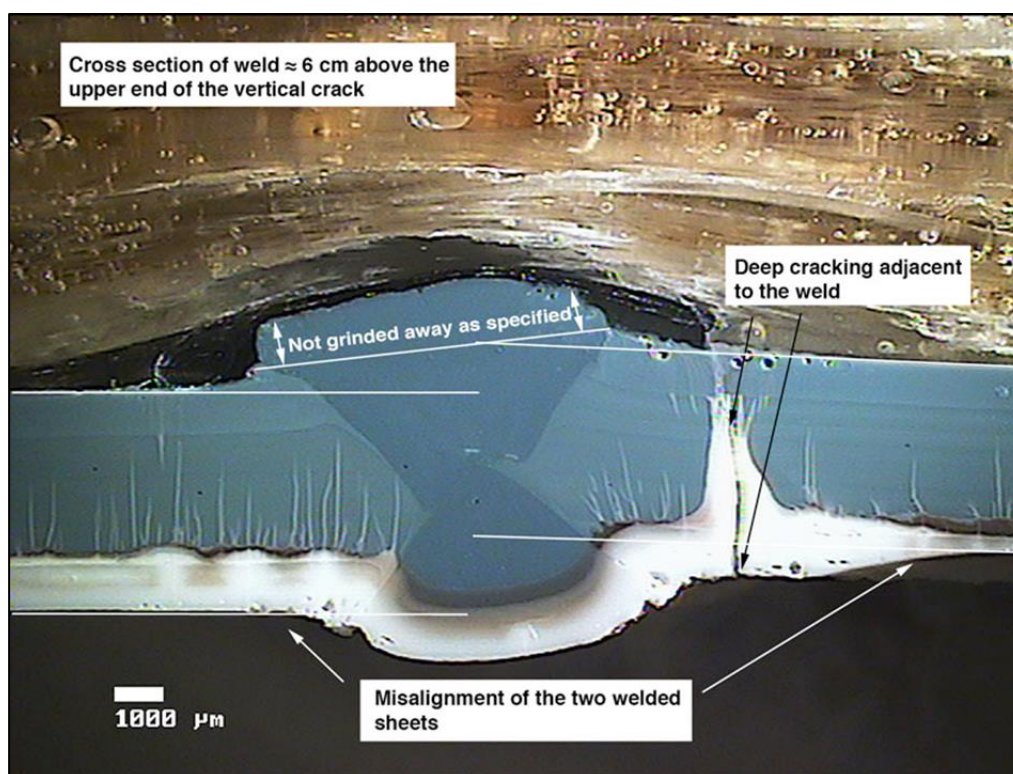


Figure 25. Weld showing significant misalignment and angle deviation of the sheet-ends. Typically, such welds showed damage of deep crack/attack adjacent to the weld.

The following factors have an influence on the service life of CPVC equipment for handling chlorine dioxide solutions.

- Temperature.
- Concentration of ClO₂.
- CPVC grade
- Thickness of the installed CPVC i.e. pipe wall or tank wall.
- The quality of the weld or socket joints.
- CPVC can behave brittle and is therefore sensitive to pressure shocks or external impact.
- Service temperature up to 90°C is possible.

When installing equipment for a service life of 10 years or more, a sample should be collected after half of the planned service life to verify that the rate of corrosion is not higher than expected. Note that for piping it is important that the pipe thickness (pressure rating) is chosen correctly for the service pressure and temperature even for short term use.

3.3 Evaluation of welding techniques

Samples joined using various joining techniques, such as solvent welding, butt welding, hot gas welding and IR-welding have been exposed in the Karlsborg test station and then evaluated from a corrosion point of view, Figure 26. The same type of corrosion effects as has been seen in samples from long term

service, see examples in Figure 4, Figure 5, Figure 6 and Figure 27, have been seen which shows that the test method is relevant. It has thus been possible to generate comparable results for different grades, which is important in order to build up a better understanding of how a piping system should be constructed. Some of the data is still being analysed and samples are also kept in the spent acid test station longer to get more effect. Still even at this stage it is clear that welding techniques such as butt welding and IR-welding are much less sensitive to corrosion effects compared to socket cemented samples. The hot gas welds do not show any significant corrosion attack compared to the piping material but as discussed above misalignment could result in cracking due to stress concentrations. This was also seen in the samples shown in Figure 5.

