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CICLO XXXVI

Messa a punto di un metodo di sanificazione di ambienti e contesti urbani tramite l'impiego di acqua elettrolizzata a basso impatto ambientale: verifica degli aspetti di sostenibilità chimica

Development of a method for sanitising urban environments and contexts through the use of electrolysed water with low environmental impact: assessment of chemical sustainability aspects

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#### Abstract

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The experimental campaign described and summarized in this PhD is an assessment of the chemical and sustainability aspects of HOCl as a disinfectant, produced by GATE srl, Ferrara. The work is twofold: a compatibility test on several reference materials, connected with the eventual presence/deposition of NaCl over them and an LCA assessment, comparing HOCl with another commercial disinfectant.

Analyzing the large amount of experimental data gathered during the PhD activities gave interesting results. Where the exposure of non-metallic materials or steel did not lead to compatibility issues, bare metals showed degradation due to salt deposition.

On the other hand, the experimental LCA analysis showed the clear ecological advantage of HOCl vs other commercial products.

The experimental work was carried out at the ENEA DISPREV lab, in Bologna.


Keywords: HOCl disinfectant, salt deposition, $L C A$, corrosion.

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## Introduction

## 1: General

When facing emerging infectious diseases and the continuous evolution of pathogens, developing effective disinfectants has become crucial in maintaining public health and preventing the spread of infections. Hypochlorous acid ( HClO ), a weak acid with powerful antimicrobial properties, has gained significant attention recently for its remarkable disinfectant capabilities. Unlike traditional disinfectants, HClO offers a unique combination of high efficacy and low toxicity, making it a promising candidate for various applications in healthcare, food safety, water treatment, and beyond. This introduction provides an overview of the properties, mechanisms [1, 2, 3], and applications of HClO as a disinfectant, highlighting its potential to address the challenges posed by infectious microorganisms, as well as its chemical compatibility with a targeted environment. [4, 5, 6, 7] HClO exists in equilibrium with its conjugate base, hypochlorite ion $\left(\mathrm{ClO}^{-}\right)$, in aqueous solutions. A weak acid dissociates partially, forming reactive species, including hypochlorous acid molecules $(\mathrm{HOCl})$ and hypochlorite ions. The balance between HOCl and $\mathrm{ClO}^{-}$is influenced by factors such as pH , temperature, and the presence of other substances. This equilibrium is essential in determining the disinfectant potency of HClO , as HOCl is more effective in microbial inactivation than its ionised counterpart. [17, 18, 19, 20 , 21]

Hypochlorous acid $(\mathrm{HOCl})$ could be proposed as a promising disinfectant candidate. There is wide literature [22, 23, 24, 25] demonstrating its efficacy against a broad range of microorganisms, including spores and viruses. HOCl is an endogenous substance in all mammals, usually produced by white blood cells to surround pathogens, e.g., when the skin is injured, and pathogens begin to invade. Its mechanism of action relates to the destruction of the cytoplasmic membrane and the cell wall of the bacteria, due to its small molecular dimensions, such as the water molecule, and neutral charge, not repelled by bacteria. For decades, chlorination has been securing the microbiological quality of drinking water. One of the recent advancements in chlorine-based disinfection is its utilization in the form of electrolyzed water (EW). This method became attractive due to its proven simplicity, biocidal efficiency, and convenience of in situ production, which reduces the hazard of handling and transporting concentrated chlorine reagents [26, 27]. EW is usually produced by passing a dilute salt solution $(\mathrm{NaCl})$ through an electrolytic cell, subjected to a DC voltage. The spontaneous reduction of hypochlorous acid to chloride, after the disinfection process via oxidation, accelerated if exposed to light and air, assures the absence of residual effects or damages on the environment [28, 29].

In recent years, while EW liquid solution has been widely accepted for disinfection by different sectors, such as medical, agricultural, food processing and sanitary industries, its application as the aerosolized dry fog is still barely known and few studies have investigated its potentiality for indoor environments and surfaces disinfection.

The antimicrobial activity of HClO stems from its ability to disrupt vital cellular components and processes in microorganisms. HOCl , being a potent oxidizing agent, can react with cellular proteins, lipids, nucleic acids, and enzymes. These reactions lead to the denaturation of proteins, peroxidation of lipids, and fragmentation of nucleic acids, ultimately causing cell death. Furthermore, HClO can penetrate bacterial cell walls and biofilms, making it effective against a wide range of microorganisms, including bacteria, viruses, fungi, and protozoa [33].
Microorganisms can colonize all surfaces, independent of the type of material and environmental conditions. Although some may be safe (i.e. Lactobacilli), others, due to their nature of human pathogens, or their number, can be strongly harmful and have to be completely removed. Surface adhesion or absorption mechanisms by micro-organisms can be influenced by several factors, namely temperature, pH , and relative humidity of the environment, as well as by surface properties, such as porosity, composition, roughness, and hydrophilicity. Among indoor surfaces, floors are one of the most susceptible to microbial contamination, due to the high probability of exposure to sources of contamination and dirt, and to the presence of breakages that can retain moisture and nesting microbial colonies. In this regard, studies carried out in hospitals, schools and public spaces have shown that contaminated floors increase the probability of being infected not only by direct contact but also by inhaling them as aerosols. While walking on contaminated floors, microorganisms can be resuspended in the air to man-height, increasing the microbial charge of indoor air up to $15 \%$. [ 34 , 35].
The versatility of HClO as a disinfectant has led to its incorporation into various applications. In healthcare settings, it is used for surface disinfection, wound care, and sterilization of medical instruments. In the food industry, HClO is employed for sanitizing fruits, vegetables, and food processing equipment, ensuring food safety and preventing foodborne illnesses. Moreover, $\mathrm{HClO}-$ based disinfectants are utilized in water treatment processes, providing safe drinking water and controlling the spread of waterborne diseases [37]. Additionally, its application extends to air purification systems, where it helps eliminate airborne pathogens and create healthier indoor environments. [38, 39, 40, 41]
In Hospitals, HOCl is commonly used:

- Disinfection of Surfaces: HOCl can be used to disinfect surfaces in hospitals, including patient rooms, operating rooms, and medical equipment. It is effective against a wide range of pathogens, including bacteria like MRSA (Methicillin-resistant Staphylococcus aureus) and viruses like influenza.
- Hand Sanitizers: Some hospitals use HOCl-based hand sanitizers as an alternative to alcoholbased sanitizers. HOCl is gentle on the skin and can be used by healthcare workers who have sensitive skin or allergies to other types of hand sanitizers.
- Wound Care: HOCl is used in wound care to clean and disinfect wounds. It helps in preventing infections and promotes faster healing of wounds.
- Sterilization of Medical Instruments: HOCl can be used for sterilizing medical instruments. Its antimicrobial properties ensure that the instruments are free from harmful microorganisms before they are used in medical procedures.
- Air Disinfection: HOCl generators can be used to disinfect the air in hospital rooms. This is particularly important in areas where there are patients with compromised immune systems who are more susceptible to infections.
- Water Disinfection: HOCl can be used to disinfect water used in hospitals for various purposes, ensuring that the water supply is free from harmful pathogens.
- Infection Control: HOCl can be incorporated into infection control protocols in hospitals to prevent the spread of infections. This is especially important in healthcare settings where patients with contagious diseases are treated. [42, 43, 44, 45]

Hypochlorous acid $(\mathrm{HOCl})$ can be produced through electrochemical methods, specifically by using a process called electrolysis. Electrolysis involves passing an electric current through a solution to drive a chemical reaction. In the case of HOCl production, electrolysis of a sodium chloride $(\mathrm{NaCl})$ solution (common salt) is often employed. This method has several advantages, including the production of a stable and effective disinfectant without the need for hazardous chemicals [35, 36].

The main advantages of electrochemical production are high purity, Scalability, and On-site generation. [38, 39]

On the other hand, disadvantages are Energy consumption: Electrolysis requires significant energy input; Corrosion: Electrolytic cells are prone to corrosion.; Chlorine gas release: If not controlled, electrolysis can result in the release of chlorine gas, which is toxic.

HOCl can also be produced through chemical reactions, such as the reaction between chlorine gas and sodium hydroxide $(\mathrm{NaOH})$. This method, known as the Hooker process, involves the controlled reaction between $\mathrm{Cl}_{2}$ and NaOH to produce HOCl and sodium chloride $(\mathrm{NaCl})$. While this method
has been widely used historically, it is gradually being replaced by electrolytic processes due to environmental concerns associated with the use and transportation of chlorine gas.

The chemical equation for this reaction is:

$$
\mathrm{Cl}_{2}+\mathrm{H}_{2} \mathrm{O} \rightleftharpoons \mathrm{HOCl}+\mathrm{HCl}
$$

The equilibrium between HOCl and its conjugate base, hypochlorite ion ( OCl -), can be influenced by controlling pH , temperature, and the initial concentration of $\mathrm{Cl}_{2}$. A very simple approach, usually not leading to high purities.
In recent years, there have been significant advancements in HOCl production technologies, aimed at enhancing efficiency and minimizing environmental impact. One such innovation is the use of membrane electrolysis, which separates the anode and cathode compartments with a membrane, preventing the mixing of chlorine gas and hydrogen gas. This technology improves the purity of the generated HOCl and reduces the formation of harmful by-products.
Another promising approach is the development of electrochemical cells with specialized electrodes and catalysts, like the method used for the solution in this experimental campaign. These cells facilitate the direct conversion of chloride ions into HOCl , bypassing the formation of chlorine gas altogether. Such advancements not only increase production efficiency but also reduce the environmental footprint associated with traditional methods.

In the context of HOCl , the process involves the electrolysis of a sodium chloride solution, usually referred to as brine. At the anode, chloride ions $(\mathrm{Cl}-\mathrm{Cl}-)$ are oxidized, leading to the formation of chlorine gas (Cl2Cl2):

$$
2 \mathrm{Cl}-\rightarrow \mathrm{Cl}_{2}+2 \mathrm{e}^{-}-2 \mathrm{Cl}^{-} \rightarrow \mathrm{Cl}_{2}+2 e^{-}
$$

Subsequently, chlorine gas reacts with water molecules $(\mathrm{H} 2 \mathrm{OH} 2 \mathrm{O})$ to produce HOCl and hydrochloric acid ( HClHCl ):

$$
\mathrm{Cl}_{2}+\mathrm{H}_{2} \mathrm{O} \rightarrow \mathrm{HOCl}+\mathrm{HCl}
$$

This reaction is pH -dependent, with more acidic conditions favouring the formation of HOCl over hypochlorite ions ( $\mathrm{OCl}-\mathrm{OCl}-$ ). Proper control of pH is vital in maximizing the yield of HOCl during electrolysis.

The choice of electrode material significantly influences the efficiency of HOCl production. Common electrode materials include graphite, platinum, and various metal oxides. Electrodes with high surface area and good conductivity enhance the reaction kinetics, leading to increased HOCl yields.

The concentration of sodium chloride in the solution affects the conductivity and overall efficiency of the electrolysis process. Higher concentrations of NaCl generally result in higher HOCl production rates. However, overly concentrated solutions can lead to the formation of undesired by-products, necessitating a balance between concentration and purity.
Also, maintaining the appropriate pH level is critical for controlling the ratio of HOCl to $\mathrm{OCl}-\mathrm{OCl}-$ ions. pH adjustment can be achieved by adding acids or bases to the electrolyte solution, ensuring that the desired HOCl concentration is attained.

Catalytical methods can be coupled with electrochemical production methods and involve the use of specific catalysts to facilitate the production of HOCl . These catalysts accelerate the reaction kinetics without being consumed in the process. One common catalytic reaction involves the activation of hydrogen peroxide ( H 2 O 2 H 2 O 2 ) with chloride ions in the presence of a catalyst to produce HOCl :

$$
\mathrm{H}_{2} \mathrm{O}_{2}+2 \mathrm{Cl}^{-}=2 \mathrm{HOCl}
$$

Metal-based catalysts are commonly used, including transition metals like iron ( Fe ) and copper $(\mathrm{Cu})$, which have been explored for catalytical HOCl production. These metals, in specific oxidation states, serve as active sites for the reaction, enhancing the yield of HOCl .
Non-metal catalysts, such as carbon-based materials (graphene, carbon nanotubes) and certain metal oxides, have shown promise in catalyzing the production of HOCl . These materials possess unique surface properties that facilitate the reaction between H 2 O 2 H 2 O 2 and chloride ions.

The precise mechanisms underlying catalytical HOCl production are a subject of ongoing research. In general, the catalyst provides a surface for the interaction between $\mathrm{H}_{2} \mathrm{O}_{2}$ and chloride ions, lowering the activation energy of the reaction and facilitating the conversion to HOCl . Understanding these mechanisms is crucial for catalyst design and optimization.

Hypochlorous acid $(\mathrm{HOCl})$ is a powerful, yet environmentally friendly disinfectant that has gained attention for its efficacy and ecological advantages. HOCl is a weak acid with a chemical formula HClO , and it is produced through the electrolysis of saltwater, making it a sustainable choice. Its unique properties make it a suitable alternative to traditional disinfectants, and there are key ecological advantages of $\mathrm{HOCl} .46,47,48,49,50$ ]

- Biodegradability: HOCl is a natural substance formed from the reaction between water and salt, and it degrades into harmless components, primarily salt and water, within a relatively
short period. This natural degradation process ensures that HOCl does not persist in the environment, reducing its ecological footprint.
- Minimal chemical residue: unlike some other disinfectants that leave chemical residues on surfaces, HOCl leaves no harmful residue behind. This is particularly important in healthcare facilities and food processing industries, where the absence of chemical residues is critical for patient and consumer safety.
- Low toxicity: HOCl is known for its low toxicity to humans and animals, which is a significant advantage when compared to disinfectants that may pose health risks to both users and those who come into contact with treated surfaces. It is safe for use on food contact surfaces, reducing the risk of contaminating food products.
- Effectiveness against a wide range of pathogens: HOCl is highly effective against a broad spectrum of pathogens, including bacteria, viruses, and fungi. Its rapid kill rate and ability to penetrate microbial cell walls make it a potent disinfectant. As a result, it can often be used in lower concentrations, reducing the overall environmental impact.
- Reduced energy consumption: the production of HOCl through the electrolysis of saltwater consumes less energy compared to the production of some other disinfectants, making it a more sustainable choice.

While hypochlorous acid ( HOCl ) offers numerous ecological advantages, it is essential to acknowledge certain challenges and considerations associated with its use.

- Stability: HOCl is sensitive to light and heat, which can reduce its stability over time. Proper storage and handling are crucial to maintain its efficacy.
- Regulatory Standards: The regulatory landscape regarding disinfectant use is complex and varies globally. Clear guidelines and standards are necessary to ensure the responsible production, distribution, and application of HOCl .
- Public Awareness and Education: Proper education about the advantages and correct usage of HOCl is vital. Users must be aware of its benefits and limitations, as well as the correct concentrations and application methods to ensure effective disinfection. Public awareness campaigns can contribute significantly to promoting responsible use. One of the goals of this work is to define a "good practice" for the operator, to minimize impurities release.
- Integration into Existing Systems: Transitioning from traditional disinfectants to HOCl may require changes in infrastructure and practices. Integrating HOCl into existing systems, such as healthcare facilities, water treatment plants, and food processing industries, necessitates
careful planning and collaboration between stakeholders. A recent example of integration has been shown using advertising videos in regional trains: automated nebulization systems for disinfectant inside coaches for COVID-19-exposed surfaces were shown.
- Research and Development: Ongoing research and development are essential to improving the production, stability, and application of HOCl . Continued scientific inquiry can lead to innovations that enhance its efficacy and address existing limitations.

Disinfectants play a crucial role in maintaining hygiene and preventing the spread of infections in various settings, including hospitals, households, and public spaces [51, 52, 53, 54]. A brief comparison between Hypochlorous Acid $(\mathrm{HOCl})$ and other common disinfectants, chlorine-based and other ammonium products, highlighting their efficacy, safety, and environmental impact could be summarized by the following points:

## Efficacy:

- $\mathrm{HOCl}: \mathrm{HOCl}$ is highly effective against a broad spectrum of microorganisms, including bacteria, viruses, and fungi. Its oxidizing properties disrupt cell walls and membranes, leading to microbial inactivation.
- Chlorine-based Disinfectants: Chlorine-based disinfectants, like sodium hypochlorite, work through the release of hypochlorite ions ( $\mathrm{OCl}-$ ) in water. They are also effective against a wide range of pathogens.
- Quaternary Ammonium Compounds (Quats): Quats disrupt the cell membrane, leading to microbial death. They are effective against bacteria and some viruses but may be less effective against certain fungi and spores.


## Safety:

- $\mathrm{HOCl}: \mathrm{HOCl}$ is non-toxic to humans and animals at appropriate concentrations. It is nonirritating to the skin and eyes, making it safe for use in various applications.
- Chlorine-based Disinfectants: Chlorine-based disinfectants can produce harmful by-products like chloramines, which can be toxic and irritating. Exposure to these by-products can cause respiratory issues and other health problems.
- Quaternary Ammonium Compounds (Quats): Quats are generally safe to use but may cause skin and respiratory irritation in some individuals. Prolonged or high-level exposure can lead to adverse health effects.

