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EFFECTS OF PASSIVE AND ACTIVE DECONTAMINATION ON METAL MATERIALS CONTAMINATED BY SULPHUR MUSTARD (YPERITE)

This paper reports the results of the experimentally determined effects of decontaminating agents on metal surfaces resulting from passive and active decontamination after sulphur mustard (Yperite) contamination. The paper includes an analysis of the experimentally obtained results for each metal (Zinc, Nickel, Aluminium, Brass, Steel, Copper).

Keywords: *decontamination, yperite, metal, surface, pH potential*

1. Introduction

Decontamination refers to a set of methods, procedures and means used to remove effectively contaminating substances. Since the complete removal of contaminating substances is rarely perfect (due to residual / secondary contamination), the definition can be amended by saying that the goal of decontamination is to reduce the harmful effect of contamination to a safe level or to eliminate it.

This paper deals with the effect of decontaminating agents on the surfaces of decontaminated metals contaminated with sulphur mustard (HD), known as active decontamination, or uncontaminated with HD, the so-called passive decontamination. Knowledge of the effects may indicate the necessity to use a different material or surface treatment for the selected metal.

The most frequently used chemical procedures for decontamination during the liquid phases are strong oxidizing agents in hydrogen peroxide type solutions, ozonization and decomposition with strong acids or alkalis. Decontaminating agent application then depends directly on the form and extent of decontamination and on the type of the decomposed substance.

2. Experiments

For the purpose of the experiments, the decontaminating solutions Hvezda SCH [1-2] a two-component agent with combined decontaminating effects, were selected. The component trade name CC contains in particular hydrogen peroxide, while the component trade name AB includes an ethoxylated fatty alcohol, sodium hydroxide. The key component is quaternary alkyl (C_{12}-C_{16}) benzyl dimethyl ammonium chloride and a hypochlorite mixture - solution containing 2.5 % by weight active chlorine and 2 % by weight sodium hydroxide.

During the experiments, the focus was on the materials used for the construction of critical infrastructure, specifically on those used for the construction of Prague's Metro, an important constituent part of municipal transport in Prague. Thanks to the long-time cooperation with the Prague Public Transport Company, the operator of Prague's Metro, the surface testing samples of materials, which were actually used, were acquired, see Table 1.

3. Passive decontamination

Surfaces of the samples were scanned using digital microscopes. Time of exposure to decontaminating solutions was 1 and 3 hours, and the solutions were applied by manual spraying. The surfaces of metal samples (0.4 m^{-2}) were divided into 4 areas with defined circular zones for testing the content of 7 cm^{-2}. The H1 and H3 regions were reserved for the Hvezda solution with the times of exposure 1 and 3 hours, while the hypochlorite mixture was applied to the N1 and N3 regions with the times of exposure 1 and 3 hours. After exposure to decontaminating solutions, the surfaces of individual samples were dried up, washed with distilled water and scanned. A total of 8 samples were processed in the aforementioned manner. The scanned images were compared. Changes on the surfaces were so significant that it was decided to have these changes examined and assessed at the Department of Material Engineering at VSB - Technical University of Ostrava.

Both of the used decontaminating solutions were alkaline (pH 13-14) with oxidizing nature (having the potential metals $E_{cor} \approx 0.5\text{-}1$ V if a standard hydrogen electrode is used). Based on the E-pH diagrams, it was possible to assess the thermodynamic possibility of formation (stability) and the type of corrosion products in the given region. However, E-pH diagrams do not allow the rate of corrosion formation (kinetics) to be determined. Both peroxide and hypochlorite have the strong oxidizing effects. The pH values of individual environments were ascertained directly by measurement or calculated based on composition. The value of potential taken up by the metal was determined as a

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***Table 1** Overview and designation of used materials*

No.	Name	No.	Name
K 1	Zinc-plated metal sheet	K 5	Stainless steel (18/8)
K 2	Nickel	K 6	Stainless ferritic steel (Cr12)
K 3	Aluminium (99 %)	K 7	Copper (99 %)
K 4	Brass (CuZn30)	K 8	Zinc - iron