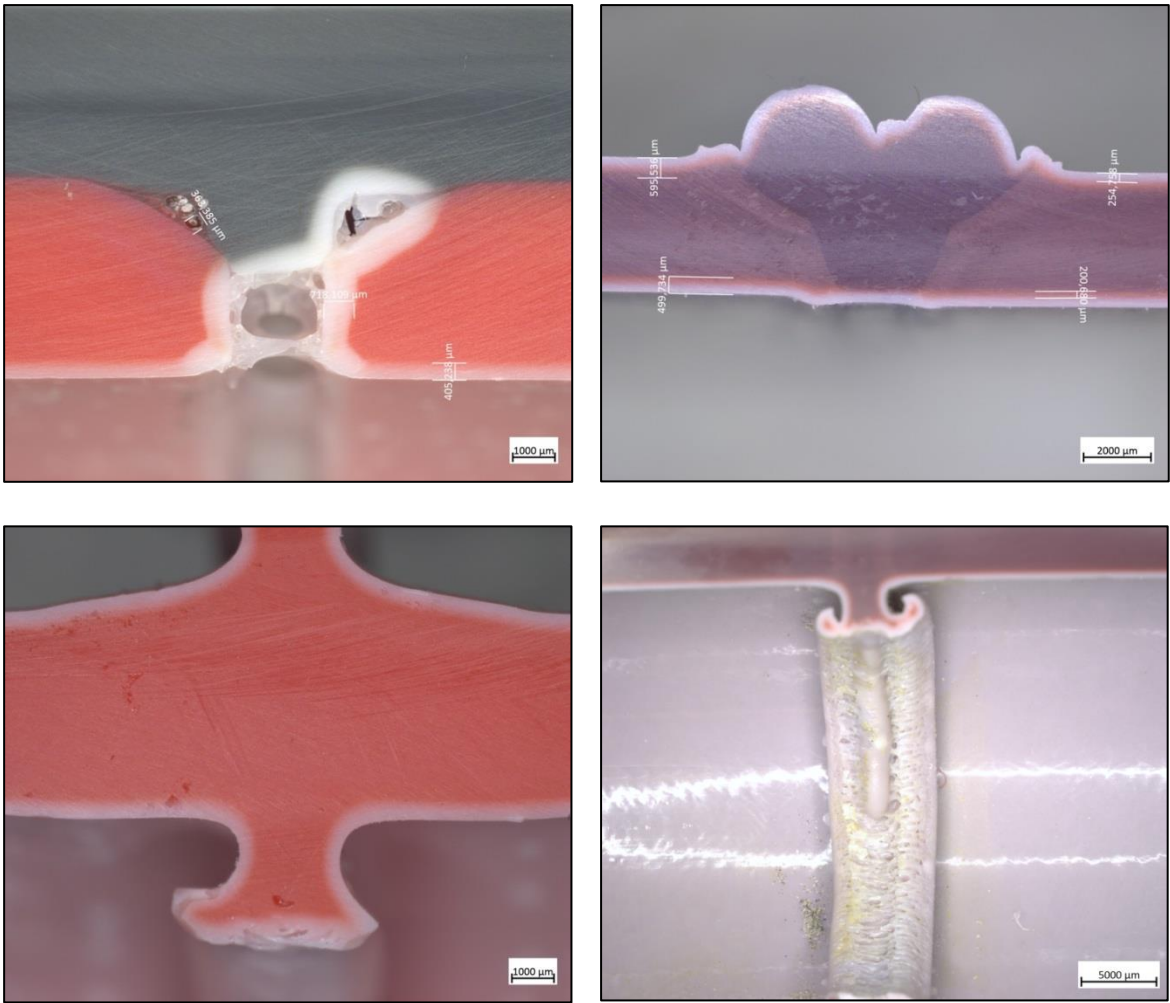


Figure 26. Joints using solvent welding, butt welding and hot gas welding in Dekadur plus and Troisdorf red PVC after exposure in the spent acid test station for one year.