Environmental Impact:

- $\mathrm{HOCl}: \mathrm{HOCl}$ breaks down into water and salt, leaving no harmful residues. It does not contribute to the formation of chlorinated by-products in water, making it environmentally friendly.
- Chlorine-based Disinfectants: Chlorine-based disinfectants can react with organic matter to form harmful chlorinated by-products, such as trihalomethanes (THMs) and haloacetic acids (HAAs), which are environmental pollutants.
- Quaternary Ammonium Compounds (Quats): Quats can persist in the environment, potentially affecting aquatic life. Their accumulation in water bodies can disrupt the ecosystem and harm aquatic organisms.

Resistance:

- HOCl : There is a low likelihood of microbial resistance to HOCl due to its multiple modes of action, including cell membrane disruption and DNA damage.
- Chlorine-based Disinfectants: Microorganisms can develop resistance to chlorine-based disinfectants, especially if not used at appropriate concentrations or if used continuously without rotation with other disinfectants.
- Quaternary Ammonium Compounds (Quats): Some bacteria can develop resistance to quats, potentially reducing their effectiveness over time.
Deactivation by Organic Matter:
- HOCl : While HOCl can be deactivated by organic matter, its efficacy is generally more stable in the presence of organic materials compared to chlorine-based disinfectants.
- Chlorine-based Disinfectants: Chlorine-based disinfectants are more susceptible to deactivation in the presence of organic matter. This can lead to reduced effectiveness in realworld, organic-rich environments.
- Quaternary Ammonium Compounds (Quats): Quats are less affected by organic matter than chlorine-based disinfectants but can still experience reduced efficacy in the presence of high organic loads.

Residual Activity:

- $\mathrm{HOCl}: \mathrm{HOCl}$ does not leave a persistent residual activity, which means its antimicrobial effects dissipate after application. This lack of residual activity can be an advantage, especially in situations where complete removal of the disinfectant is essential.
- Chlorine-based Disinfectants: Chlorine-based disinfectants can provide residual activity, which means they continue to disinfect surfaces even after application. This residual effect can be beneficial in certain settings.
- Quaternary Ammonium Compounds (Quats): Quats provide some residual activity, offering prolonged protection on surfaces. However, this residual effect can lead to the development of resistant microorganisms over time.

Cost and Accessibility:

- HOCl : The production of HOCl through electrolysis is generally cost-effective and accessible. The raw materials (salt and water) are widely available and relatively inexpensive.
- Chlorine-based Disinfectants: Chlorine-based disinfectants are cost-effective and commonly used. However, the costs associated with managing harmful by-products and potential environmental damage must also be considered.
- Quaternary Ammonium Compounds (Quats): Quats are relatively affordable and readily accessible. However, their cost-effectiveness might be affected by the need for frequent applications due to potential resistance issues.

In this short comparison between HOCl and other disinfectants, it becomes evident that HOCl offers a compelling combination of efficacy, safety, environmental friendliness, and accessibility. While each disinfectant has its unique advantages, HOCl's ability to provide robust antimicrobial action, coupled with its minimal environmental impact and safety for both humans and animals, positions it as a leading choice in the quest for effective, sustainable, and responsible disinfection solutions in various applications, from healthcare to public spaces and beyond. [55, 56, 57]

The goal of this work is to deepen the knowledge on the topics of NaCl release and materials compatibility.

## Introduction, 2: the need for compatibility tests

As previously stated, HClO aqueous solution is considered a powerful yet environmentally friendly disinfectant. In the literature, different terms are reported to present water solutions that are produced by the electrolysis of salts, such as electrochemically activated solutions (ECAS), electrolyzed oxidising water (EOW) or simply electrolyzed water (EW). The main species formed by electrolysis of an aqueous NaCl solution is hypochlorous acid ( HOCl ), an unstable hydroxyl radical in a pH range from 2 to 7 . HOCl has been indicated for years as a biocide agent for enhancing cutaneous wound healing and in the safe treatment of eyes, nose and ear infections. Several studies have also demonstrated that HOCl is effective in water, air and surface sanitization or disinfection. Depending
on the desired HClO concentration, NaCl can be added to water or it is also possible to use the amount present in groundwater and drinking water (usually $<200 \mathrm{ppm}$ ).
As a function of the quality of HClO production from NaCl electrochemical production, salt residual traces could be found in the sprayed product, thus leading to possible salt deposition over surfaces, in time and subsequent eventual corrosion phenomena. Given the low relative acidity of the HOCl solution, the combined effects of NaCl presence and acidic environment could be the key factors for eventual corrosion mechanisms.

Metal corrosion is a natural process that occurs when metal reacts with its environment. This reaction leads to the deterioration of the metal's properties and can result in structural damage, decreased functionality, and economic losses. Corrosion can occur in various forms, such as rusting in iron and steel, tarnishing in silver, and pitting in aluminum. Understanding the scientific principles behind metal corrosion is essential for developing effective prevention and mitigation strategies. [4, 5, 6, 7, 8, 9, 10, 11].

Corrosion reactions generally involve the metal, an electrolyte (usually water), and an oxidizing agent, such as oxygen or other chemicals present in the environment. The corrosion process can be explained through electrochemical reactions, where the metal undergoes oxidation, releasing electrons, and the oxidizing agent gains electrons, reducing its state.

The most common form of corrosion is rusting, which occurs in ferrous metals like iron and steel. In the presence of oxygen and water, iron reacts with oxygen to form iron oxide (rust) according to the following chemical reaction:

$$
4 \mathrm{Fe}+3 \mathrm{O}_{2}+6 \mathrm{H}_{2} \mathrm{O} \rightarrow 4 \mathrm{Fe}(\mathrm{OH})_{3} 4 \mathrm{Fe}+3 \mathrm{O}_{2}+6 \mathrm{H}_{2} \mathrm{O} \rightarrow 4 \mathrm{Fe}(\mathrm{OH})_{3}
$$

This reaction demonstrates the electrochemical nature of corrosion, involving both oxidation and reduction half-reactions. The presence of electrolytes, especially salts, enhances the rate of corrosion by providing ions that facilitate electron flow in the electrochemical cell.

Several factors influence metal corrosion, including environmental conditions (such as humidity, temperature, and pollution levels), the presence of corrosive substances (acids, bases, salts), and the type of metal and its alloy composition. Galvanic corrosion, another common type, occurs when two dissimilar metals are in contact in the presence of an electrolyte, leading to accelerated corrosion of the more reactive metal. [12, 13, 14, 15]

Preventing metal corrosion involves various methods, including the application of protective coatings (paints, platings), the use of corrosion-resistant alloys, cathodic protection, and controlling
environmental factors. Researchers continue to explore innovative materials and techniques to develop more efficient corrosion prevention strategies, considering both economic and environmental sustainability.[79, 80]
Studying metal corrosion scientifically is crucial for industries such as construction, transportation, and manufacturing, where metals are extensively used. Ongoing research in corrosion science aims to improve the understanding of corrosion mechanisms, develop advanced materials, and design effective corrosion inhibitors to prolong the lifespan and reliability of metal-based structures and products.

Corrosion is a pervasive issue in various industries and infrastructures. Among the many corrosioninducing agents, sodium chloride $(\mathrm{NaCl})$ stands out as a significant contributor.

Factors Influencing Corrosion Rate are the NaCl concentrations, leading to more aggressive corrosion due to increased Cl - ion availability. Moreover, elevated temperatures and humidity levels may enhance the corrosive impact of NaCl . High temperatures accelerate chemical reactions, while humidity sustains the presence of the aqueous NaCl solution, prolonging the corrosion process.

Iron and steel are susceptible to rapid corrosion in the presence of NaCl , leading to rust formation. The formation of iron chloride compounds accelerates the deterioration process. [81, 82]

Non-ferrous metals also corrode in NaCl environments, but the corrosion products and mechanisms vary. For instance, aluminum forms a protective oxide layer, but chloride ions can breach this layer, causing localized corrosion. This work considers both metals and non-metallic materials, to screen inside a reference environment.

When starting this PhD work, a "generic" Hospital Operating Room has been chosen as a reference environment where HOCl would be used as a disinfectant. Different structural or constituting materials inside such an environment were then listed and selected for exposure.

The hospital operating room (OR) is a critical environment where complex medical procedures are performed with utmost precision and care. The materials inside the OR play a pivotal role in ensuring the success of surgeries, the safety of patients, and the well-being of medical professionals. This is the very reason why assessing their compatibility with the sprayed/nebulized disinfectant is a critical topic.

Surgical instruments, for example, are the backbone of any operating room. These tools are made from high-quality materials such as stainless steel, titanium, and specialized alloys, ensuring
durability, corrosion resistance, and strength. Precision instruments like scalpels, forceps, and scissors are essential for the intricate tasks performed by surgeons. Thus, stainless steel is one of the selected materials to test. A choice that extends to positioning tripods and operating tables too.

Also, inside the modern operating room, advanced medical imaging and diagnostic equipment are indispensable. Electronic monitors and control panels in the OR are constructed using materials that ensure electrical safety and durability. These devices, often encased in high-impact plastics or metal alloys, provide vital information about the patient's vital signs, anaesthesia levels, and other critical parameters. Copper, connectors, polymeric and electronics parts were selected too, to define possible compatibility and corrosion effects over them.

Corrosion, the gradual degradation of materials due to chemical or electrochemical reactions with the environment, is a significant concern across various industries and sectors. One of the most common corrosive agents is sodium chloride $(\mathrm{NaCl})$, a ubiquitous salt found in natural environments, de-icing agents, and industrial processes. NaCl corrosion, often referred to as salt corrosion, is a complex phenomenon with far-reaching implications on the structural integrity, safety, and economic aspects of structures and equipment. In this work, we have considered candidate materials that could be found in a medical/surgery room: electrical and electronic parts, structural metals, and polymers.

NaCl corrosion initiates through a series of electrochemical reactions. When salt particles come into contact with a metal surface and water is present, an electrochemical cell is formed. NaCl dissociates into sodium ions $\left(\mathrm{Na}^{+}\right)$and chloride ions $\left(\mathrm{Cl}^{-}\right)$, and these ions facilitate the flow of electrical current within the cell. The metal surface acts as an anode, where oxidation occurs, leading to the release of metal ions and electrons. Chloride ions migrate to the anode and participate in reactions that accelerate the corrosion process. This electrochemical activity is further exacerbated by the presence of oxygen, leading to the formation of metal chlorides and oxides, which weaken the material's structure and integrity. In the case of metals, NaCl corrosion results in the formation of rust, weakening the material and causing structural failures. This has significant implications for bridges, pipelines, and other infrastructures, leading to compromised safety and costly repairs, as well as for electric devices, plugs, and wires, where damages to critical instrumentation could occur.

NaCl corrosion usually involves several complex processes:

- Saltwater Electrolysis: In the presence of moisture, saltwater forms an electrolyte. When metal is submerged in this solution, an electrochemical cell is created. Anodic oxidation occurs at
the metal surface, leading to metal ions in the solution. Concurrently, reduction reactions take place, resulting in the formation of products like rust in the case of iron and steel.
- Pitting Corrosion: NaCl corrosion often leads to pitting, a localized form of corrosion where small pits or craters form on the metal surface. Pitting corrosion can be particularly dangerous, as it can cause structural failures even in the early stages of degradation.
- Galvanic Corrosion: When dissimilar metals are in contact with the presence of NaCl , galvanic corrosion can occur. The more noble metal remains relatively unaffected, while the less noble metal corrodes rapidly. This process is commonly observed in alloys and mixedmetal structures.

Considering the common practices for the nebulization of products like HOCl , pitting corrosion, possibly coupled with electrochemical corrosion appears to be the most predictable mechanism for the considered metal samples.

Pitting corrosion initiates the breakdown of the protective passive film on a metal surface, exposing a small area to the corrosive environment.

Normally, metals develop a thin, protective oxide film that prevents further corrosion. Pitting corrosion occurs when this film breaks down in a localized area, leaving the metal vulnerable to corrosion. Within the pit, anodic reactions occur, causing the metal to dissolve into ions. These reactions are highly localized, leading to the formation of the characteristic pits.

Moreover, pits often have a limited oxygen supply, creating an environment conducive to aggressive chemical reactions. This accelerates metal dissolution within the pits, making them deeper and wider over time.

Corrosion not only affects the durability of materials but also has environmental implications. Rust, for instance, can contaminate soil and water, leading to environmental degradation. As industries strive for sustainability, corrosion testing methods are evolving to assess not only the durability of materials but also their environmental impact. Researchers are developing eco-friendly corrosion inhibitors and materials with minimal environmental consequences, as well as, as it will be for this present work, effective procedures and recommendations for materials protection.

Several reference materials were selected, exposed to HClO in a controlled series of exposure tests and then analyzed employing SEM EDS morphological analysis.

SEM-EDS offers the best characteristics for morphological studies as well as semi-quantitative evaluations of materials. [74, 75, 76].

SEM provides high-resolution imaging capabilities, allowing operators and researchers to visualize the surface morphology of corroded materials at the microscale. SEM images reveal details such as pitting, crevice corrosion, and surface roughness, providing crucial information about the corrosion mechanisms. EDS analysis, integrated with SEM, enables elemental mapping of corroded surfaces. By mapping the distribution of elements, researchers can identify localized corrosion products, understand the migration of ions during corrosion, and assess the effectiveness of corrosion inhibitors. SEM-EDS assists in the identification and analysis of corrosion products. By examining the elemental composition of these products, researchers can deduce the corrosion mechanism, evaluate the effectiveness of protective coatings, and develop strategies to mitigate corrosion. [77, 78, 83].

SEM-EDS is commonly employed to study the interfaces between dissimilar materials, such as metalceramic or metal-polymer interfaces. Analyzing these interfaces helps in understanding interfacial reactions, identifying potential weak points, and optimizing material combinations for enhanced compatibility.
In compatibility testing, when materials fail due to incompatibility issues, SEM-EDS assists in failure analysis. It identifies the root cause of failure, whether it's galvanic corrosion, stress corrosion cracking, or other forms of incompatibility, guiding engineers and researchers toward informed solutions.

Also, it is instrumental in characterizing materials exposed to aggressive environments such as corrosive chemicals or high temperatures. By analyzing the material's surface composition after exposure, researchers gain valuable insights into the material's performance and degradation mechanisms.

Scanning Electron Microscopy (SEM): SEM utilizes electron beams to scan the surface of a sample. When the electrons interact with the sample, various signals are generated, including secondary electrons, backscattered electrons, and characteristic X-rays. The key components of an electronic microscope are:

- Electron Gun: Generates a beam of electrons accelerated to high energy levels.
- Electron Lenses: Focus and shape the electron beam, ensuring precision and clarity in imaging.
- Specimen Chamber: Houses the specimen and allows for precise positioning and movement.
- Detectors: Capture different signals emitted from the specimen, such as secondary electrons, backscattered electrons, and X-rays.
- Display and Imaging System: Converts the detected signals into visual images, which can be observed on a computer screen.

Energy Dispersive X-ray Spectroscopy (EDS): EDS is an elemental analysis technique that detects characteristic X-rays emitted from the sample upon interaction with the electron beam. These X-rays are unique to each element, allowing qualitative and quantitative elemental analysis. When the electron beam interacts with the atoms in the sample, inner-shell electrons are displaced, creating vacancies. Electrons from higher energy levels fill these vacancies, emitting X-rays in the process. The EDS probe consists of a solid-state detector and a semiconductor crystal. When X-rays enter the detector, they interact with the crystal, generating electrical pulses proportional to the X-ray energy. By measuring the energy and intensity of these X-rays, EDS software identifies the elements present in the sample and quantifies their concentrations.
Compatibility tests ensure that materials used in critical applications, such as medical devices and aerospace components, do not react adversely with the substances they come into contact with, ensuring user safety and preventing contamination. In this work, an accelerated corrosion test, materials are exposed to a saline mist, simulating harsh environmental conditions.

The compatibility of materials with HClO spraying is crucial for ensuring the longevity, safety, and performance of structures and devices.

The tests were carried out following the UNI EN ISO 9227. UNI EN ISO 9227 is a standard developed by the International Organization for Standardization (ISO) that provides guidelines for conducting salt spray tests, a common method for assessing the corrosion resistance of metallic and non-metallic materials.

In this work, it was chosen to perform accelerated tests, simulating long exposures of materials in a compressed time. These kinds of accelerated tests facilitate the rapid evaluation of material performance, aiding in the development of corrosion-resistant materials, coatings, and mitigation strategies. And allowed the author to perform meaningful experiments in the time frame of a PhD .

## Introduction, 3: ECHA.

One of the challenges associated with the use of hypochlorous acid $(\mathrm{HOCl})$ is the need for clear regulatory standards and guidelines. Establishing specific regulations regarding its production, usage, and disposal will ensure responsible application and prevent potential misuse or environmental contamination. Regulatory bodies and policymakers must work in tandem with scientists and industry experts to develop comprehensive guidelines that promote the safe and sustainable use of HOCl .