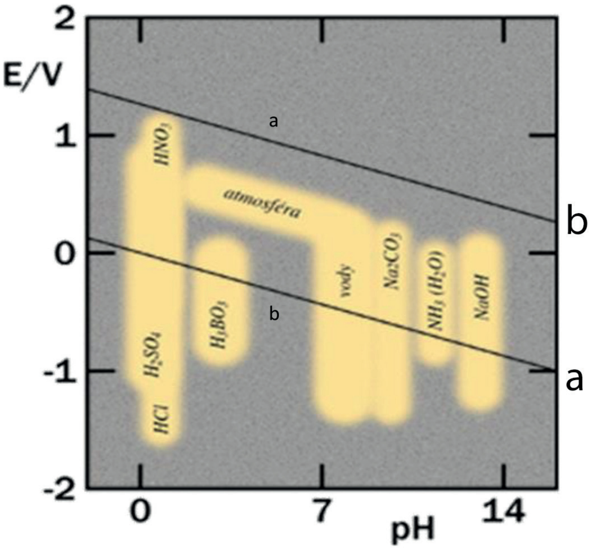

***Figure 1** The potential-pH diagrams for various environments*

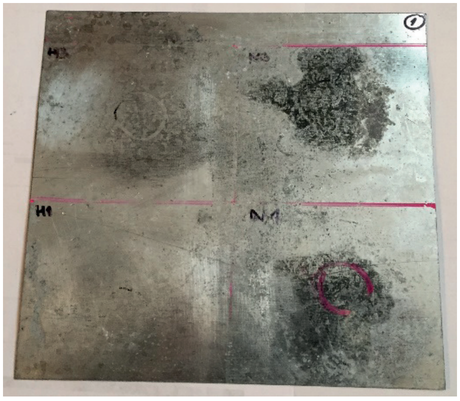

***Figure 2** The K1 sample after passive decontamination*

compromise between the oxidizing properties of the environment and the grade of the metal concerned [3].

The E potential-pH diagram, Figure 1 shows the designated regions with depicted corrosion potentials of metals in selected environments. The higher the value of (corrosion) potential metals, the stronger the oxidizing effect of the environment. Aerated waters and solutions have their potential in the upper part of the respective region, while deaerated ones in the lower part of the respective zone (highlighted in yellow). The area of thermodynamic stability is delimited by the a-b line segments. (The pH-dependent range of potential values in which the water is stable, the thermodynamically stable oxygen gas above the line b and the gaseous hydrogen below the line a).

Detailed assessment of changes in metal surfaces after the passive decontamination was carried out by the stereomicroscope and metallographic examination microscope focusing on the areas designated by the circles (magnification 400 times). Table 2 provides an overview of changes on surfaces of each metal following the passive decontamination.

Assessment of changes in the K1 sample - zinc-plated steel metal sheet, Figure 2.

In the dark areas in samples N1 and N3, clusters of microscopic corrosion pits (dots) with hemispherical profile were detected. The dark areas were formed by aggregates of the dark adhesive corrosion products. The H1 and H3 samples did not include such microscopic dots, but shallow microscopic irregular depressions with rougher inner surface were discovered in them. Under the microscope, it was further detected that the dark areas did not result from different corrosion of zinc cells with different roughness. In addition, light stains, typical of zinc corrosion products (ZnO, $Zn(OH)_2$, etc.), could be seen on the zinc-plated sheet metal.

The more intense change in the colour shade for N1 and N3 (compared to H1 and H3) corresponds to the corrosive effect of chlorides on the exposed zinc-plated surfaces. The Zinc corrosion can proceed in both acidic and alkaline environments (pH 12-14).

Assessment of changes in the K2 sample - nickel. The surface of the K2 metal remained unchanged after having been exposed to the decontaminating agents.

Assessment of changes in the K3 sample - aluminium (99 %), Figure 3.

Numerous darker stains (with the size of 0.01-0.1 mm) and numerous dark dots (with the diameter ranging from 1 to 10 μm) can be seen under the microscope, when the gauge line is observed in the forming process direction on the original surface not exposed to the decontaminating agents. After the exposure to the decontaminating solutions, all regions (H1-N3) were covered with thin, uneven, nearly continuous layers of the light grey deposits of salts, very likely of the $Al(OH)_3$ based corrosion products. According to the E-pH diagram Figure 4, aluminium and its alloys are subject to corrosion in alkaline environments (pH ≥13). On the surface of the regions under review, black dots were observed in the field of view of the stereomicroscope, as well.

The observed surface included microscopic pits and corroded borders of grains, which were greater the longer they were exposed and for the hypochlorite mixture [4]. The more extensive affected areas H1 and H3, compared to N1 and N3, result from application of the tenside that increases the wettability of