Figure 27, a failed socket cemented weld in a PVC line used for spent acid

4 Chlorine dioxide solutions

Chlorine dioxide is a neutral chlorine compound. It is very different from elemental chlorine, both in its chemical structure and in its behavior. One of the most important qualities of chlorine dioxide is its high water solubility, especially in cold water. Chlorine dioxide does not hydrolyze when it enters water; it remains a dissolved gas in solution. Chlorine dioxide is approximately 10 times more soluble in water than chlorine. A concentration of chlorine dioxide in water of a bit more than 20 g/l is normally produced in a reactor. Chlorine dioxide is a preferable bleaching agent used in the production of elemental chlorine-free (ECF) bleached chemical wood pulp all over the world, because it selectively oxidizes lignin without degrading cellulose fiber, and increases pulp yield and strength.

4.1 PVC

In general the same mechanisms are expected in the reactor, in spent acid and in chlorine dioxide solutions, the rate will be determined by the concentration of the chlorine dioxide, the temperature and the type of PVC used.

It is important to note that different PVC grades can have very different corrosion rates in chlorine dioxide. For unknown grades the suitability of the material should be verified by experiments or practical experience before it is used.

The following factors have an influence on the service life of PVC equipment for handling chlorine dioxide solutions.

- Temperature.
- Concentration of ClO_2 .
- PVC grade
- Wall thickness of the installed PVC.
- The quality of the weld or socket joints.

- PVC can become brittle and is therefore sensitive to pressure shocks or external impact.
- Service temperature is limited to 60-70°C due to the materials softening temperature. At elevated temperatures an external FRP reinforcement should be applied, at least for long-term use.
- Surface cracking and local attack possible.

The influence of temperature on the corrosion rate is high. For ClO₂ solutions (10-15 g ClO₂/l) a corrosion rate of 0.9 mm/(year)^{0.5} at 30-40°C has been observed. At 5-10°C the corrosion rate can be as low as 0.3 mm/(year)^{0.5}.

In bleaching environment (D0-stage pulp, pulp consistency 5%, estimated ClO₂ concentration 1%, temperature 68-75°C) the corrosion rate of DEKA PVC red (Troisdorf) and standard grey were about 0.7 and 0.8 mm/year^{0.5}, respectively.

When installing equipment for a service life of 10 years or more a sample should be collected after half of the planned service life to verify that the rate of corrosion is not higher than expected. Note that for piping it is important that the pipe thickness (pressure rating) is chosen correctly for the service pressure and temperature even for short term use.

4.2 CPVC

In general, the same mechanisms are expected in the reactor, in spent acid and in chlorine dioxide solutions, the rate will be determined by the concentration of the chlorine dioxide, the temperature and the type of PVC used.

Just as for PVC it is important to note that different CPVC grades can have very different corrosion rates in chlorine dioxide and it is important that the suitability of the material is verified by experiments or practical experience before it is used.

The following factors have an influence on the service life of CPVC equipment for handling chlorine dioxide solutions.

- Temperature.
- Concentration of ClO₂.
- CPVC grade
- Thickness of the installed CPVC i.e. pipe wall or tank wall.
- The quality of the weld or socket joints.
- CPVC can behave brittle and is therefore sensitive to pressure shocks or external impact.
- Service temperature up to 90°C is possible.

In bleaching environment (D0-stage pulp, pulp consistency 5%, estimated ClO₂ concentration 1%, temperature 68-75°C) the corrosion rate of DEKA CPVC was about 0.3 to 0.4 mm/year^{0.5}.

When installing equipment for a service life of 10 years or more a sample should be collected after half of the planned service life to verify that the rate of corrosion is not higher than expected. Note that for piping it is important that the pipe thickness (pressure rating) is chosen correctly for the service pressure and temperature even for short term use.

5 Chlorine and Hypochlorite

As was discussed in the general introduction, it is important to realize that chlorine is not constant through the pH range from 1 to 14. Figure 3 shows a diagram of the chemical composition balance of sodium hypochlorite (NaOCl), hypochlorous acid (HOCl) and chlorine (Cl₂) as a function of the pH.

Hypochlorite is an ion composed of chlorine and oxygen, with the chemical formula ClO⁻. It can combine with a number of counter ions to form hypochlorites, which may also be regarded as the salts of hypochlorous acid. Common examples include sodium hypochlorite (household bleach) and calcium hypochlorite (bleaching powder, swimming pool "chlorine").

Hypochlorites are frequently quite unstable in their pure forms and for this reason are normally handled as aqueous solutions. Their primary applications are as bleaching, disinfection and water treatment agents but they are also used in chemistry for chlorination and oxidation reactions.