The European Chemicals Agency (ECHA) is an independent EU agency that plays a key role in the implementation of the European Union's regulation concerning the Registration, Evaluation, Authorization, and Restriction of Chemicals (REACH). Established in 2007, ECHA is headquartered in Helsinki, Finland. Its primary purpose is to ensure a high level of protection for human health and the environment, as well as to promote the free movement of chemicals within the European Single Market.


Fig. 1: the ECHA website with search tools.

Key Functions and Responsibilities of ECHA:

REACH Regulation Implementation: ECHA oversees the implementation of the REACH regulation, which requires companies to register information about the properties and uses of their chemical substances. ECHA evaluates the registration dossiers submitted by companies, assesses hazardous properties of chemicals, and ensures the proper dissemination of information about these substances. Biocidal Products Regulation (BPR): ECHA also administers the BPR, which regulates the use of biocidal products in the EU market. Biocidal products are those intended to destroy, deter, render
harmless, or control harmful organisms. ECHA evaluates active substances used in biocidal products and assesses their safety and efficacy.

Classification, Labeling, and Packaging (CLP) Regulation: ECHA is responsible for the CLP regulation, which ensures that the hazardous properties of chemicals are communicated through standardized labels and safety data sheets. This helps protect consumers, workers, and the environment from the risks associated with hazardous chemicals.

Authorization and Restriction of Chemicals: ECHA evaluates applications for authorization of substances of very high concern (SVHC) to ensure that their use is adequately controlled, and it also proposes restrictions on certain chemicals when necessary to protect human health or the environment.

Candidate List and Authorization List: ECHA maintains the Candidate List of substances that may have serious effects on human health or the environment, which are potential candidates for authorization. ECHA also maintains the Authorization List (Annex XIV of REACH), specifying substances for which authorization is required to be used within the EU.

Chemical Safety Assessment: ECHA provides guidance and tools for chemical safety assessments and helps companies comply with their obligations under REACH. This includes developing guidelines, databases, and software tools to support the assessment and management of chemical risks.

Research and Development: ECHA conducts research and develops methodologies to improve the understanding of chemical safety and to enhance the implementation of regulations related to chemicals.

Information Exchange Forum (Forum): ECHA facilitates cooperation and exchange of information among EU Member States, industry, and NGOs through the Forum. The Forum supports consistent enforcement of chemicals legislation across the EU.

ECHA's work is essential for achieving the EU's goal of ensuring the safe use of chemicals, protecting human health, and preserving the environment. Through its regulatory activities, research initiatives, and collaborative efforts, ECHA contributes significantly to advancing chemical safety within the European Union.

Challenges and Future Directions for ECHA:

1. Data Availability and Quality: One of the ongoing challenges for ECHA is the availability and quality of data on chemical substances. Ensuring that companies provide accurate and comprehensive data is crucial for the agency to assess the risks associated with different chemicals effectively.
2. Substance Evaluation and Risk Management: ECHA needs to continuously refine its methods for substance evaluation and risk management. This includes identifying substances of concern, evaluating their risks comprehensively, and implementing necessary risk management measures. Striking a balance between regulatory stringency and industrial innovation is a delicate challenge.
3. International Cooperation: Collaborating with non-EU countries and aligning regulations with global standards is a growing necessity. Many chemicals and products cross international borders, and harmonizing regulations help ensure the safety of products in the global market.
4. Emerging Substances and Technologies: With the continuous development of new substances and technologies, ECHA must adapt to assess the risks associated with these emerging chemicals effectively. This includes addressing nanomaterials, advanced materials, and substances with unknown or complex properties.
5. Transparency and Communication: Maintaining transparency in decision-making processes and effectively communicating the implications of regulations to various stakeholders, including the general public, is crucial. Ensuring that information is accessible and understandable fosters trust and cooperation.
6. Climate Change and Circular Economy: Considering the environmental impact of chemicals, particularly concerning climate change and the circular economy, is becoming increasingly important. ECHA plays a vital role in promoting sustainable practices and supporting the transition toward a circular economy by regulating the use of hazardous substances and encouraging the use of safer alternatives.
7. Digitalization and Big Data: Embracing digital technologies and leveraging big data can enhance ECHA's ability to process vast amounts of information, making regulatory processes more efficient. Data analytics and artificial intelligence can assist in risk assessment, substance identification, and trend analysis, enabling proactive regulatory decisions.
8. Public Awareness and Education: Raising public awareness about chemical safety, the importance of proper handling and disposal of chemicals, and the role of ECHA is vital. Educated consumers can make more informed choices and advocate for safer products, encouraging industries to adopt environmentally friendly practices.

All experimental data gathered for this present work can be usefully listed and categorized, following the ECHA scheme and methodology.

## Introduction, 4: environmental impact and LCA

In an era where sustainable development is imperative, businesses, policymakers, and researchers are increasingly turning to Life Cycle Assessment (LCA) as a comprehensive tool to evaluate the environmental impact of products and processes. LCA is a systematic analysis methodology that quantifies the environmental impact of a product or service throughout its entire life cycle, from raw material extraction to production, use, and disposal.

LCA offers a comprehensive view, considering not only the production phase of the considered product or item, but also the entire life cycle, including material extraction, manufacturing, distribution, use, and end-of-life disposal or recycling. This comprehensive perspective is vital for identifying potential environmental hotspots and making informed decisions.

Moreover, LCA provides valuable insights for businesses and policymakers to make informed decisions about product design, process optimization, and policy formulation. By comparing the environmental impact of different options, stakeholders can choose sustainable alternatives, reducing their ecological footprint.

LCA findings influence the development of environmental policies and regulations. Governments use LCA data to set standards, promote eco-labelling, and incentivize industries to adopt environmentally friendly and sustainable practices.

The first step in LCA involves clearly defining the goals and scope of the assessment. This includes determining the purpose of the study, specifying the boundaries (cradle-to-gate, cradle-to-grave), and identifying the functional unit for comparison.

Then, it involves compiling a detailed inventory of all inputs and outputs at each stage of the product's life cycle. This includes raw materials, energy, water, emissions, and waste. LCA software and databases assist in collecting and organizing this vast amount of data.
The LCIA evaluates the potential environmental impacts identified in the LCI phase. Impact categories, such as greenhouse gas emissions, water pollution, and resource depletion, are assessed using established characterization factors. LCIA results provide a quantitative measure of the environmental burden associated with the product or process.

The final step involves interpreting the results and drawing conclusions. Stakeholders will then analyze the findings, considering uncertainties and limitations, to make informed decisions and identify areas for improvement, in the case of this campaign for HOCl as a disinfectant.

Studies carried out in hospitals, schools and public spaces have shown that contaminated floors increase the probability of being infected not only by direct contact but also by inhaling them as
aerosols. While walking on contaminated floors, microorganisms can be resuspended in the air to man-height, increasing the microbial charge of indoor air up to $15 \%$.

In this study, the HOCl electrochemical system has been integrated into a wash-and-dry machine for floor cleaning treatment. Such an innovative machine has been used for floor cleaning and sanitation, to evaluate the microbial charge and organic dirt removal capacity of HOCl in comparison with a machine charged with traditional Ecolabel standard detergent. The quartz-concrete floor has been tested in this study. Due to its durability and resistance, it is the most used floor material for industrial floors, varying from food to heavy industries. The surface damage potentially caused by prolonged HClO applications on quartz concrete has then been investigated through a Scanning Electron Microscope (SEM). Results have been compared with coated hardwood floors, usually considered more sensitive.

Furthermore, a comparative Life Cycle Assessment (LCA) analysis has been carried out to evaluate the environmental impact of cleaning operations using HOCl-based and detergent-based wash-anddry machines. Life Cycle Assessment (LCA) is a systematic and holistic approach used to evaluate the environmental aspects and potential impacts of a product, process, or service throughout its life cycle stages, from raw material extraction to disposal. In an era marked by increasing concerns about climate change and environmental degradation, LCA plays a pivotal role in guiding industries, policymakers, and researchers toward sustainable practices and innovations. LCA is a standardized methodology (ISO 14040, ISO 14044 and ISO14067) for the verification of appropriate sustainability along the overall production and use of the life cycle of a product, process or service.
n the intersection of environmental, ethical, and socio-economic Life Cycle Assessment (LCA), the concept of sustainable development comes to the forefront. Sustainable development aims to meet the needs of the present without compromising the ability of future generations to meet their own needs. Integrating environmental, ethical, and socio-economic dimensions into LCA practices is essential for achieving sustainable development goals:

Integrating environmental, ethical, and socio-economic LCA data allows for balanced decisionmaking. When businesses, policymakers, and consumers have access to comprehensive information, they can make choices that minimize environmental impact, uphold ethical standards, and contribute positively to social and economic well-being.

By considering all three dimensions, LCA contributes to the development of resilient systems. Sustainable development ensures that economic growth is stable, social well-being is enhanced, and environmental resources are preserved. Resilient systems can withstand challenges and adapt to changing conditions, ensuring long-term sustainability.

The intersection of ethical and socio-economic considerations highlights the importance of social equity and environmental justice. It ensures that the benefits of development are distributed fairly, addressing historical disparities and empowering marginalized communities. By promoting social equity, sustainable development becomes inclusive and just.

Integrating ethical and environmental considerations often leads to innovation. Businesses are incentivized to develop eco-friendly technologies and adopt ethical practices. Sustainable development fosters a culture of continuous improvement, encouraging the development of cleaner processes, renewable energy solutions, and socially responsible business models.

GATE srl, a spinoff company of the University of Ferrara, has been producing HClO disinfection devices for many years. During the COVID-19 pandemic, several experimental programmes were financed to study different disinfectants for the virus. In the "POR FESR 2014-2020" frame, ENEA (the Italian National Agency for New Technologies, Energy and Sustainable Economic Development) and GATE srl, together with other partners, participated in common scientific activities. From that common experience, the work performed in this PhD took shape.

The rationale of this work is twofold:

- a compatibility/corrosion test with reference materials, i.e. the most common surfaces where HClO would be sprayed, coupled with SEM-EDS analyses;
- A comparison with other disinfectants, as far as environmental impact and LCA are concerned.

All experimental activities were performed at the ENEA DISPREV laboratory in Bologna, part of the ENEA Division for Models and Technologies for risks reduction.

The Division develops models and delivers measurements for the assessment of policies, plans and strategies for the adaptation and mitigation of risks deriving from natural causes, especially seismic, with a particular focus on climate change, extreme events and air quality.

Activities are carried out in three labs: "Climate Modelling and impacts", "Atmospheric Pollution", "technologies for Structure Dynamics and seismic and hydrogeological risk prevention".

This ENEA Division works in several scientific areas:

- Development of models and systems for the analysis of scenarios for the assessment of anthropogenic impacts and the reduction of natural hazards at local and national scales.
- Development of numerical models for describing interactions between greenhouse gas emissions, air pollution, climate change, energy and technology scenarios to assess relevant economic and social impact, and propose strategies for the adaptation and mitigation of risks.
- Development, design and validation of innovative anti-seismic systems and technologies, with built resilience analysis and application of geomatic techniques to the protection of land, landscape and architectural heritage.
- Research and development on seismic input characterisation and seismic microzonation, with investigations for the definition and control of geomorphological and hydrogeological risk and surface erosion. Research on the preservation of water resources.

Facilities and platforms:

- Instrumentation for the chemical-physical characterisation of Atmospheric Particulate Matter for the identification of different sources. Transportable laboratory equipped for sampling with offline determination methods of the main air quality parameters and online monitors for high temporal resolution.
- MINNI Integrated Assessment Modelling System of Atmospheric Pollution on a national scale, consisting of two main components:
- The Atmospheric Modelling System produces hourly three-dimensional fields of meteorological variables and concentrations of major pollutants in forecast and hindcast mode at the following link: http://airqualitymodels.enea.it/.
- The GAINS-Italy System, develops emission scenarios at national and regional levels for analysing impacts on air quality and costs of abatement/mitigation measures.
- The modelling system of daily climate/marine projections is viewable at the following link: https:// giotto.casaccia.enea.it/forecasts/
- Seismic Hall at C. R. Enea Casaccia with vibration table with passive 3D motion capture system dedicated to seismic tests. There are also two electrodynamic shakers and a contrast wall with two actuators for dynamic or pseudo-static tests.

Non-destructive diagnostic equipment for assessing the state of damage to structures.

- Scanning Electron Microscope (SEM) for morphological analysis of electron microscopy and semi-quantitative microanalysis (the facility used in this work). Remote Sensing and Image Processing.


## 2. Materials and methods

## 1. HClO production

As stated in the introduction, Hypochlorous acid ( HOCl ) is a powerful oxidant that exhibits microbicidal activity towards a broad spectrum of microorganisms and for this reason, it is used, in many cases, as a disinfectant.
HOCl used as a disinfectant can be produced as a water solution electrolyzed (EW). EW is produced by electrolysis of a dichloride solution sodium $(\mathrm{NaCl})$. During the electrolysis process, positively charged ions are formed, the sodium ion $\left(\mathrm{Na}^{+}\right)$and the hydrogen ion $\left(\mathrm{H}^{+}\right)$, which move towards the cathode, where they receive electrons with the generation of sodium hydroxide $(\mathrm{NaOH})$ and hydrogen $\left(\mathrm{H}_{2}\right)$. Charged ions negatively that are formed, chloride ions $\left(\mathrm{Cl}^{-}\right)$and hydroxide ions $\left(\mathrm{OH}^{-}\right)$, instead move towards the anode, where chlorine gas $\left(\mathrm{Cl}_{2}\right)$ is generated. From the hydrolysis of chlorine gas produced, they form hypochlorous acid and hypochlorite ion $\left(\mathrm{OCl}^{-}\right)$. The reactions can be summarised as follows:

$$
\begin{gathered}
2 \mathrm{Cl}^{-}(\mathrm{aq}) \longrightarrow \mathrm{Cl}_{2}(\mathrm{~g})+2 e^{-} \quad \text { (anode) } \\
\mathrm{Cl}_{2}(\mathrm{~g})+\mathrm{H}_{2} \mathrm{O}(\mathrm{l}) \longrightarrow \mathrm{Cl}^{-}(\mathrm{aq})+\mathrm{HOCl}_{\mathrm{aq})+\mathrm{H}^{+}(\mathrm{aq})} \\
\mathrm{HOCl}(\mathrm{aq})
\end{gathered} \longrightarrow \mathrm{H}^{+}(\mathrm{aq})+\mathrm{OCl}^{-}(\mathrm{aq}) \mathrm{l}
$$

The ratio with which hypochlorous acid and hypochlorite ion are generated depends on the pH of the solution (Figure 1). If the solution has a pH between 3 and $7, \mathrm{HOCl}$ is the predominant species, while at higher pH values the concentration of $\mathrm{OCl}^{-}$gradually increases until it becomes prevailing, ending in being $100 \%$ at pH 10 . At pH less than 4 , in addition to HOCl , there is also chlorine in the aqueous phase and chlorine gas, the concentration of which increases greatly at pH lower than 3 . Hypochlorous acid at pH 6 turns out to be $98 \%$ free chlorine and at $\mathrm{pH} 783 \%$, and then decreases and is only $14 \%$ at pH 8.5 .


Fig. 1: Scheme of the electrochemical cell for HOCl production from tap water.


Fig. 2: active Cl concentrations as a function of pH .

The microbicidal and disinfectant activity of EW can be attributed to the Hypochlorous acid concentration, which is known to be 100 times more reactive and a stronger disinfectant than $\mathrm{OCl}^{-}$ The greater germicidal power of hypochlorous acid can be attributed to its ability to pass through the cell membrane, unlike the hypochlorite ion. $\mathrm{OCl}^{-}$, being charged negatively, is unable to cross the bacterial cell membrane formed by a hydrophobic lipid bilayer and therefore acts only from the outside of the cell. Hypochlorous acid, on the other hand, given its electrical neutrality and modest molecular dimensions, manages to cross the lipid bilayer of the membrane by passive diffusion. Consequently, it can carry out its activity both from inside and outside the cell, with a significant increase in germicidal capacity. Their activity is thought to be due to the inhibition of enzymes essential for bacterial growth, membrane damage and DNA, and probably also to damage to membrane transport systems.

Therefore, EW at $\mathrm{pH} 6 / 7$, with a preponderance of hypochlorous acid, is an excellent disinfectant with advantageous characteristics compared to other substances used. First of all, it is environmentally friendly and non-toxic for the staff who have to use it, as it is produced from scratch from water and sodium chloride $(\mathrm{NaCl})$, and after use it returns to its initial condition.

The concentration of free chlorine decreases following oxidation reactions with 19 organic substances. It can also be produced on-site, allowing for savings in transportation and storage costs. Another advantage is its bactericidal activity against a broad spectrum of microorganisms and, in addition, does not appear to induce the growth of bacterial strains.

## 2. The SEM-EDS lab at ENEA.

The SSPT-MET-DISPREV Scanning Electron Microscopy laboratory is equipped with a Quanta "Inspect S" FEI SEM, coupled to an Oxford Instruments Xplore microanalysis (fig. 2). This equipment is characterized by a particularly innovative technology and constitutes an extremely advanced system.

It is possible to perform direct morphological analysis of samples up to $5-10 \mathrm{~cm}$ in diameter in a nondestructive and non-invasive way, with a maximum resolution of 3 nanometers, without any preparation and metallization treatment.
The electron gun is a Tungsten filament with and maximum resolution range between $3 \mathrm{~nm}(30 \mathrm{kV}$ in high vacuum conditions, SE and BS Everhart-Thornley detector) and $12 \mathrm{~nm}(3 \mathrm{kV}$ in low vacuum, GSE Large Field detector). As it is well known, the scanning electron microscope uses a focused
beam of high-energy electrons to generate a variety of signals at the surface of solid specimens. The signals that derive from electron-sample interactions reveal information about the sample including external morphology (texture), chemical composition, crystalline structure and orientation of materials making up the sample. In most applications, data are collected over a selected area of the sample surface, and a two-dimensional image that displays spatial variations is generated: areas ranging from approximately 1 cm to $5 \mu \mathrm{~m}$ in width can be imaged in a scanning mode using conventional SEM techniques (magnification ranging from 20X to approximately 30.000 X , spatial resolution of $50-100 \mathrm{~nm}$ ). The FEI Inspect $S$ can handle both conductive and non-conductive sample types.
The recent update with a new microanalysis OXFORD model, which does not require liquid Nitrogen for operation, allows the semi-quantitative recognition of the elements present on the sample, the creation of maps and profiles of their distribution and, thanks to the great sensitivity, also the detection of light chemical elements.

The main technical characteristics of SEM and microanalysis are:

- Mapping at count rates $>1,000,000 \mathrm{cps}$
- Quantitative analysis at count rates $>100,000 \mathrm{cps}$
- Resolution $<129 \mathrm{eV}$ at $100,000 \mathrm{cps}$
- Detector range Boron (B) Californium (Cf)
- Ultra-thin SATW polymer window for best performance at low power consumption LN2 - vibrationfree Peltier Cooling with power supply only
- No external chillers with compressors or gas lines.
- Aztec EDS software for users with more advanced EDS requirements, equipped with several navigators designed to help you perform analysis tasks step by step, so you get the same high-quality results every time.
- Possibility of analysing in Analyzer Navigator/Step (Spectrum Acquisition) Point\&ID Navigator/Step (Spectrum Acquisition)
- it is possible to quickly analyze morphology/structure, chemical characterisation, and perform mapping of chemical elements on many materials.


Fig 3: EDS Inspect $S$ and Oxfoprd EDS probe at ENEA DISPREV, Bologna.

Scanning Electron Microscopy (SEM) is a powerful technique used for high-resolution imaging and microanalysis of materials. In SEM, a focused electron beam scans the surface of a sample, and various interactions between the electrons and the sample surface produce signals that are used to create detailed images and obtain information about the sample's composition and structure.
Tungsten (W) filaments are commonly used as electron sources in SEM instruments. Tungsten filaments serve as the electron source in SEM instruments. When a high voltage is applied across the tungsten filament, it emits electrons through a process called thermionic emission. In this process, electrons gain enough thermal energy to overcome the work function of tungsten and are emitted into the vacuum.

The emitted electrons are then focused into a fine, focused beam using electromagnetic lenses. These lenses use magnetic fields to concentrate the electrons into a tight spot, which can then be scanned across the surface of the sample.
When the focused electron beam strikes the sample, several interactions occur, including secondary electron emission, backscattered electron emission, and X-ray emission.

- Secondary Electrons (SE): When the primary electrons penetrate the sample surface, they can knock loose other electrons from the atoms in the sample. These secondary electrons are collected to create the SEM image. SE imaging provides detailed surface morphology information.
- Backscattered Electrons (BSE): High-energy primary electrons can also bounce back (scatter) from the sample surface. BSE imaging provides compositional contrast, as elements with higher atomic numbers tend to backscatter more electrons.
- X-ray Emission: When the primary electrons interact with the sample, they can dislodge inner shell electrons from atoms. When outer shell electrons fill these vacancies, characteristic Xrays are emitted. X-ray spectroscopy (EDS or Energy Dispersive X-ray Spectroscopy) can be used to analyze the energy and intensity of these X-rays, providing information about the sample's elemental composition.

The signals generated by these interactions are detected, amplified, and converted into images or spectra. SEM images provide high-resolution, three-dimensional surface information, while EDS analysis provides qualitative and quantitative elemental composition data.
Tungsten filaments are favoured for SEM electron sources due to their high melting point, allowing them to operate at high temperatures without evaporating, and their long lifespan, providing stable and reliable performance over extended periods of use. These properties make tungsten filaments
essential components in SEM instruments, enabling scientists and researchers to explore the microscopic world in great detail.

The EDS Oxford probe represents the key tool and application improvement for the instrumentation at ENEA in Bologna, adding to the morphological imaging of the actual semi-quantitative elemental composition of the specific sample area.

When excited under an electron beam, each element within a sample emits a unique and characteristic X-ray signal. The number of X-rays emitted by each element is loosely related to the concentration of that element and its atomic (Z) number. The role of the EDS system is to capture the X-rays as they are emitted from the sample, convert these X-rays into a series of electrical voltage pulses whose amplitudes reflect the energy of the detected X-rays, and pass these pulses to a multichannel analyser that creates.

The energy-dispersive X-ray Spectroscopy (EDS) probe is an analytical technique used for elemental analysis of materials. In traditional EDS systems, a detector cooling system involving liquid nitrogen is often used to cool the detector and reduce electronic noise, allowing for better energy resolution. However, there are newer EDS systems available that operate without the need for liquid nitrogen cooling. These systems are based on advanced detector technologies and improved electronic components that allow for efficient operation at room temperature. Some of the main technological advantages of liquid nitrogen-free EDS are:

- Traditional EDS detectors use a silicon-drift detector (SDD) or a lithium-drifted silicon ( $\mathrm{Si}(\mathrm{Li})$ ) detector. Newer EDS systems without liquid nitrogen cooling often use Silicon Drift Detectors (SDDs). SDDs are made from high-purity silicon and have a small active area, allowing them to operate at room temperature without significant degradation in performance.
- Instead of relying on liquid nitrogen, these advanced EDS detectors incorporate thermoelectric cooling systems. Thermoelectric coolers use the Peltier effect, where an electric current passing through two different conductors or semiconductors creates a temperature gradient, leading to one side becoming cooler. This cooling method is sufficient to maintain the detector at the required low temperatures for optimal performance.
- Modern EDS systems employ digital pulse processing techniques to enhance the signal-tonoise ratio. Digital pulse processors process the electrical pulses generated by the detector when X-rays interact with the material being analyzed. These processors can distinguish between genuine X-ray events and noise, improving the accuracy of the analysis.
- Advances in electronics design have led to the development of low-noise, high-speed signal processing circuits. These circuits are essential for processing the signals from the detector efficiently. By minimizing electronic noise, these systems can achieve excellent energy resolution and sensitivity without the need for cryogenic cooling.
- EDS systems without liquid nitrogen cooling rely on precise calibration procedures and sophisticated software algorithms. Calibration corrects any minor deviations in the detector response, ensuring accurate elemental analysis. Advanced software algorithms help in realtime background subtraction, peak deconvolution, and quantification, leading to reliable results.

The automated peak identification software determines the elements present in the histogram before quantification routines calculate the relative concentrations present. These quantification routines consist of several steps, including spurious peak removal, background removal, net peak intensity calculation, and matrix corrections for the relative effects of absorption, fluorescence, and atomic number variance $(Z)$ of the different elements within the sample. As a final step, the EDS system software coordinates the chemical information from the EDS spectra with the electron beam position, enabling point identification, line-scanning, and X-ray elemental mapping.

Etching is a widely used technique in materials science for preparing samples for corrosion tests, particularly when studying the microstructure and corrosion behaviour of metals and alloys. The process involves selectively removing thin layers of material from the sample's surface to reveal its internal structure. Proper etching techniques are crucial for obtaining accurate and reliable results in corrosion studies.

For the sake of consistency, in the case of the present study, it was decided to avoid any kind of etching, given both the different nature of the substrates and the forecasted weakness of eventual scales at the interface.

## 3. The procurement of reference materials and the rationale of the exposure tests.

As stated in the introduction, the materials to be tested were selected with a hospital operation room as a reference environment:

1. Samples of AISI 304 stainless steel, chosen as it is very common in metal structures present in a hospital, such as instrument supports, bed or cabinet structures, pipes or other objects;
2. Samples of an aluminium alloy, similar to that used for window frames;
3. Samples of copper cable, used for electrical networks;
4. Samples of electronic boards (kindly provided by ALMA Elttronica srl), typically inside computers or instruments;
5. Samples of "touch screen" type plastic panels, which ALMA usually uses for hospital instrumentation;
6. Plastic samples of electrical sockets, "Ticino" type, obviously external to the copper electrical cables.


Fig.4: pictures of the different specimens. From the top left, clockwise: electronics and connector, touchpanel, Copper wire, "Ticino" plastic, AISI304 Stainless Steel, Aluminum, anodized.

As quoted above, the electronics were provided by ALMA Elettronica Srl, a local company manufacturing industrial devices. Metals and plastics are commercial items.

The Alma Elettronica S. r. 1., company was born in September 1997 with the purpose of furnishing products and services in the electronic control ambit and generally in the industrial electronics ambit. The company produces and sells two devices (NEX and PTC, essentially used in the electrotechnical sector) and new devices are in an optimizing phase.

## 4. The compatibility tests.

The use of electrolyzed water, in liquid or atomized form, could cause compatibility or degradation problems on the materials on which it is applied. The effects that can be expected are summarized as: - Corrosion or degradation effects of electrolyzed water in liquid form on steel or metals.

- Effects of corrosion or degradation by HOCl in an atomized form on the main materials present in a surgical site (electrical materials, particular devices, metals, monitors, etc.) and also materials present in environments for civil use, wood, furniture, and fabrics.

Standardizing corrosion tests on such different materials is quite complex. The effects that must be verified and quantified are:

- The effects due to the deposition of residual chloride
- The effects of degradation or corrosion due to exposure to electrolyzed water.
- The possible correlation between delivery times and deposition kinetics of the residual chloride present in the nebulized product
- The possible correlation between delivery times/action of the electrolyzed water and corrosive/degradation phenomena on the surfaces
- The subsequent verification of the optimal concentrations to minimise the corrosion/degradation effects for each material

The materials mentioned above will have different times and methods of exposure to HOCl and, as regards electrical/electronic materials and their insulators, also different temperatures. Naturally, surgical instruments and utensils made of medical or special steel are excluded from this experimental campaign, as they are all single-use and sealed "disposable" objects.
The essential test parameters to be defined will therefore be, for the selected materials, the average exposure time of each type of material and the operating temperature.
Typically, a corrosion test is carried out following precise and simple ISO reference standards. A sample of the material of interest, of appropriate dimensions, is weighed when "new" and is then exposed to the potentially corrosive or degrading environment in the conditions of temperature and concentration of the chemical agents of normal use, for a time appropriate to its standard use. At the end of the exposure, it is prepared for weighing following the test, necessary to evaluate the kinetics of any corrosion mechanism, and then its morphology is studied via SEM-EDS electronic microscopy. In summary, as regards metals and steels, the corrosion mechanisms can be direct attack (or chemical corrosion) if the metallic material is attacked by particular chemical substances in the presence of water (in the form of liquid water or water vapour); of electrochemical corrosion, if the corrosion occurs between two metal parts placed in contact (if the metals placed in contact are of a different
nature, this is in particular called galvanic corrosion); of mechano-chemical corrosion, if the corrosion is caused by the participation of electrochemical causes and mechanical stress.

Corrosion can be diffuse, localized or selective, intragranular or intergranular as regards steels.
The degradation mechanisms for plastic, wood or other materials are different and specific for each of them. SEM observation is fundamental for their determination. The degradation of a wooden material, for example, occurs mainly through oxidation of the lignin ("greying" of the wood) and subsequent loss of its mechanical properties. However, the wood is painted, so it will have to be verified how the hydrolyzed water first acts on the surface polyurethane layer and then on the wood. Carrying out these tests presents non-trivial implementation difficulties, both in terms of the availability and production of the samples and in carrying out the tests themselves.

The typical dimensions of a sample, for example, both weightings on an analytical balance and for observations in electron microscopy, are a few cm 2 . If the client is interested, for example, in studying the degradation effects of HOCl on the monitor of an electronic instrument in the room, an ad hoc method must be identified to carry out the test.

On the other hand, the corrosion/degradation mechanisms in a mildly acidic aqueous environment of steels and the aforementioned materials are rather slow, when present, especially at room temperature. Normally, ISO standards allow us to simulate and accelerate corrosion behaviour by acting on the temperature and concentration of the corrosive agent. Also, it will not be possible to influence temperatures by testing plastics, elastomers and synthetic materials.

The rationale for the test, to perform comparable and accelerated tests over all the specimens, can then be summarised as follows:

- Samples are selected and sized. After machining, the metal samples, are also degreased in acetone.
- The samples are weighed.
- The samples are immersed in a concentrated solution at 2000 wppm of HOCl for $50,100,200$, and 750 hours.
- After exposure, the samples are dried in an oven at low temperature and then weighed.
- The concentration of the hypochlorous solution is measured before and after each single test, for each type of material.
- Morphological analysis under SEM is carried out.
- The metal samples are washed in acetone, to remove any layers or deposits, and observed again under SEM

Exposure times were chosen because of their scalability to realistic usage times. It has been assumed, for example, that hypochlorous can typically be nebulized in a hospital setting every 5 minutes. 750 hours ( 45,000 minutes) are therefore equivalent to 9,000 applications at the maximum possible concentration, equal to almost 5 years.

The meaning of the subsequent weightings, according to the quoted UNI standard, is to establish any mass gains/losses on the samples, as a consequence of deposit or corrosion/erosion phenomena. Measuring the concentration of the solution before and after the test allows you to monitor how it degrades as a function of the material with which it comes into contact and as a function of time.
The samples are observed under SEM without interventions or washing, to avoid introducing random analytical errors into the observation. Washing/pickling following the test is a debated topic and only empirical techniques can be envisaged.

## 5. LCA assessment

In section 5.1 the experimental area set-up where the cleaning and sanitation tests have been conducted is described, together with additional information about the wash-and-dry machines used. In section 5.2 we will describe how the HOCl solution has been prepared for these specific tests. Cleaning and microbiological test procedures have been reported in sections 5.3 and 5.4, respectively. Finally, in sections 5.5 and 5.6 respectively, the experimental set-up of SEM and the LCA framework is described.

All experimental segments are needed to obtain quantitative data supporting the discussion about the cleaning and sanitation performance of HOCl -based in comparison with the detergent-based wash-and-dry machine.

### 5.1 Experimental area description and sampling plan

The test floor area has been marked out with strips in 4 tracks of $1.5 \times 5.0 \mathrm{~m}$ each, previously cleaned and wiped (Fig. 4).


Fig. 5: the marked floor.

The floor area is made of quartz concrete. Wash-and-dry machine (MMG Plus, FIMAP, Italy) has a washing opening of 0.5 m and was equipped with one washing brush PPL 0.60 with a plastic disc diameter of 410 mm and height of 125 mm . Operating parameters have been reported in Table 1.

| Parameter | Machine setting |
| :--- | :--- |
| Washing brushes push $(\mathrm{kg}) 70$ |  |
| Speed rate $(\mathrm{km} / \mathrm{h})$ | 3 |
| Flow rate (L/min) | 0.9 |
| Cleaning yield $\left(\mathrm{m}^{2} / \mathrm{h}\right)$ | 2,250 |
| EW consumption | 2.4 |
| $\left(\mathrm{~L} / 100 \mathrm{~m}^{2}\right)$ |  |
| Specific pressure $\left(\mathrm{g} / \mathrm{cm}^{2}\right)$ | 37 |

Table 1. Operating parameters of the wash-and-dry machine used for the experimental tests.

Wash-and-dry machine integrated with HOCl production system

The wash-and-dry machine has been integrated with 2 electrochemical cells for the in-situ production of HOCl solution. Each electrochemical cell has a flow-through tubular shape (Figure 2),
consisting of cylindrical coaxial parts. An internal anodic rod (external diameters 8 mm , length 173 mm ), provided with a noble metal oxide-based catalytic coating and an external cathodic titanium cylinder (internal diameter 14 mm , length 232 mm ) were used.