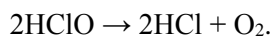
Hypochlorous acid is a weak acid with the chemical formula HClO. It forms when chlorine dissolves in water, and it is HClO that actually does the disinfection when chlorine is used to disinfect water for human use. It cannot be isolated in pure form due to rapid equilibration with its precursor. HClO is an oxidizer.

A bleach solution is most stable at pH >11 where the decomposition rate is nearly independent of pH. In this region, the decomposition rate has a second order dependence on the concentration of hypochlorite. It also increases with increasing ionic strength. Thus concentrated solutions decompose much faster than dilute solutions. The decomposition results in chloride and chlorate ions:



Below pH 11, the decomposition rate becomes dependent on pH and the mechanism becomes more complicated. The rate increases greatly as the pH decreases from 11 to 7 where the rate reaches a maximum. As the pH decreases from 7 to 3, the rate decreases. Below pH 3 the rate becomes reasonably slow but still considerably faster than at pH 11. The mechanisms are not well known, and they may be different in each of these pH ranges. In all cases, the decomposition rate increases greatly with temperature and with a second- or higher-order dependence on the concentration of hypochlorous acid and/or hypochlorite.

HClO can also be decomposed to form oxygen:



The presence of light or transition metal oxides of copper, nickel, or cobalt accelerates this exothermic decomposition into hydrochloric acid and oxygen.

Due to the variation in chemical composition the reactivity also varies with pH. The chlorine concentration is most often reported as the active chlorine concentration, which is the total concentration of Cl₂, HClO and ClO⁻. It is not only the pH which determines the relative concentration between the species but also the temperature and concentration of the Hypochlorite solution.

For lab testing in HClO it is very important to control the pH. This normally requires a circulating loop system with pH control. This is due to gaseous products forming resulting in further drop in pH. Since this control has not always been made, some literature data is confusing.

As mentioned above, in drinking water the maximum allowed level of total chlorine concentration is 4 ppm which, at the pH value of drinking water, is a mixture of HClO and ClO⁻. The chlorine is normally

added by bubbling chlorine gas (low pH) or by adding NaClO (or Ca(ClO)₂) as a liquid (high pH) and then regulate pH to the suitable one using HCl or H₂CO₃ to decrease pH, if necessary, or NaOH to increase it. The NaClO used has a concentration often around 25 or 12.5%, i.e. 250 000 or 125 000 ppm, with a pH of around 12.5. At a pH below 11.8, the pH will drop on storage resulting in an unstable solution. The hypochlorite solution at high pH will also decrease in concentration upon storage due to the following reaction (which will not affect the pH):



This degradation is accelerated by increased concentration and temperature.

5.1 Chlorine production

Chlorine can be made by various processes that utilize brine to create chlorine and sodium hydroxide. In the European chlorine production market, the membrane cell process dominates today, as it is the most environmentally sound and energy efficient process existing for industrial scale production. The process involves an electrolysis cell which is constituted of an anode and a cathode separated by an ion-exchange membrane which is most commonly made of perfluorinated polymer. The saturated brine solution is de-chlorinated as sodium ions pass through the cation selective membrane. The chlorine ions in the pure brine are pumped into the anode compartment and are oxidized to form chlorine gas. In the cathode compartment, water is reduced to form the hydroxide ions while hydrogen gas is formed. A portion of the produced sodium hydroxide is extracted while the remaining solution is diluted with deionized water and recirculated. (Euro Chlor, u.d.) Presented in Figure 28 and Figure 29 are two illustrations of the process.