HOCl in an aqueous solution is produced by an electrochemical reaction generated by a voltage of 24 V . In the presence of NaCl , usually present in tap water, in Italy, at a concentration of 25-30 ppm, oxygen $\left(\mathrm{O}_{2}\right)$ and chlorine $\left(\mathrm{Cl}_{2}\right)$ are synthesized at the anode of the electrochemical reactor, both in gaseous form. Once formed, the two gases follow different paths. As oxygen moves away from the reaction environment, chlorine can dissolve in water, producing $\mathrm{HOCl} . \mathrm{HOCl}$, in aqueous solution, is always in equilibrium with the corresponding hypochlorite ion, $\mathrm{ClO}^{-}$

$$
\mathrm{HOCl}<->\mathrm{OCl}^{-}+\mathrm{H}^{+}
$$

The pH of the solution determines which forms of chlorine will be present $\left(\mathrm{HOCl} / \mathrm{OCl}^{-} / \mathrm{Cl}_{2}\right)$ and represents the key factor to explain the sanitizing effectiveness of the solution coming out of the electrochemical cell. If the pH of the solution is kept below the value 7,8 , it is guaranteed the presence of $>95 \% \mathrm{HOCl}$, which is, among the 3 possible forms of chlorine, the most oxidizing and therefore most effective as a sanitiser [52]. At an average $25-30 \mathrm{ppm}$ chloride concentration in tap water, the electrochemical cells' yield of conversion is about $30 \%$, obtaining a final HOCl concentration of 10 ppm. HOCl concentration was checked using the photometric DPD (N, N-diethyl-pphenylenediamine) assay [53].

## Cleaning test: removal of organic dirt from the surface

The test strips have been divided into six sub-areas of $0.42 \mathrm{~m}^{2}$ each, marked with coloured tape strips. Each sub-area has been nebulized with 15 ml of a protein and lipid-based standard solution and left to dry naturally. After 24 hours, cleaning conditions, such as organic dirt removal capacity, were measured in three sub-areas using a qualitative clean test kit [54]. The clean test consists of a buffer for the detection of organic residues (proteins, fats and sugars) specifically designed to check the level of cleanliness of a given work surface. The test provides qualitative data based on photometric indications. The product is composed of test tubes plastic test tubes containing a buffer, a vial (reagent A: bicinchoninic acid-BCA) and a floppy disc (reagent disc (reagent B: $\mathrm{CuSO}_{4}$ ).

Using the procedure previously described in 2.3, the remaining three sub-areas were sampled using RODAC (Replicate Organism Detection and Counting) contact Petri plates (Liofilchem, Italy). Adhered microorganisms were transferred directly to the plates via direct contact under standardized conditions (applying $0.02 \mathrm{~kg} / \mathrm{cm}^{2}$ of constant pressure for 10 s ). The plates had a surface area of 24 $\mathrm{cm}^{2}$ and a bottom grid to facilitate the counting of colonies. Mesophilic bacteria and fungi were detected. Selected cultivation media were used for bacteria (Plate Count Agar at $\mathrm{pH}=7.0 \pm 0.2$ ), and fungi (Sabouraud Chloramphenicol Agar at $\mathrm{pH}=5.6 \pm 0.2$ ) [55]. Mesophilic bacteria and fungi were incubated at $37^{\circ} \mathrm{C}$ for 48 hours and $22^{\circ} \mathrm{C}$ for 120 hours, respectively.

RODAC plates were then incubated within 2 h , and colonies were counted after 24-48 h. All sampling was carried out in triplicate.

A total of 144 samples were collected. Samples were transported to the laboratory in refrigerated insulated bags ( $4{ }^{\circ} \mathrm{C}$ ). Microbial density was expressed in terms of CFUs (Colony-Forming Units)/ $100 \mathrm{~cm}^{2}$ and calculated as:

$$
\mathrm{R}=\mathrm{Ut}-\mathrm{At}
$$

where:
$\mathrm{R}=$ microbial charge reduction
$\mathrm{Ut}=$ average value of the number of colonies recovered on the control surface (track D) after 24 hours, expressed as $\log 10$
$\mathrm{At}=$ average value of the number of colonies they were recovered on the treated surface (tracks A, B or C) after 24 hours, expressed as Log 10 .

Finally, R\% has been derived from the following formula:

$$
\begin{equation*}
\mathrm{R} \%=\left(1-10^{-\mathrm{R}}\right) \times 100 \tag{3}
\end{equation*}
$$

The microbial density, based on INAIL (Istituto Nazionale Assicurazione Infortuni sul LavoroNational Institute for Insurance Against Industrial Injuries) standard protocols for civil environments should be also expressed in terms of CFU $100 \mathrm{~cm}^{2}$, calculated by dividing the count result ( N , number of colonies/plate) by the contact area of the plate with the test surface $\left(24 \mathrm{~cm}^{2}\right)$ :

$$
\mathrm{CFU} / 100 \mathrm{~cm}^{2}=\mathrm{N} / 24 * 100
$$

A very slight growth ( $<40$ colonies $/ 100 \mathrm{~cm} 2 \cong 10 \mathrm{CFU} / 24 \mathrm{~cm}^{2}$ ) were considered acceptable for the standard.

## Surface damage evaluation with SEM

Surface damages caused by corrosion can be visually assessed and studied using morphological tests, including techniques like Scanning Electron Microscopy (SEM) and energy-dispersive X-ray Spectroscopy (EDS). These methods provide valuable insights into the corrosion products, surface features, and elemental composition of corroded materials.
As for the exposure tests, a Scanning Electron Microscope equipped with an EDS (Energy Dispersive System) probe (Oxford Instruments, Abingdon, UK) belonging to the ENEA lab, was used. A small sample of quartz concrete ( $10 \times 10 \mathrm{~mm}$ ) and coated hardwood floor ( $10 \times 10 \mathrm{~mm}$ ) were softly cleaned to remove any layers or deposits of dust. Samples were then sprayed with a concentrated HOCl solution at 2000 ppm , appropriately created by adding NaCl to water. After exposure, the samples were wiped, to simulate the wash-and-dry operation. For observation under the SEM microscope, samples were placed on conventional aluminium stubs and made conductive with a carbon adhesive disc. To gather significant elemental mapping, the SEM parameters were set to 30 Kv and spot 7 , allowing a faster and more accurate EDS acquisition.

Energy Dispersive X-ray Spectroscopy (EDS) elemental mapping is a powerful analytical technique used in conjunction with scanning electron microscopy (SEM) to visualize the spatial distribution of elements within a sample. EDS elemental mapping provides detailed information about the elemental composition and distribution at the micrometre to nanometer scale.
When the high-energy primary electrons from the SEM interact with the sample, they can dislodge inner shell electrons from the atoms. When outer shell electrons fill these vacancies, characteristic Xrays are emitted. Each element emits X-rays at specific energies, allowing for the identification of elements based on their unique X-ray spectra.

- An EDS detector positioned near the sample collects the characteristic X-rays emitted from the sample. The detector processes these X-rays and produces a spectrum showing the intensity of X-rays at different energies.
- The obtained EDS spectrum helps identify the elements present in the sample. The characteristic peaks in the spectrum correspond to specific elements.
- Elemental mapping involves scanning the electron beam across the sample while simultaneously collecting EDS spectra at each pixel location. The software analyzes these spectra and identifies the elements present at each point on the sample's surface.
- The resulting elemental maps visually represent the spatial distribution of elements within the sample. Each pixel in the map corresponds to a specific element, and the intensity of the colour or grayscale indicates the elemental concentration. Bright regions in the elemental maps represent areas with higher concentrations of the corresponding element.

This kind of analysis has been implemented for the LCA study over selected floors.

## LCA methodology

In this study LCA follows the standardised method, regulated by ISO 14040 series, which consists of four stages: (1) goal and scope definition; (2) life cycle inventory construction; (3) environmental impact assessment: and (4) interpretation of the results. [58, 59, 60] LCA was carried out using OpenLCA ${ }^{\text {TM }}$ software (Green Delta, Berlin, Germany), applying the CML Baseline 4.4 method. The goal and scope was the quantification of the Global Warming Potential (GWP) of a wash-and-dry machine used for cleaning service in civil buildings in Italy. According to the General Programme Instructions for Environmental Product Declarations ver. 3.0, of the PCR 2021:07 ver. 1.0 "Machinery for professional cleaning") and 14040: 2006 (Environmental management - Life Cycle Assessment - Principles and framework), the functional unit (FU) is 1 hour worked by a wash-and-dry machine equipped with an HOCl production system in comparison with a traditional detergent-based machine. Data collection for life cycle inventories included specific data, collected directly during the cleaning tests, whereas all background data on the production of electricity, materials and transport, was derived from the Ecoinvent 3.8 database. All the data used refers to 2023, the year in which the service was provided. The system boundaries include:

- Upstream processes: raw materials production for machine construction and packaging
- Core processes: supply chain and transportation of raw materials, production of electricity and water consumption for semi-finished and finished machine assembling,
- Downstream processes: machine use and maintenance, transportation to the experimental site, waste management and machine end-of-life

For the present study, it has been assumed that the following characteristics were identical in the compared systems and consequently excluded by the boundaries:
the transport of personnel involved and personnel technical vests, the plants for machine construction
the total area of the plant
data quality
The output of the analysis GWP evaluates the contribution at a time horizon of 100 years to the greenhouse effect provoked by greenhouse gases emitted in the atmosphere as a consequence of the process under study, measured as $\mathrm{kg} \mathrm{CO}_{2}$ equivalent ( $\mathrm{kgCO}_{2}$ eq.) per FU .

The impact assessment has been limited to a single impact category because of the lack of reliable data for calculating other impact categories. [61, 62, 63]

## 3. Experimental

## 1 Weight measurements

Corrosion, the gradual destruction of materials by chemical or electrochemical reactions with their environment, is a pervasive issue affecting industries worldwide. The study and understanding of corrosion mechanisms are crucial to developing effective corrosion prevention strategies. Weight measurements during corrosion tests serve as a cornerstone in this endeavour. In this PhD work, materials are exposed to HOCl , as defined in the introduction, with an accelerated method. The rationale of this choice resembles the need to simulate in the best possible way the use of the product in the "real world", together with the need for a test performance in a defined time. In brief, HOCL in the highest concentration has been put over the reference materials for an exposure time that simulates one year of daily spraying. Given the possible presence of saline impurities in the concentrated product, a possible weight change in the samples might be expected.

Corrosion mechanisms can be complex and influenced by various factors such as temperature, humidity, the chemical composition of the environment, and mechanical stress. Therefore, the choice between a parabolic or linear model, the two common mechanisms for saline exposure, depends on the observed corrosion behaviour under specific conditions.

Linear corrosion occurs when the rate of metal loss is constant over time. This means that a consistent amount of metal corrodes at a steady rate. Linear corrosion can happen under certain conditions, especially when the corrosion rate is relatively uniform, and there are no significant changes in the environment or other influencing factors. Linear corrosion is relatively straightforward to model and predicts, assuming the conditions remain stable.

Parabolic corrosion, on the other hand, describes a situation where the rate of corrosion increases over time. This type of corrosion often occurs when a protective layer, such as an oxide or passivation layer, forms on the metal surface. Initially, this layer protects the metal, but as it breaks down or gets damaged, the corrosion rate accelerates. Parabolic corrosion is common in materials like aluminium and stainless steel.

In real-world scenarios, corrosion mechanisms can be complex and influenced by various factors such as temperature, humidity, the chemical composition of the environment, and mechanical stress. Therefore, the choice between a parabolic or linear model depends on the observed corrosion behaviour under specific conditions. The assessment of possible weight variations and related models is the first step when trying to define a corrosion process.

The following tables summarise the test matrix and the results.

| Specimen | Exposure time | Specimens <br> Number (total) |
| :--- | :--- | :--- |
| Inox AISI 304 | $\mathrm{t}_{0} ; 50 \mathrm{~h} ; 100 \mathrm{~h} ; 200 \mathrm{~h} ; 750 \mathrm{~h} ;$ | 15 |
| Al Alloy | $\mathrm{t}_{0} ; 50 \mathrm{~h} ; 100 \mathrm{~h} ; 200 \mathrm{~h} ; 750 \mathrm{~h} ;$ | 15 |
| Copper wire | $\mathrm{t}_{0} ; 50 \mathrm{~h} ; 100 \mathrm{~h} ; 200 \mathrm{~h} ; 750 \mathrm{~h} ;$ | 15 |
| Electronics | $\mathrm{t}_{0} ; 50 \mathrm{~h} ; 100 \mathrm{~h} ; 200 \mathrm{~h} ; 750 \mathrm{~h} ;$ | 15 |
| Touch screen | $\mathrm{t}_{0} ; 50 \mathrm{~h} ; 100 \mathrm{~h} ; 200 \mathrm{~h} ; 750 \mathrm{~h} ;$ | 15 |
| Electric plug plastic | $\mathrm{t}_{0} ; 50 \mathrm{~h} ; 100 \mathrm{~h} ; 200 \mathrm{~h} ; 750 \mathrm{~h} ;$ | 5 |

Table 1: Summary of the exposure test matrix.

| Sample | $\begin{aligned} & \mathrm{T} 0(\mathrm{~g}) \\ & \text { Test } 1 \end{aligned}$ | T100h (g) | $\begin{aligned} & \mathrm{T} 0(\mathrm{~g})- \\ & \text { Test } 2 \end{aligned}$ | T200h (g) | $\begin{aligned} & \mathrm{TO}(\mathrm{~g})- \\ & \text { Test } 3 \end{aligned}$ | T750h (g) | $\begin{aligned} & \text { T0(g)- } \\ & \text { Test } 4 \end{aligned}$ | T50h(g) |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Steel1 | 15,7494 | 15,7504 | 15,7005 | 15,7003 | 15,7294 | 15,7296 | 15,7382 | 15,7384 |
| Steel2 | 15,7793 | 15,7814 | 15,7582 | 15,7580 | 15,7883 | 15,7884 | 15,9277 | 15,9279 |
| Steel3 | 15,6599 | 15,6615 | 15,8836 | 15,8841 | 15,7635 | 15,7630 | 15,7346 | 15,745 |
| Al1 | 5,5399 | 5,4258 | 5,5635 | 5,5973 | 5,5353 | 5,5798 | 5,5406 | 5,5701 |
| Al2 | 5,4258 | 5,473 | 5,5227 | 5,5870 | 5,5501 | 5,6124 | 5,5086 | 5,5296 |
| Al3 | 5,5320 | 5,5864 | 5,4946 | 5,5381 | 5,4627 | 5,5186 | 5,2903 | 5,3202 |
| Cu1 | 0,0555 | 0,0559 | 0,0542 | 0,0548 | 0,0541 | 0,0544 | 0,0558 | 0,0560 |
| Cu2 | 0,0540 | 0,0543 | 0,0540 | 0,0539 | 0,0540 | 0,0541 | 0,0535 | 0,0542 |
| Cu3 | 0,0558 | 0,0547 | 0,0544 | 0,0553 | 0,0542 | 0,0552 | 0,0550 | 0,0553 |
| El1 | 4,7087 | 4,7455 | 4,5360 | 4,5625 | 3,6054 | 3,6215 | 2,7780 | 2,7759 |
| E12 | 4,0358 | 4,0749 | 4,8424 | 4,8603 | 3,2003 | 3,2137 | 2,9866 | 2,9943 |
| El3 | 4,0626 | 4,0679 | 2,7857 | 2,7891 | 3,1106 | 3,1163 | 3,6046 | 3,6195 |
| Touch1 | 3,3403 | 3,3498 | 3,5242 | 3,5385 | 3,9217 | 3,9769 | 2,7221 | 2,7394 |
| Touch2 | 4,0683 | 4,0749 | 4,1118 | 4,1492 | 2,4644 | 2,4726 | 3,2733 | 3,2874 |
| Touch3 | 3,6418 | 3,6477 | 4,9096 | 4,9590 | 3,5010 | 3,5113 | 3,6601 | 3,6696 |
| Plastic | 1,0596 | 1,1534 | 1,2220 | 1,1270 | 1,8503 | 1,8615 | 1,0407 | 1,0447 |

Table 2: summary of the weight variations tests, $\mathrm{T} 1,2,3$, and 4 are the different exposure times for each material.

For a quicker data analysis and understanding, average variations tables for each material were done:

| Specimen/time | Average var. (g) |
| :--- | :--- |
|  |  |
| Steel 50 h | 0,0048 |
| Steel 100 h | 0,0016 |
| Steel 200 h | 0.0003 |
| Steel 750 h | 0 |


| Specimen/time | Average var. (g) |
| :--- | :--- |
|  |  |
| Al 50 h | 0,0542 |
| Al 100 h | 0,0719 |
| Al 200 h | 0,0258 |
| Al 750 h | 0,0542 |

Tables 3 and 4: average values for Steel (AISI 304) and Al alloy.

| Specimen/time | Av. var. (g) |
| :--- | :--- |
| Cu 50 h | 0,0552 |
| Cu 100 h | 0 |
| Cu 200 h | 0,0547 |
| Cu 750 h | 0,0546 |


| Specimen/time | Av. var. (g) |
| :--- | :--- |
|  |  |
| El 50 h | 0,0065 |
| El 100 h | 0,0027 |
| El 200 h | 0,0159 |
| El 750 h | 0,0073 |


| Specimen/time | Av. Var.(g) |
| :--- | ---: |
|  |  |
| Touch 50 h | 0,0136 |
| Touch 100 h | 0,0007 |
| Touch 200 h | 0,0337 |
| Touch 750 h | 0,0272 |

Tables 5, 6 and 7: Average values for Cu , Electronics and Touch screen.
From the above data, it is not possible to derive trends, whether linear or parabolic. Aluminum and Copper show the most significant weight increases. All data variations are within the analytic balance sensitivity.
It must be underlined that the actual concentration of HOCl varies with time. The chosen starting value of 2000 ppm was continuously checked during the exposures.

|  | $\mathbf{5 0} \mathbf{h}$ | $\mathbf{1 0 0} \mathbf{h}$ | $\mathbf{2 0 0} \mathbf{~ h}$ | $\mathbf{7 5 0} \mathbf{~ h}$ |
| :--- | :--- | :--- | :--- | :--- |
| Original | 1140 ppm | 1420 ppm | 1030 ppm | 662 ppm |
| $\mathbf{C u}$ | 1160 ppm | 1260 ppm | 1000 ppm | 524 ppm |
| Al | 760 ppm | 420 ppm | 139 ppm | 69 ppm |
| Touch | 1120 ppm | 1060 ppm | 500 ppm | 229 ppm |
| Electronics | 1070 ppm | 840 ppm | 810 ppm | 133 ppm |
| Plastic | 1150 ppm | 1150 ppm | 810 ppm | 466 ppm |

Table 8: HOCl concentration variations with time of HOCl solution and HOCl in contact with the specimens.

Oddly, Aluminum shows the strongest variation when compared to the other samples. It could be related to its electronegativity properties, but the same behaviour is then observed with the plastic specimens, which are electrically neutral. Such variations in concentration must then be connected with casual errors during the exposures.

## 2 Morphology studies

Given the impossibility of quantifying a corrosion mechanism, the main interest of the exposure tests is shifted to SEM imaging.

SEM operates on the principles of electron microscopy, utilizing a focused electron beam to interact with the sample's surface. As electrons strike the sample, they generate signals, including secondary electrons, backscattered electrons, and characteristic X-rays. Detectors capture and convert these signals into images. Interpreting SEM images primarily involves the recognition and analysis of morphological features. These features can vary widely depending on the type of sample and research objective. Common morphological characteristics include surface roughness, particle size and distribution, crystal morphology, porosity, fracture surfaces, and more.

In this study, specimens are analyzed as they are. There is no specific sample preparation or coating/sputtering, given the capabilities of the FEI Inspect $S$ instrumentation.

Moreover, after each exposure, each specimen is Acetone washed and air-dried, without any etching.

Enlargements, main parameters and impacting energy are the same for all materials, as quoted in each picture.

In Scanning Electron Microscopy (SEM), the energy of the electron beam, often referred to as the "accelerating voltage" or "source energy," plays a crucial role in determining various aspects of the imaging process. The accelerating voltage influences several factors in SEM imaging:

- Higher accelerating voltages result in electrons with greater kinetic energy. Electrons with higher energy can penetrate deeper into the sample. This is particularly useful when imaging thick or dense specimens because higher-energy electrons can penetrate the surface layers and provide information from deeper regions of the sample.
- Spatial resolution in SEM refers to the ability to distinguish between two points that are very close to each other. Lower accelerating voltages generally provide higher spatial resolution. At lower energies, the electron beam interacts more strongly with the atoms in the sample, resulting in a narrower interaction volume. This increased interaction at lower energies enhances the imaging resolution and allows for detailed imaging of surface features.
- Depth of field refers to the range along the optical axis (depth) within which the specimen remains in acceptable focus. Lower accelerating voltages lead to a larger depth of field. This means that more features within the sample can be in focus simultaneously, making it easier to obtain sharp images of irregular or uneven surfaces.
- Higher accelerating voltages generate higher-energy electrons that can produce more secondary and backscattered electrons upon interaction with the sample surface. Consequently, higher-energy beams can produce stronger signals, leading to brighter and clearer images. However, this may come at the cost of reduced surface sensitivity.
- Charging effects occur when the electron beam builds up a charge on the insulating or poorly conducting sample surface. Higher accelerating voltages can reduce charging effects because high-energy electrons can penetrate the surface and dissipate the charge effectively.
- Higher-energy electron beams can cause more electron-induced sample damage, especially in sensitive or organic samples. Lower accelerating voltages are often preferred for imaging delicate specimens to minimize electron beam-induced damage.

The choice of the voltage/energy parameters has been made considering both the need to carry on non-destructive imaging over the different surfaces, balancing with the need for sufficient energy for the EDS studies. Higher accelerating voltages result in higher-energy electrons that can excite innershell electrons in the sample atoms, leading to the production of characteristic X-rays. These X-rays
can be analyzed using Energy Dispersive X-ray Spectroscopy (EDS) to determine the sample's elemental composition.

AISI 304

No corrosion phenomena are observed on the steel samples, as previously confirmed by the weight measurements. There are evident traces of salt deposits, which do not produce visible effects on the surface of the substrate. Even after washing in acetone, no damage from salt corrosion was apparent.


Fig. 6 AISI304 exposed for 50 h


Fig. 8: salt depositions


Fig. 7 AISI304 exposed for $50 h$


Fig. 9: detail


Fig. 10: detail

Salt deposition on stainless steel AISI 304 is a complex phenomenon influenced by multiple factors. It occurs through various mechanisms, such as hygroscopic growth, deliquescence, and efflorescence. Hygroscopic growth involves salt particles absorbing moisture from the air and adhering to the steel surface. Deliquescence occurs when salts absorb moisture, forming a solution that corrodes the steel. Efflorescence happens when salts crystallize on the steel surface due to evaporation. Several factors influence salt deposition, including environmental conditions (humidity, temperature, and pollution levels), surface roughness, and exposure duration.
Salt deposition compromises the passive oxide layer on stainless steel AISI 304, leading to localized corrosion. This weakens the material, reducing its mechanical strength and structural integrity. Consequently, it affects the performance and longevity of stainless steel components
The saline scales observed after 100 hours appear less localized than the former ones.


Fig. 11: AISI 304 exposed to 200 ore


Fig. 12: Detail of salt concretions


Fig. 13: detail of salt concretions


Fig. 15: 12.000 $\times$ Enlargement


Fig. 14: Salt deposition enlargement


Fig. 16: AISI 304 exposed for 750 ore


Fig. 18: detail of salt scales



Fig. 17: AISI 304 exposed for 750 ore


Fig. 19: detail of salt scales

Fig. 20: detail of salt scales, $12.000 x$ enlargement

AISI 304; 750 h after Acetone washing/etching (24h)


Fig. 21: AISI304 exposed for 750 after Acetone wash


Fig. 23: AISI304 exposed for 750 after Fig.24: Salt traces

Acetone wash

Fig. 25: Salt traces, $12.000 x$

## The Aluminum alloy

Aluminium is certainly the material that has shown the most macroscopic phenomena. After exposure, the samples appear covered by a thick whitish and non-compact layer, probably a mixture of salt and alumina ( $\mathrm{Al}_{2} \mathrm{O} 3$ ), a typical product of surface oxidation of non-anodized aluminium.
SEM observation allows us to identify (fig. 30 and 31) the points at which the oxidative/corrosive phenomenon starts and begins to "scale" the surface of the metal. Also visible in Figure 49, after washing in Acetone.

Corrosion mechanisms by salt $(\mathrm{NaCl})$ could create structural damage, following different possible behaviours.

- Electrochemical Processes: Aluminum corrosion in saltwater primarily occurs through electrochemical reactions. In a saline environment, water acts as an electrolyte, enabling the flow of electric current. The key reactions involved are the anodic oxidation of aluminium:

$$
\text { Aluminum (Anode): } 2 \mathrm{Al}(\mathrm{~s}) \rightarrow 2 \mathrm{Al}^{3+}(\mathrm{aq})+6 \mathrm{e}^{-}
$$

And the cathodic reduction of water and oxygen:

Water (Cathode): $6 \mathrm{H}_{2} \mathrm{O}(\mathrm{l})+6 \mathrm{e}^{-} \rightarrow 3 \mathrm{H}_{2}(\mathrm{~g})+6 \mathrm{OH}^{-}(\mathrm{aq})$
Oxygen (Cathode): $\mathrm{O}_{2}(\mathrm{~g})+4 \mathrm{H}^{+}(\mathrm{aq})+4 \mathrm{e}^{-} \rightarrow 2 \mathrm{H}_{2} \mathrm{O}(\mathrm{l})$

The net reaction is the formation of Aluminum hydroxide $\left(\mathrm{Al}(\mathrm{OH})_{3}\right)$ and the release of hydrogen gas.

- Pitting Corrosion: Pitting corrosion is a severe form of localized corrosion and is particularly insidious for Aluminum in salt environments. It initiates defects or imperfections on the Aluminum's surface and is accelerated by chloride ions, leading to the formation of small pits that can penetrate the material.
- Galvanic Corrosion: When Aluminum comes into contact with other metals in a salt environment, galvanic corrosion can occur. This phenomenon results from the difference in the electrochemical potential between Aluminum and other metals, which drives the corrosion of the more anodic material (usually Aluminum).

When considering the reference "operating room" where HOCl is sprayed, Al alloys are not part of extremely critical components, for example, windows, small PC holders etc. This is why simple operating instructions could be enough to avoid severe damage.

## 50 hours



Fig. 26 Al exposed for 50 ore. Scales formation.


Fig. 27: Al exposed for 50 ore. Scales formation.


Fig. 28: Scales detail


Fig. 29: Scales detail


Fig. 30: Scales detail, $12.000 \times$


Fig. 31: Clear scales formation


Fig. 33: Scales details


Fig. 35: Salt crystals, $12.000 x$


Fig. 32: Scales details


Fig. 34: Scales details


Fig. 36 Damages on the surface and scales


Fig. 38: Damages on the surface and scales



Fig. 37 Damages on the surface and scales


Fig. 39 Damages on the surface and scales

Fig. 40: Damages on the surface and scales, $12.000 x$

## 750 hours



Fig. 41: Damages and scales


Fig. 43: Damages and scales


Fig. 45: damages and scales


Fig. 42: damages and scales


Fig. 44: damages and scales


Fig. 46: Scales detail

750 hours after Acetone washing, 24 hours


Fig. 47: traces of scales after washing


Fig. 1: Scales after etching: cracks


Fig. 48: traces of scales


Fig. 2: Scales details


Fig. 3: Scales details enlargement

Fig. 5 Scales details enlargement, $24.000 x$



Fig. 4: Scales details enlargement

## The Copper wire

Being part of electrical wires, connectors and electronics, Cu is the most interesting material to test with HOCl in this work. In salt-laden environments, copper is susceptible to corrosion, posing significant challenges in maintaining its integrity and functionality.

The corrosion processes can be summarised as follows:

- Electrochemical Processes: Copper corrosion in saltwater primarily occurs through electrochemical reactions. In the presence of chloride ions, copper undergoes oxidation at the anode:

$$
\begin{gathered}
\text { Copper (Anode): } \mathrm{Cu}(\mathrm{~s}) \rightarrow \mathrm{Cu}^{2+}(\mathrm{aq})+2 \mathrm{e}^{-} \\
\text {Meanwhile, water is reduced at the cathode, forming hydroxide ions: } \\
\text { Water (Cathode): } 2 \mathrm{H}_{2} \mathrm{O}(\mathrm{l})+2 \mathrm{e}^{-} \rightarrow \mathrm{H}_{2}(\mathrm{~g})+2 \mathrm{OH}^{-}(\mathrm{aq})
\end{gathered}
$$

These reactions lead to the formation of copper ions and corrosion products like copper oxide and copper hydroxide.

- Pitting Corrosion: Similar to aluminium copper is susceptible to pitting corrosion in salt environments. Localized imperfections or impurities on the copper surface facilitate the initiation of pits, which can lead to severe structural damage over time.
- Galvanic Corrosion: When copper comes into contact with dissimilar metals in a salt environment, galvanic corrosion can occur due to the difference in electrochemical potential. This process accelerates copper corrosion, especially when coupled with more anodic metals. All the mechanisms mentioned above could lead to potential damages:
- Reduced Conductivity: Corroded copper surfaces impede electrical conductivity, affecting the performance of electrical systems and devices.
- Structural Degradation: Corrosion weakens the structural integrity of copper components, leading to material loss and potential failures in plumbing systems and architectural elements.
- Environmental Contamination: Corrosion products can leach into the surrounding environment, polluting water sources and soil, and posing environmental and health risks.

When considering the reference "operating room", the mentioned damages can become critical.
The observed Copper specimens clearly show a widespread layer of salt deposits, mixed with a probable layer of mixed oxides.

The deposit progressively increases with exposure time, showing some lacerations/laminations in some places.

Unlike Aluminium, the deposit appears compact and not washed by acetone.

## 50 hours



Fig. 6: Salt deposits


Fig. 8: Salt deposits


Fig. 7: Salt deposits


Fig. 9: Salt deposits, details


Fig. 10: Salt deposits detail

## 100 hours



Fig. 12: Wire exposed for 100 hours


Fig. 14: Wire detail


Fig. 11: Salt crystals


Fig. 13: Wire enlargement


Fig. 15: Salt depositions


Fig. 16: Salt depositions, $12.000 x$

## 200 hours



Fig. 17: Copper wire exposed for 200 hours


Fig. 19: depositions details


Fig. 18: Salt depositions


Fig. 20: depositions detail, 12.000 x


Fig. 21: depositions details, salt crystals

## 750 hours



Fig. 23: Copper wire exposed for 750 hours


Fig. 25: Salt deposition, Oxidation


Fig. 22: Salt crystals, $12.000 x$


Fig. 24: Copper wire exposed for 750 hours


Fig. 26: Scales details


Fig. 28: Salt crystals
Fig. 27: Salt crystal


Fig. 29: Sclaes depletion


Fig. 30: Sacles details


| Map Sum Spectrum |  |
| :--- | ---: |
| Element |  |
| C | Weight \% |
| O | 14.16 |
| Na | 26.80 |
| P |  |
| Cl | $\mathbf{1 0 . 5 4}$ |
| Ca | 7.99 |
| Ti | 2.56 |
| Fe | 0.44 |
| Cu | 0.02 |
| Total | 0.06 |

Fig. 31: Salt crystals, $50.000 x$


Spectrum 1: EDS of a salt crystal, with elemental composition

In EDS analysis, the emitted X-rays are collected by a detector, which measures their energy (or wavelength). The detector generates a spectrum that provides information about the energy distribution of the X-rays. This energy-dispersive detection allows for the simultaneous identification of multiple elements within a sample.
In this case, a single Salt crystal was selected as the beam target and its semi-quantitative elemental composition was detected, confirming NaCl over Cu , as expected. The relatively high concentration of Oxygen suggests a parallel ongoing oxidizing process, led by HOCl and water action over the bare metal.

## 750 hours on Cu , after Acetone



Fig. 32; Cu wire after Acetone washing


Fig. 34: Scales after washing



Fig. 33: Cu wire after Acetone washing


Fig. 35: Depositions details

Fig. 36: Deposition detail: $12.000 x$

## Electronic board

The electronics board is an example of a composite sample. It is made of electronic supports, steel capacitors, electrical connection pins, and microchips.

Electronic boards, also known as printed circuit boards (PCBs), are fundamental components in electronic devices, ranging from smartphones and laptops to industrial machinery. These boards consist of intricate networks of conductive pathways, which facilitate the smooth transmission of electrical signals. The choice of materials profoundly influences the efficiency, reliability, and environmental impact of electronic boards.

Types of common materials:

## Substrate Materials:

- FR-4 (Flame Retardant 4): The most commonly used substrate material due to its excellent thermal and mechanical properties.
- Flex PCBs: Made of flexible plastic substrates, suitable for applications requiring flexibility, such as wearable devices.
- Metal-Core PCBs: Designed with metal core (aluminium or copper) for enhanced heat dissipation, ideal for high-power applications.


## Conductive Materials:

- Copper: Widely used for conductive traces due to its high electrical conductivity.
- Gold Plating: Applied to critical connectors and switches for superior conductivity and corrosion resistance.
- Silver Ink: Used in inkjet printing technologies for low-cost, flexible circuits. Insulating Materials:
- Solder Mask: Applied over conductive traces to prevent short circuits and provide mechanical support.
- Silicones and Epoxies: Used for encapsulation and potting, providing insulation and protection against environmental factors.

Exposure to HOCl shows that the metallic connection pins are the parts that undergo salt deposition and oxidation phenomena, as expected.

50 ore


Fig. 37: Electronic board, 50 exposure


Fig. 39: Salt on metallic areas


Fig. 38: Electronic board, 50 exposure


Fig. 40: salt on metallic areas


Fig. 41: Electronic boards, 100 exposure

Fig. 43: Salt depositions over metallic pins



Fig. 42: Salt depositions over metallic pins


Fig. 44: Salt depositions over metallic pins, $12.000 x$.