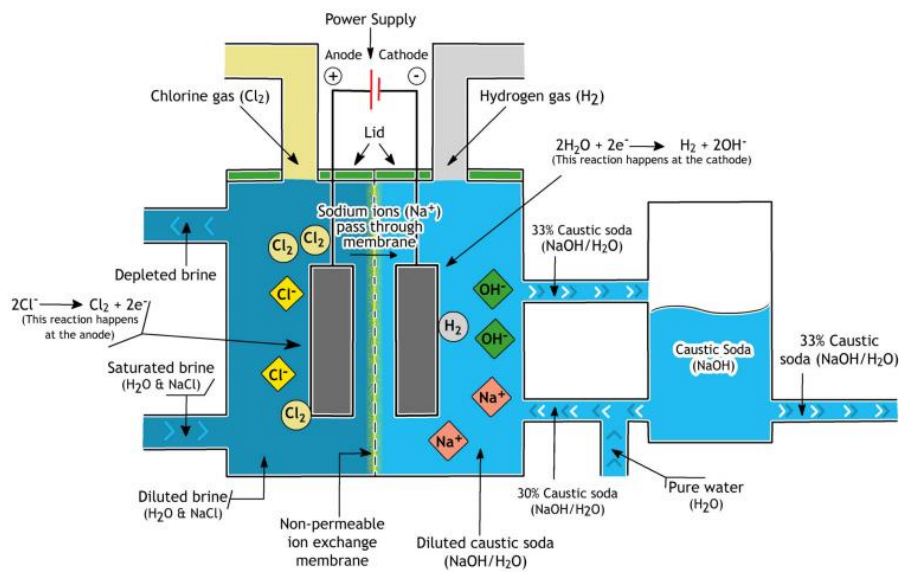


Figure 28: Illustration of The membrane cell process. Picture from www.eurochlor.org.

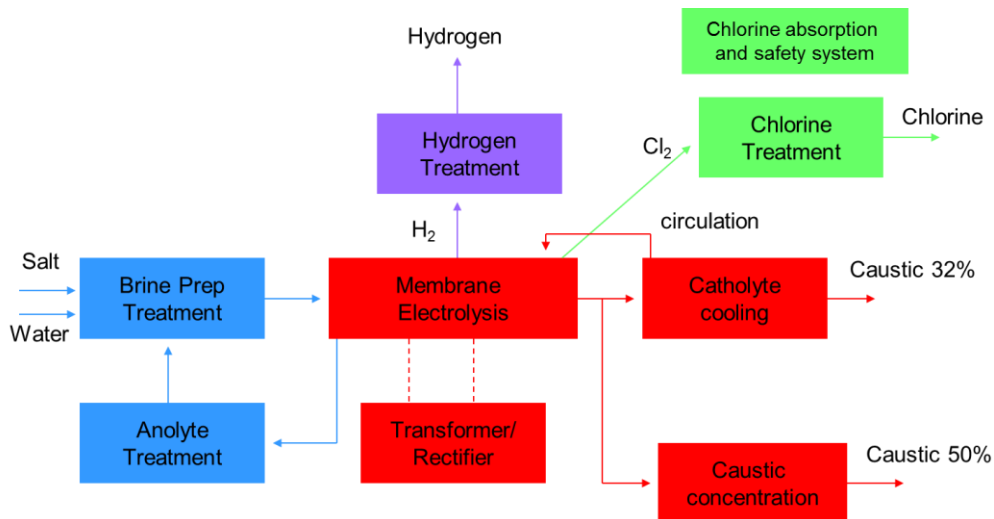


Figure 29: Schematic illustrations of the flows in, through and out of the plant.

This method produces very pure sodium hydroxide at concentration of 30-35 % but on the other hand it also requires very pure brine. The sodium hydroxide can be further concentrated, typically up to 50 %, using evaporators.

The produced chlorine leaves the cell with depleted brine, which also contains dissolved chlorine, and the purity can be increased by adding hydrochloric acid to reduce the oxygen content. The chlorine gas is cooled and filtered and can be feed directly to the consumer plant or it can be dried and compressed before being shipped to the consumer.

Plastic materials are often used in chlorine plants as the temperature is low enough to permit it and the environment very corrosive for metallic materials. The most difficult positions are the piping for the hot wet chlorine gas from the cells and the depleted brine and for the chlorine absorption and safety system where hypochlorite is being formed.

5.1.1 PVC

PVC can be attacked by the radicals formed in HClO and is not recommended as long as there is a high concentration HClO present in the solution. Figure 30 shows a PVC lining from a scrapped chlorine absorption tower at a chlorine plant. In this tower chlorine gas is reacted with NaOH to form NaClO . The pH should be high but it must have decreased locally so that HClO was formed attacking the PVC. At high pH, i.e. in ClO^- , PVC with external reinforcement of FRP is known to have a long service life, up to more than 25 years (GF DEKA).



Figure 30. A PVC lined FRP tank for hypochlorite at a chlorine plant. The pH is normally kept high (above 10) but had varied locally which resulted in radical attack from HClO and material thinning.