Fig. 45: Electronic board, 200 hours of exposure


Fig. 47 Electronic board, 200 hours exposure Fig. 48: Scales over metallic pins


Fig. 49: Scales over metallic pins

## 750 hours



Fig. 51: Electronic board, 750 h exposure


Fig. 53: Saline scales


Fig. 50: Scales over metallic pins, $12.000 x$


Fig. 52: Saline scales


Fig. 54: metallic weldings, scales


Fig. 55: Scales detail


Fig. 56: Scales detail


Fig. 57: metallic connectors: salt depositions


Fig. 58: metallic connectors: salt depositions


Fig. 59: metallic connectors: salt depositions


Fig. 60: metallic connectors: salt depositions


Fig. 61: metallic connectors: salt depositions


Fig. 62: metallic connectors: salt depositions

Given the complexity of such kinds of "composite" specimens, i.e. made of plastic, polymers together with metals and other compounds, the performance of an EDS map is quite interesting.

EDS mapping operates on the fundamental principles of X-ray emission and energy-dispersive detection. By scanning a sample with an electron beam, EDS detectors collect X-ray data at each point, creating elemental maps that illustrate the spatial arrangement of elements. The resulting maps offer a visual representation of elemental distribution.


EDS analysis over selected areas.


EDS maps: different colours represent different elements and their graphic distribution over the sample area-oxygen, Silicon, Sodium, Chlorine, phosphorus and Platinum Maps.


Maps for Carbom Copper, Chromium, Iron and Nickel. Oxidation and salt deposition are then graphically and qualitatively described.

## Touch Screen

The touch screens are made of plastic and show no signs of damage or corrosion, other than sporadic salt deposits.

50 hours


Fig 63: touch screen exposed for 50 ore


Fig. 64: traces of salt


Fig. 65: traces of salt
100 hours


Fig. 67: touch screen exposed for 100 ore

Fig. 69: traces of salt



Fig. 66: traces of salt

Fig. 68: traces of salt



Fig. 70: touch screen exposed for 200 hours


Fig. 72: localized depositions

Fig. 74: localize depositions



Fig. 71: localized depositions


Fig. 73: localized depositions

## 750 hours



Fig. 75: touch screen exposed for 750 h


Fig. 77: localized scales

Fig. 79: salt crystals


Fig. 76: Localized scales

Fig. 78: Salt crystals


## Electric plug plastic cover

Just like the touch screen, commercial plastic for electric plugs does not show any corrosion attack, just very localized salt depositions.

50 hours


Fig. 80: Plastic for an electric plug: traces deposition on


Fig. 82: Plastic electric rice plug: traces of depositions


Fig. 81: Plastic for electric plug: traces of deposition


Fig. 83 Plastic for an electronic plug: traces of deposition

100 hours


Fig. 84: Exposed plastic, 100 hours. No deposits

200 hours


Fig. 86. Exposed plastic, 200 hours. No deposits


Fig. 85: Exposed plastic, 100 hours. No deposits


Fig. 87. Exposed plastic, 200 hours. No deposits


Fig. 88: Exposed plastic, 200 hours. No deposits



Fig. 89: Exposed plastic, 200 hours. No deposits

Fig. 90: Exposed plastic, 200 hours. No deposits

## 750 hours



Fig. 91: plastic exposed for 750 ore. Traces of salt



Fig. 92: plastic exposed for 750 ore. Traces of salt

Fig. 93 Plastic exposed for 750 ore. Traces of salt

Being luster and chemically inert towards the HOCl solution, plastic parts show only very localized salt deposition without scales or corrosion phenomena.

## 3 LCA experimental.

The test strips have been divided into six sub-areas of $0.42 \mathrm{~m}^{2}$ each, marked with coloured tape strips. Each sub-area has been nebulized with 15 ml of a protein and lipid-based standard solution and left to dry naturally. After 24 hours, cleaning conditions, such as organic dirt removal capacity, have been measured in three sub-areas using a qualitative clean test kit. The clean test consists of a buffer for the detection of organic residues (proteins, fats and sugars) specifically designed to check the level of cleanliness of a given work surface. The test provides qualitative data based on photometric indications. The product is composed of test tubes plastic test tubes containing a buffer, a vial (reagent A: bicinchoninic acid-BCA) and a floppy disc (reagent disc (reagent B: CuSO

Sanitization test: removal of microbial charge from the surface.

Using the procedure previously described, the remaining three sub-areas were sampled using RODAC (Replicate Organism Detection and Counting) contact Petri plates (Liofilchem, Italy). Adhered microorganisms were transferred directly to the plates via direct contact under standardized conditions (applying $0.02 \mathrm{~kg} / \mathrm{cm}^{2}$ of constant pressure for 10 s ). The plates had a surface area of 24 $\mathrm{cm}^{2}$ and a bottom grid to facilitate the counting of colonies. Mesophilic bacteria and fungi were detected. Selected cultivation media were used for bacteria (Plate Count Agar at $\mathrm{pH}=7.0 \pm 0.2$ ), and fungi (Sabouraud Chloramphenicol Agar at $\mathrm{pH}=5.6 \pm 0.2$ ). Mesophilic bacteria and fungi were incubated at $37^{\circ} \mathrm{C}$ for 48 hours and $22^{\circ} \mathrm{C}$ for 120 hours, respectively.
RODAC plates were then incubated within 2 h , colonies were counted after 24-48 h. All sampling was carried out in triplicate.
A total of 144 samples were collected. Samples were transported to the laboratory in refrigerated insulated bags $\left(4^{\circ} \mathrm{C}\right)$. Microbial density was expressed in terms of CFUs (Colony-Forming Units)/100 $\mathrm{cm}^{2}$ and calculated as

$$
\mathrm{R}=\mathrm{Ut}-\mathrm{At}
$$

where:
$\mathrm{R}=$ microbial charge reduction
$\mathrm{Ut}=$ average value of the number of colonies recovered on the control surface (track D ) after 24 hours, expressed as Log 10
$\mathrm{At}=$ average value of the number of colonies they were recovered on the treated surface (tracks A, B or C) after 24 hours, expressed as Log 10 .

Finally, R\% has been derived from the following formula:

$$
\mathrm{R} \%=\left(1-10^{-\mathrm{R}}\right) \times 100
$$

The microbial density, based on INAIL (Istituto Nazionale Assicurazione Infortuni sul LavoroNational Institute for Insurance against Industrial Injuries) standard protocols for civil environments should be also expressed in terms of CFU/ $100 \mathrm{~cm}^{2}$, calculated by dividing the count result ( N , number of colonies/plate) by the contact area of the plate with the test surface $\left(24 \mathrm{~cm}^{2}\right)$ :

$$
\mathrm{CFU} / 100 \mathrm{~cm}^{2}=\mathrm{N} / 24 * 100
$$

A very slight growth ( $<40$ colonies $/ 100 \mathrm{~cm} 2 \cong 10 \mathrm{CFU} / 24 \mathrm{~cm}^{2}$ ) were considered acceptable for the standard.

## Surface damage evaluation with SEM

The Scanning Electron Microscope at ENEA DISPREV was used. A small sample of quartz concrete $(10 \times 10 \mathrm{~mm})$ and a coated hardwood floor $(10 \times 10 \mathrm{~mm})$ were softly cleaned to remove any layers or deposits of dust. Samples were then sprayed with a concentrated HOCl solution at 2000 ppm , appropriately created by adding NaCl to water. After exposure, the samples were wiped, to simulate the wash-and-dry operation. For observation under the SEM microscope, samples were placed on conventional aluminium stubs and made conductive with a carbon adhesive disc. To gather significant elemental mapping, the SEM parameters were set to 30 Kv and spot 7 , allowing a faster and more accurate EDS acquisition.

## LCA methodology

In this study LCA follows the standardised method, regulated by ISO 14040 series, which consists of four stages: (1) goal and scope definition; (2) life cycle inventory construction; (3) environmental impact assessment: and (4) interpretation of the results. [64, 65, 66]

LCA was carried out using xxxxxx software, using the xxxx method. The goal and scope was the quantification of the Global Warming Potential (GWP) of a wash-and-dry machine used for cleaning service in civil buildings in Italy. According to the General Programme Instructions for Environmental Product Declarations ver. 3.0, of the PCR 2021:07 ver. 1.0 "Machinery for professional cleaning") and 14040: 2006 (Environmental management - Life Cycle Assessment Principles and framework), the functional unit (FU) is 1 hour worked by a wash-and-dry machine equipped with an HOCl production system in comparison with a traditional detergent-based machine.

Data collection for life cycle inventories included specific data, collected directly during the cleaning tests, whereas all background data on the production of electricity, materials and transport, was derived from the Ecoinvent 3.8 database. All the data used refers to 2023, the year in which the service was provided. The system boundaries include:

1) Upstream processes: raw materials production for machine construction and packaging
2) Core processes: supply chain and transportation of raw materials, production of electricity and water consumption for semi-finished and finished machine assembling,
3) Downstream processes: machine use and maintenance, transportation to the experimental site, waste management and machine end-of-life
For the present study has been assumed that the following characteristics were identical in the compared systems and consequently excluded by the boundaries:

- the transport of personnel involved and personnel technical vests,
- the plants for machine construction
- the total area of the plant
- data quality

The output of the analysis GWP evaluates the contribution at a time horizon of 100 years to the greenhouse effect provoked by greenhouse gases emitted in the atmosphere as a consequence of the process under study, measured as $\mathrm{kg} \mathrm{CO}_{2}$ equivalent ( $\mathrm{kgCO}_{2}$ eq.) per FU .
The impact assessment has been limited to a single impact category because of the lack of reliable data for calculating other impact categories. [67, 68, 69]

## Results: Cleaning effectiveness

The effect of organic dirt removal due to treatments applied to surface tracks has been reported in Figure 142.

(a)

(b)

Fig 142 - Qualitative depiction of CLEANING TEST results (a) and test tubes results (b). Depending on the level of organic dirt, the test solution colored from violet to light blue.

Before the treatments, floor surfaces appeared very dirty, whereas, in the post-treatments, B, C and D sub-areas showed the complete removal of organic residues on surfaces, differently from the untreated track (A), as expected.

## Microbial charge reduction effectiveness

The comparison among the different sanitization protocols (i.e., with water, HOCl and detergent) has evidenced that, except for cleaning with only water, the percentage of abatement of microbial charge was found acceptable (Figure 143)

(a)

(b)

Fig 143 - Percentage of abatement of bacterial (a) and fungal (b) charges on the three selected tracks areas (B, water; C, Ecolabel detergent; $\mathrm{C}, \mathrm{HOCl}$ ) between pre-treatment and post-treatment. Data are the average of 2 independent experiments performed in triplicate (average $\pm$ standard deviation), and values are represented as a percentage of reduction.

Percentage reduction of bacterial counts was $84.9 \pm 1.2 \%, 96.9 \pm 1.9 \%$ and $96.9 \pm 2.0 \%$ for water, HOCl -based and detergent-based treatment, respectively. Percentage reduction of fungal counts is $85.6 \pm 3.1 \%, 99.3 \pm 0.5 \%$ and $99.3 \pm 0.4 \%$ for water, HOCl-based and detergent-based treatment, respectively. [70, 71, 72, 73]

Treatment based on the use of only water is significantly less effective than treatments based on the use of additives to water. The percentage of abatement using water alone is due to the effect of mechanical removal.

After treatment with both HOCl and detergent the number of $\mathrm{CFU} / 100 \mathrm{~cm}^{2}$ was $<40$ bacterial colonies ( $37.3 \mathrm{CFU} / 100 \mathrm{~cm}^{2}$ and $39.1 \mathrm{CFU} / 100 \mathrm{~cm}^{2}$ respectively), as requested to consider acceptable the microbial removal, whereas the treatment with water alone does not warrant the correct sanitization, with a residual contamination of about $306.2 \mathrm{CFU} / 100 \mathrm{~cm}^{2}$.

## SEM observation

To clarify the effect of HOCl treatment on floor surface, and consequently to evaluate the potential damages, the surface morphologies were observed using SEM before and after the treatments. Samples were over-exposed to HOCl solutions, i.e. at $\mathrm{HOCl}-2000 \mathrm{ppm}$, to test floors in the strongest possible conditions. Potential damages due to HOCl treatment have been tested on quartz concrete
and coated wooden floors as reference materials. No apparent change in the surface morphology, as well as no saline crystal deposition evidence, has been found (Figure 144).


Figure 144- Effects of 2000 ppm HOCl treatment on floor surfaces analyzed by SEM-EDS microscopies; (a) SEM image of quartz concrete untreated; (b) SEM image of quartz concrete $\mathrm{HOCl}, 2000 \mathrm{ppm}$ treatment; (c) (a) SEM image of coarted hardwood floor untreated; (d) SEM image of coarted hardwood floor HOCl, 2000ppm treatment. No salt crystals are apparent.

The following pictures ( $145 \mathrm{a}, \mathrm{b}$ ) are overlayed elemental maps. Where standard micrographies give morphological information, i.e. possible surface modifications, corrosion, scales deposition, the overlayed colour maps describe the relative distribution of the detected elements by means of the EDS probe. In this specific experiment, micrographies could have
revealed saline crystals deposition, EDS maps could have described Na and Cl distribution over the surface. Any single element si artificially depicted with a different colour.


Fig. 145- Effects of 2000 ppm HOCl treatment on floor surfaces analyzed by SEM-EDS microscopies: EDS mapping; (a) MAP on treated quartz; (b) Map on coated hardwood floor, 2000 ppm treatment.

Semi-quantitative microanalysis data from SEM-EDS show almost identical elemental composition for both materials, before and after the treatments with HOCl. Elemental mapping (figure 6; a, b) after HOCl exposure represents with artificial colours the relative concentration of the surface elements. There is no Na or Cl detectable presence. In Table 3, data spot no difference in samples regarding NaCl residual deposition, as well as the presence of traces of oxidation. All the floor samples have shown no damage effects, due to to HOCl .

1. Table 3. Semi-quantitative microanalysis data from SEM-EDS spectrum for the two-floor materials (quartz concrete and hardwood) before and after HOCl treatments.

|  | Quartz concrete |  | Hardwood floor |  |
| :--- | :--- | :--- | :--- | :--- |
| Element | Untreated | Treated | Untreated | Treated |
| C | $17.84 \pm 0.19$ | $15.81 \pm 0.16$ | $56.70 \pm 0.08$ | $56.42 \pm 0.07$ |


| O | $43.51 \pm 0.11$ | $43.92 \pm 0.10$ | $26.61 \pm 0.07$ | $26.56 \pm 0.06$ |
| :--- | :--- | :--- | :--- | :--- |
| Na | $0.70 \pm 0.01$ | $0.77 \pm 0.01$ | - | - |
| Mg | $1.63 \pm 0.01$ | $1.63 \pm 0.01$ | $0.04 \pm 0.00$ | $0.04 \pm 0.00$ |
| Al | $6.19 \pm 0.02$ | $6.61 \pm 0.02$ | $0.61 \pm 0.00$ | $0.62 \pm 0.00$ |
| Si | $17.76 \pm 0.05$ | $19.13 \pm 0.04$ | $1.15 \pm 0.00$ | $1.16 \pm 0.00$ |
| P | $0.87 \pm 0.01$ | $0.77 \pm 0.01$ | - |  |
| S | $0.25 \pm 0.00$ | $0.28 \pm 0.00$ | $1.40 \pm 0.00$ | $1.42 \pm 0.00$ |
| Cl | $0.06 \pm 0.00$ | $0.06 \pm 0.00$ | $0.06 \pm 0.00$ | $0.06 \pm 0.00$ |
| K | $1.85 \pm 0.01$ | $1.93 \pm 0.01$ | $0.07 \pm 0.00$ | $0.07 \pm 0.00$ |
| Ca | $4.55 \pm 0.01$ | $4.22 \pm 0.01$ | $2.34 \pm 0.01$ | $2.43 \pm 0.01$ |
| Ti | $0.37 \pm 0.00$ | $0.39 \pm 0.00$ | $4.11 \pm 0.01$ | $4.24 \pm 0.01$ |
| Mn | $0.12 \pm 0.00$ | $0.12 \pm 0.00$ | - | - |
| Fe | $4.04 \pm 0.01$ | $4.08 \pm 0.01$ | - | - |
| Zn | $0.18 \pm 0.01$ | $0.15 \pm 0.01$ | - | - |
| Sr | $0.07 \pm 0.02$ | $0.07 \pm 0.02$ | $0.11 \pm 0.01$ | $0.11 \pm 0.01$ |
| Ba | - | - | $6.80 \pm 0.02$ | $6.92 \pm 0.02$ |
| Total | 100 | 100 | 100 | 100 |

The high presence of oxygen $(\mathrm{O})$ is because metals are usually in the form of inorganic oxides. In particular, quartz is a crystalline mineral composed of silica dioxide. Concrete is composed of silica $(\mathrm{Si})$, iron $(\mathrm{Fe})$, aluminium $(\mathrm{Al})$ and calcium ( Ca ) oxides, whereas titanium ( Ti ) and barium $(\mathrm{Ba})$ are used as common elements in wood paints. Parquet floors are never rough wood made, but nitrocellulose or polyurethane painted. Metals are commonly part of such kinds of paints.

It must be underlined that possible salt deposition is a normal consequence of the HOCl application method but the effect is strongly dependent on surface roughness. Both coated hardwood floors and quarts-concrete are characterized by smooth surfaces, allowing a very effective mechanical cleaning of the surfaces.

## LCA analysis

The upstream processes inventory has shown that the two machines have been built with identical components, except for the two-electrochemical cells unit in the HOCl -based machine, resulting in a higher weight ( 218.67 kg vs. 214.18 kg ), and consequently in a higher GWP value (Table 4).

Table 4. GWP (as $\mathrm{kgCO}_{2} \mathrm{eq} / \mathrm{FU}$ ) related to the main processes and phases of the life cycle of the wash-and-dry machines compared in the present study

| Process | Phase | HOCl-based wash-and-dry machine ( $\mathrm{kgCO}_{2} \mathrm{eq} / \mathrm{FU}$ ) | Detergentbased wash-and-dry machine $\left(\mathrm{kgCO}_{2} \mathrm{eq} / \mathrm{FU}\right)$ |
| :---: | :---: | :---: | :---: |
| Upstream | Raw materials production | 0.533 | 0.548 |
| Core | Supply chain and transportation of raw materials <br> Electricity and water consumption for machine assembling | v0.043 e0.046 | 0.046 0.046 |
| Downstream | Use - energy consumption | 0.395 | 0.488 |
|  | Use - water consumption | 0.011 | 0.011 |
|  | Use - detergent consumption | $0.570$ | - |
|  | Transportation to the experimental area | $0.005$ | 0.005 |
|  | Machine maintenance | 0.095 | 0.095 |
|  | Machine end-of-life | 0.009 | 0.009 |
|  | Waste management | 0.016 | 0.016 |
|  | TOTAL GWP | 1.72 | 1.26 |

The cradle-to-grave analysis carried out on the two wash-and-dry systems has evidenced that the use of HOCl -based machines leads to an overall GWP reduction of about $30 \%$ per hour worked. The higher impact of the detergent-based system is related to the use of detergent, corresponding to about $34 \%$ of the overall impact, whereas, the HOCl -based machine generates higher emissions in the upstream phase, due to the increased weight of the electrochemical cells and in the downstream
for higher electricity consumption (corresponding to about $44 \%$ and $39 \%$ of the overall GWP, respectively). Water consumption, machine maintenance, waste management and machine end-oflife do not significantly contribute to the overall GWP impact.

## 4. Discussion

## 1: salt deposition and Copper Corrosion

As stated before, Copper represents the key problem when NaCl deposits after HOCl nebulization. It is the only reference material part of internal components inside the considered standard "operating room".

The common use of a sprayed disinfectant is a very common procedure: spray/wipe/dry. All the considered materials undergo this procedure: any NaCl unwanted deposition is then minimized. But, if the material is inside electronics or electric plugs, no wiping or drying by the operator happens and impurities accumulation starts.

Despite its excellent corrosion resistance in many environments, copper materials are vulnerable to corrosion when exposed to salt-containing media. Salt corrosion can compromise the structural integrity and aesthetic appeal of copper, making it imperative to understand the underlying mechanisms and devise effective corrosion mitigation strategies.
The experimental data shown in this chapter represent a screening test over reference materials. Some of the chosen materials can be regarded as "not critical", i.e. Aluminium, used for example for windows, small tripods, stainless steel, part of solid structures, or plastic plates in walls. The spray of HOCl could indeed lead to possible damages, still not being troublesome for the chosen environment. On the other hand, bare metals, like Cu or connectors in electronics can cause criticalities when corroding, leading to possible malfunctioning of important instrumentations.

This is why the evidence of saline corrosion over Cu substrates is the most important information gathered from this experience. Salt corrosion of Copper occurs through electrochemical processes, primarily driven by the presence of chloride ions.

The primary mechanisms include:

- Pitting corrosion: localized corrosion in the form of pits or holes on the copper surface.
- Crevice corrosion: occurs in confined spaces where stagnant electrolytes accumulate, facilitating localized corrosion.
- Stress Corrosion Cracking (SCC): a combination of tensile stress and the presence of chloride ions can induce SCC in copper.

There are several factors influencing the rate and severity of salt corrosion in copper:

- Chloride concentration: higher chloride levels in the environment increase the risk of corrosion.
- Temperature: elevated temperatures can accelerate the corrosion rate.
- Oxygen levels: the presence of oxygen is crucial for the formation of copper oxides, which protect against corrosion.
- pH levels: the pH of the environment can significantly impact corrosion rates.

In the present case of HOCl nebulization, the Chlorine part of an oxidizing acidic solution is the key factor of the depicted corrosion process over the surface of the bare metal. Pitting corrosion is the main mechanism observed.

Pitting corrosion often starts with a localized defect in the protective oxide layer on the metal's surface. This defect can be caused by various factors, including surface contamination, mechanical damage, or imperfections in the metal's crystal structure.

Several factors contribute to pitting corrosion:

- Presence of chlorides (e.g., salt): Chloride ions, such as those found in salt (sodium chloride), are known to be particularly aggressive in causing pitting corrosion. They can penetrate the protective oxide layer and facilitate the breakdown of the metal's structure.
- Local Variations in Environment: Pitting corrosion can occur in areas where there are local variations in environmental conditions, such as differences in oxygen concentration, pH , or temperature.

Once a pit forms, it acts as a miniature electrochemical cell. In the presence of an electrolyte (e.g., saltwater, as in this case), anodic and cathodic areas are established within the pit. This leads to the dissolution of metal ions from the anodic areas and their migration to the cathodic areas, resulting in the continuous expansion of the pit. In the end, pitting corrosion can significantly compromise the structural integrity of the metal.

The corrosion process of copper in the presence of NaCl can be explained by the following electrochemical reactions:

Anode Reaction (Oxidation): $\mathrm{Cu} \rightarrow \mathrm{Cu}_{2}++2 \mathrm{e}-\mathrm{Cu} \rightarrow \mathrm{Cu}_{2}++2 \mathrm{e}^{-}$
Cathode Reaction (Reduction): $2 \mathrm{H}_{2} \mathrm{O}+\mathrm{O}_{2}+4 \mathrm{e}-\rightarrow 4 \mathrm{OH}-2 \mathrm{H}_{2} \mathrm{O}+\mathrm{O}_{2}+4 \mathrm{e}-\rightarrow 4 \mathrm{OH}-$

Overall Reaction:

$$
\mathrm{Cu}+2 \mathrm{H}_{2} \mathrm{O}+\mathrm{O}_{2} \rightarrow \mathrm{Cu}_{2}++4 \mathrm{OH}-\mathrm{Cu}+2 \mathrm{H}_{2} \mathrm{O}+\mathrm{O}_{2} \rightarrow \mathrm{Cu}_{2}++4 \mathrm{OH}^{-}
$$

In this process, copper $(\mathrm{Cu})$ reacts with water $\left(\mathrm{H}_{2} \mathrm{O}\right)$ and oxygen $\left(\mathrm{O}_{2}\right)$ in the presence of chloride ions $\left(\mathrm{Cl}^{-}\right)$to form copper ions $\left(\mathrm{Cu}^{2+}\right)$ and hydroxide ions $\left(\mathrm{OH}^{-}\right)$. Just like iron corrosion, copper corrosion involves the dissolution of the metal into the surrounding electrolyte.

The chloride ions play a crucial role in accelerating the corrosion of copper. They destabilize the passive film that typically forms on the copper surface, making the metal more susceptible to further corrosion. Additionally, chloride ions can catalyze the reduction of oxygen, which promotes the formation of copper ions and hydroxide ions.

Furthermore, copper corrosion products, such as copper chloride compounds, can form on the surface of the metal, leading to pitting corrosion. Pitting occurs when localized areas of the metal surface are attacked, leading to the formation of small pits or craters. This type of corrosion can significantly compromise the structural integrity of copper-based components.

On Copper itself, even though not strictly part of this work, several mitigating strategies are commonly considered:
a. Alloying: Copper can be alloyed with elements such as tin, aluminium, or nickel to improve its corrosion resistance. For example, copper-nickel alloys ( $\mathrm{Cu}-\mathrm{Ni}$ ) have found extensive use in marine applications due to their exceptional resistance to saline corrosion.
b. Protective Coatings: The application of protective coatings, such as epoxy or polyurethane paints, can further shield copper from direct contact with saltwater and enhance its longevity. c. Cathodic Protection: Cathodic protection systems, such as impressed current and sacrificial anodes, can be used to provide an external source of electrons, thereby preserving the integrity of copper structures by controlling the corrosion potential.
d. Design Considerations: Proper design and drainage systems can minimize the accumulation of stagnant saltwater, which can exacerbate corrosion.
e. Environmental Monitoring: Regular monitoring of environmental conditions and corrosion rates helps to identify and address issues before significant damage occurs.
"e" is the key point here: where impurities in the nebulized disinfectant cannot be forecasted or well controlled using production quality assessments, the only way to avoid damages is to physically protect the bare metals, using simple plastic covers.

Surface finishing plays a crucial role in protecting metals from corrosion, including the specific case of sodium chloride $(\mathrm{NaCl})$ corrosion, which is commonly referred to as salt corrosion. The main experimental outcome of this experimental campaign is the evidence of pitting corrosion over bare metals, most on Copper, enhanced by the presence of NaCl in the nebulized product.

The corrosion behaviour, mainly consisting of the formation of mixed compositions' scales and layers over the surface is thus strictly bonded to the type of surface finishing.

As an example, usually, steel tripods or Aluminium alloy fixtures are machined, polished and glossy materials. The corrosion resistance of such substrates is enhanced more using anodizing or chroming processes.

On the other hand, Cu electric wires or bare metal conductors/connectors inside electronics are not surface machined or modified, leaving the porous interface exposed to degradation and corrosion. Coupling this physical macroscopic fact with their electronegativity properties, the occurrence of pitting corrosion must be regarded as expected.
Common approaches for the mitigation of such processes are:

- Material Selection: Choosing corrosion-resistant alloys, such as stainless steels with higher chromium and molybdenum content, can significantly reduce the susceptibility to pitting corrosion.
- Protective Coatings: Applying protective coatings, such as paints or specialized corrosionresistant coatings, can act as a barrier against chloride ions.
- Proper Design: Designing structures and components in a way that avoids crevices and areas where stagnant solutions can accumulate helps prevent pitting corrosion.
- Controlled Environment: Limiting the exposure of susceptible metals to chloride-rich environments, especially in applications like industrial equipment and pipelines, can mitigate pitting corrosion.
Of course, none of the above methods are applicable in the present case, but the last.

It has to be underlined, as quoted in the introduction, that pitting corrosion is enhanced by electrochemical processes. In the case of electric Cu wire, this is the case.

In this work, however, only the simple compatibility test was assessed, still being a good screening for a good practice operator manual.

Performing accelerated exposure tests with a water solution and a 220 v current attached is beyond the technical possibility of our facilities.

Considering the interaction between bare metal and nebulized HOCl , the only possible strategy to avoid unwanted corrosion problems and subsequent damage to the instrumentation would be a "good practice" suggestion to the operator. Such a list of actions and behaviours might appear trivial, but they indeed are crucial when avoiding damage to critical devices is necessary.

The operator should:

- Identify areas with electrical wires and electronic devices. These include offices, computer rooms, laboratories, and production areas. Being especially cautious around power outlets, switches, and exposed wiring.
- Familiarize yourself with the layout of the space in cleaning. Knowing the locations of electrical outlets and electronic devices helps to plan the cleaning route effectively.
- Whenever cleaning around electrical outlets or equipment is necessary, turn off the power if it doesn't disrupt essential operations. This minimizes the risk of electrical shock and equipment damage.
- Place warning signs or cones around areas where cleaning is in progress, especially if power cannot be turned off. This alerts others to be cautious and helps prevent accidental contact with electronic equipment.
- Microfiber cloths are ideal for cleaning electronic devices and screens. They capture dust particles without scratching sensitive surfaces.
- Use a damp (not wet) microfiber cloth for cleaning electronic surfaces. Avoid excess moisture, as it can seep into devices and cause damage. For keyboards, use specialized cleaning brushes or compressed air to remove debris.
- Use permanent or removable plastic covers for open plugs and unprotected electronics fan grids.
- Ensure cleaning carts are stable and have designated compartments for cleaning solutions, tools, and waste disposal.
- Conduct training programs for cleaning operators, emphasizing the importance of proper cleaning techniques around electronics. Provide demonstrations and simulations to reinforce learning.
- Encourage cleaning operators to report any damaged or malfunctioning electronic equipment immediately. Prompt reporting allows for quick assessment and repair, minimizing potential risks, especially as far as operating room electronics are concerned.

The most common strategy to avoid corrosion processes is the modification of the properties of the substrates, making them more resistant and inert. This is impossible in the present case, where the mitigation of the damages over materials must be, as was summarized in the proposed "good practice manual", part of the product application method.

## 2 LCA study

The use of chemical-based detergents and disinfectant agents has rapidly increased in the last year, especially since the COVID-19 pandemic, despite their potential toxicity to humans and the environment. In addition, the habit of disinfection has become part of cleaning practice, even in sectors where cleaning has traditionally been seen as the removal of inorganic and organic dirt, rather than the removal of microorganisms.

In this study, the cleaning and sanitizing performance of an innovative system based on HOCl and a traditional eco-labelled detergent have been compared. HOCl has the advantage of leaving no chemical residues on the surfaces or in the residual water, because, once it has oxidized the dirt and microorganisms, it is deactivated and reverts to NaCl . In the present application, an HOCl concentration of 10 ppm was achieved by using only the concentration of NaCl normally present in tap water, without the need for an external salt solution supply. The wash-and-dry machine equipped with electrochemical cells is capable of cleaning and sanitising floor surfaces using tap water only, properly activated. Results have shown no significant differences in both organic dirt and microbial removal between the Ecolabel detergent and HOCl-based systems. The two treated tracks (C and D) were found acceptably cleaned and sanitized, and the effectiveness of the HOCl-based system has always been comparable to the Ecolabel detergent.

Moreover, HOCl-based solution has shown not to damage floor surfaces even after more than thousands of applications and to be safe also for sensitive surfaces used as control. Unlike bleach or chlorine solutions, HOCl is not corrosive on surfaces or equipment, because of slightly acidic pH conditions. The optimal pH range with $>95 \%$ of HOCl in solution was between 5.5 and 6.5 . Theoretically, at this interval, HOCl is the predominant chlorine form. In contrast, alkaline conditions ( $\mathrm{pH}>8.0$ ) cause hypochlorite ions to predominate, and very low pH favours the formation of chlorine gas, both toxic and corrosive. Moreover, extensive research has confirmed that HOCl is the most effective antimicrobial form of chlorine.

Quartz concrete is the most used floor material in both commercial and recreational spaces, and it has to be tough and durable. SEM-EDS images have shown that HOCl does not damage the surface floor at all, even after several applications. The specific wash-and-dry cleaning method operated by the machine also avoids NaCl deposition on the floor surface.

The comparative LCA analysis showed that the use of the HOCl system integrated into the wash-anddry machine for floor cleaning and sanitization permits avoiding about $30 \%$ of emissions per hour worked compared to the use of Ecolabel detergent. The environmental value added of the $\mathrm{HOCl}-$ based machine is even more clear if the scenario of application on an annual basis is considered. Based on the comparative analysis, the cleaning service provided with the HOCl -based machine leads to a reduction of $2,760 \mathrm{kgCO}_{2} \mathrm{eq} / \mathrm{year}$, considering an average of 6,000 hours worked by a single machine. Even with the higher emissions in the upstream processes due to the inclusion of electrochemical cells, the complete elimination of the detergent determines a significant reduction in environmental impact.

## 5. Conclusions

The very origin of this work starts from COVID-19-related activities. ENEA, the partner of a POR FESR program financed by Regione Emilia Romagna, coordinated by GATE srl, started the first collaborations with GATE in that context. Now named ERDF, The Emilia-Romagna ERDF Regional Programme (ERDF RP) is the programming document that defines strategy and operations for the use of funds allocated to the Region by the European Regional Development Fund (ERDF).

The goal of the present experimental campaign, which became a PhD , was the attempt to assess the compatibility of HOCl with reference materials, as well as to define precisely its ecological advantages versus other similar disinfectants.

The inner complexity of the chosen reference environment in terms of different possible materials of interest is the origin of a sort of twofold finding.

Where the ecological advantages of HOCl are confirmed by the LCA analysis exercise, the possible damages of salt, the presence of which is connected with HOCl production methods and quality controls, might be a concern for some of the pointed substrates.

Some of the considered materials did not show any degradation due to exposure, while metals, especially Cu , showed scales and corrosion phenomena. A "good practice" manual for the operator, to avoid NaCl deposition inside critical points is the best option to avoid damage to the instrumentation.

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