5.1.2 CPVC

5.1.2.1 Low pH < 3.5

CPVC has been found to be a suitable material for both chlorine and depleted brine (salt solution with dissolved Cl_2) at low pH values <3.5 in chlorine plants, Figure 31. The temperature can be as high as 88°C. In one plant, a CPVC pipe for depleted brine was in service for more than 20 years at 80°C with a Cl_2 concentration of 500 mg/l dissolved Cl_2 .



Figure 31. A CPVC/FRP pipe section for a chlorine header.

The CPVC will be attacked and a brittle degraded white layer is formed. Below this there is a plasticized layer in which there seems to be HCl formation, presumably due to dehydrochlorination, see Figure 32 which shows a CPVC pipe after 8.5 years in service.

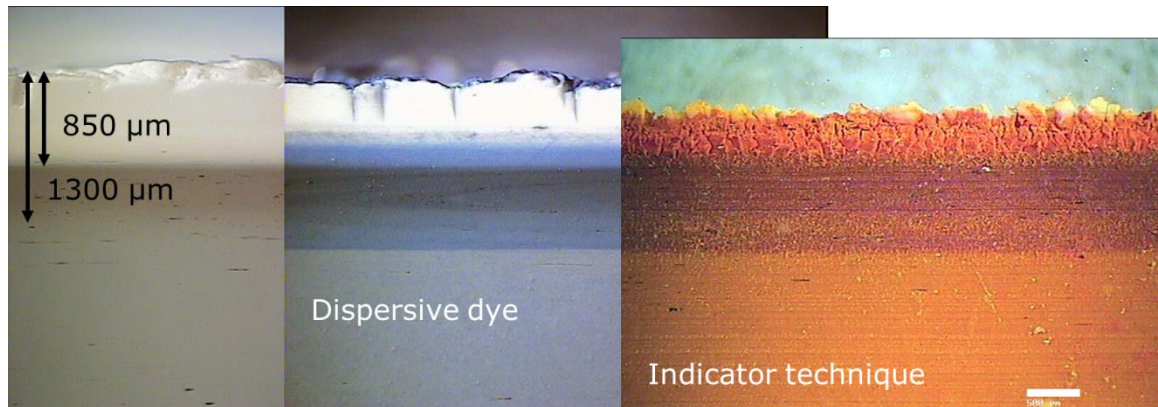


Figure 32. Corrosion of CPVC exposed to Cl_2 after 8.5 years in service

5.1.2.2 Welding

Due to the fading-out of Pb, there has been a strong need to develop an appropriate alternative to the welding rod Trovidur HTX. Swerea KIMAB has been involved in the testing of four different welding rods including two prototypes and HTX. One of the prototypes which is a high Vicat and Pb - free welding rod which complies with the established DVS welding guidelines was chosen after this. The performance of HTX welding rod is met in all tested cases and appears to be superior to HTX in Chlorine environments. There is a suspicion that Pb in the HTX rod could be the reason for severe local degradation seen in weld rods in brine solutions where the pH has been 3.5. This could be due to lead accelerating the decomposition of HClO into reactive species, just as other transition metals are known to do. The new welding rod has been tested and accepted by all major dual laminate processors in Europe. It is commercially available since 1st July 2016. Still, just as has been shown above, also in chlorine environments it is important that misalignments are avoided, see Figure 33.

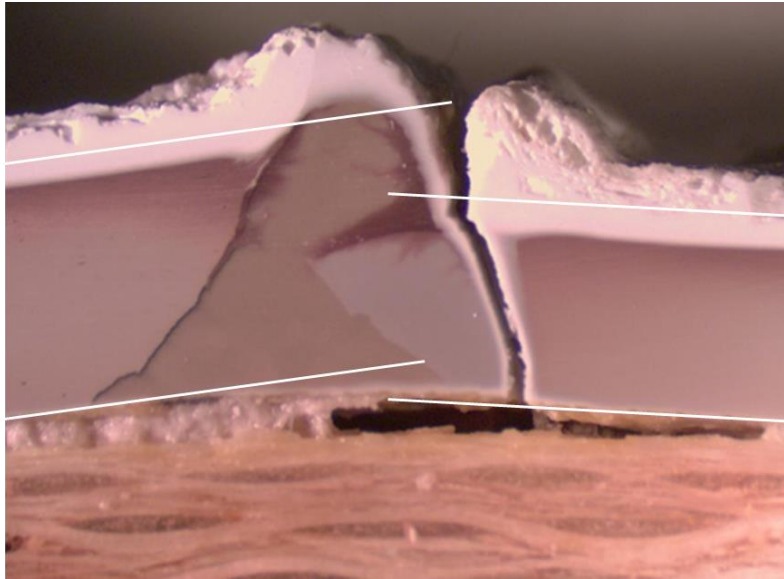


Figure 33. Cracked CPVC hot gas weld in a chlorine pipe. There is a clear misalignment of the two pipe sections welded together.

5.1.2.3 Mid pH range

At pH-values above 4 there is, however, a risk of rapid degradation of the CPVC, e.g. in regions of stagnant flow in chlorine or brine piping, where the pH increases so that HClO is formed. As can be seen in Figure 34 which shows a CPVC/FRP pipe for anolyte (brine with dissolved Cl₂) there is severe degradation in just one region. The rest of the CPVC has been attacked but by Cl₂ but this is much less harmful to CPVC than the HClO.

At lower concentrations, like in potable water, it works fine for many years, but at high concentrations it is not recommended. It will last longer than a polyolefin but still have limited service life.



Figure 34, Two different CPVC/FRP pipes for analyte (brine with dissolved Cl_2) i.e. in the low pH range of the hypochlorite balance. Both pipes have regions where the flow was stagnant, and the pH increased so that $HClO$ was formed. This resulted in rapid degradation of the material. The rest of the CPVC has been attacked but by Cl_2 but this is much less harmful to CPVC than the $HClO$.

5.1.2.4 High pH >10

At high pH (> 10), there can be a reaction with the impact modifier resulting in embrittlement, so CPVC is not recommended for long term use for the high pH range.

5.1.3 Important considerations in Chlorine and Hypochlorite

The following are some important considerations when evaluating the chemical resistance of PVC and CPVC materials in chlorine and hypo solutions:

- pH - value
 - The reactivity varies dramatically with pH. Despite this, it is often not mentioned in case studies and other reports.
- Purity of the solution
 - Does it contain other chemicals like surfactants?
- Stability of the solution
 - Hypo solutions are not stable.
- The quality of the polymer and the processing
 - Large variations are normal in the performance of polymers, both as raw material depending on composition, additives and the processing of the material.
- Joining
 - The failures most often occur in the welds and joints of plastic equipment and piping systems. This is particularly so for hypo solutions.

6 Final remarks

PVC is the world's third-most widely produced synthetic plastic material, after polyethylene and polypropylene. Interestingly, this relatively low-cost bulk polymer has some outstanding properties in chlorinated chemicals, where it often outperforms the much more expensive fluoroplastics. CPVC is, for example, for many the material of choice in chlorine containing anolyte in a chlorine plants, with reported service lives of more than 20 years. It has also been used successfully in hot wet chlorine gas. For hypo solutions PVC has been reported to have service lives of more than 30 years. Also, in the pulp and paper industry using chlorine dioxide for bleaching, PVC materials show much better service lives than most other materials.

One of the key factors to the success of the PVC materials is the low diffusion of the small molecules Cl_2 , HClO and ClO_2 . When the fluoroplastics might not be degraded by these chemicals the small molecules will diffuse through them and cause various problems. In the PVC materials there is instead often a reaction with the polymer and/or the additives but as long as this is not decreasing the mechanical properties too much and that there is a corrosion allowance then this is often to be preferred compared to the diffusion.

The goal for this project was to better understand the corrosion process of PVC and CPVC materials in chlorine environments. The results are aimed to support users and suppliers of process equipment with a better fundamental understanding about the behaviour of these materials in chlorine containing environments. One important part in this deeper understanding is knowledge about the chemical environments. This is why they have been presented in some detail in this report.

It has been shown that the new grades of PVC and CPVC without lead stabilisers seems to be as good or even better in chlorinated environments. Still, the main obstacle to a successful use of the PVC and CPVC materials in chlorine environments is the joining. In particular, the hot gas welds are the main cause for failures in CPVC-lined equipment and has been found also in PVC piping. Care must be taken to avoid misalignment. In the comparative study made on PVC welds in spent acid, it was found that welding techniques such as butt welding and IR-welding are much less sensitive to corrosion effects compared to socket cemented samples. The hot gas welds did not show any significant corrosion attack compared to the piping material, but as mentioned above misalignment can result in cracking due to stress concentrations.