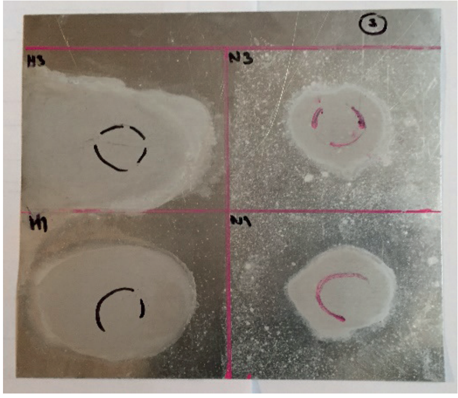

Figure 3 *The K3 sample after passive decontamination*

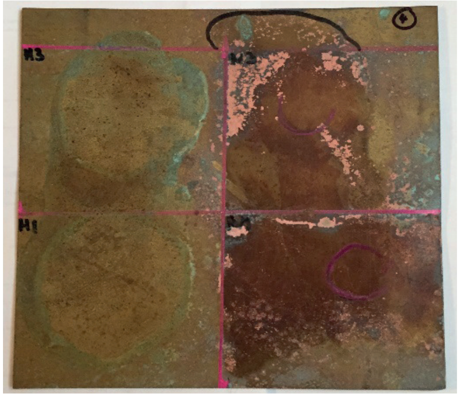

Figure 5 *The K4 sample after passive decontamination*

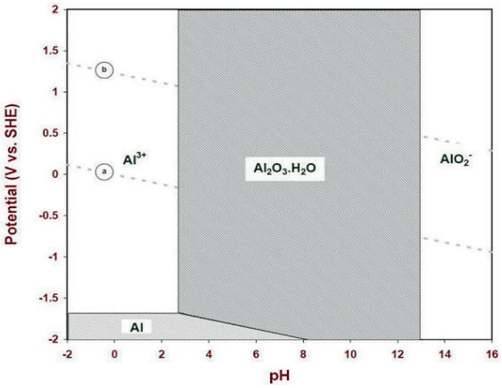

Figure 4 *The E-pH diagram (Pourbaix) for aluminium exposed to water, area “Al” - Immunity region, area “Al^{3+} and AlO_2^-”- Corrosion region, area “$Al_2O_3.H_2O$”- Passive region*

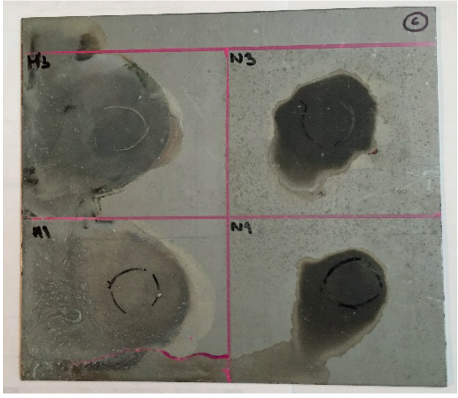

Figure 6 *The K6 sample after passive decontamination*

the surface where the solution was applied (with the application of the same quantity of solution in all cases).

Aluminium Al (Standard potential E_o = -1.66 V) is well resistant to atmospheric exposure and effects of the neutral solutions, since in the given environment (with pH values ranging from 4 to 10), it is protected by a thin layer of oxide and which is thermodynamically stable. In acidic or alkaline environments, Al oxides dissolve and Al metal corrodes faster emitting hydrogen. Solutions containing Cl^- ions ($Cl_xO_y^-$) cause pit corrosion (pitting) where the passive decontamination is applied (Al_2O_3) [5].

Assessment of changes in the <u>K4 sample - brass (CuZn30)</u>, Figure 5.

Outside the exposed areas, under the microscope, depressions of mechanical origin (bruises, scratches), lengths of the order of tenths of millimeters and widths of the order of hundredths of a millimeter, were found. This concerns a copper alloy containing zinc with the concentration of 30 % by weight (CuZn30). The alloy contains copper with a high electrochemical grade and zinc with a low electrochemical grade. Brass is generally resistant to atmospheric corrosion. This resistance is slightly worse than in the case of pure copper and decreases with the increasing content of zinc. This alloy is prone to the selective (extraction) corrosion of zinc in certain environments due to the transport of zinc atoms to the solution or due to the development of corrosion products, the so-called surface dezincification.

The E-pH diagram for the specified brass probably exists. However, it is possible to use the E-pH diagram for copper and zinc where corrosion can be expected in alkaline aqueous solutions with oxidizing effect, leading to the anodic stripping of the ZnO_2^{2-} and CuO_2^{2-} anions (see section covering zinc-plated sheet metal and copper). The greenish or green and blue areas may be deposits of chlorides (hypochlorites) of copper.

Assessment of changes in <u>the K6 sample -Stainless ferritic steel sheet,</u> Figure 6.

Depending on the degree of darkening of the exposed areas, increasing the time of exposure increases the degree of surface corrosion; further, the solution that includes sodium hypochlorite has the more intense effects. The K6 sample included numerous microscopic pits (with the diameters ranging from 0 to 50 μm, with the depth ranging from 10 to 20 μm), which were the same inside the exposed regions as well as outside of them. The pits were formed during the final treatment of the sheet metal and not as a result of exposure to the solutions. The surfaces also included light dots in these places. The microscope revealed local deposits of salts under which areas with a metallic lustre had formed with the same pits as in other areas.

According to the E-pH diagram, Figure 7 and other findings, steel materials are passivated in oxidizing environments. If the solution with oxidizing effects contains chlorides, or where applicable hypochlorite, the pit corrosion develops particularly in solutions with oxidizing effects.

Because the Diagram E-pH for the steel sample CR12 shows a diagram for steel AISI 304 (CrNi18-10) and 316 (CrNiMo17-11-2), areas of uniform corrosion, immunity, pit corrosion (dots)

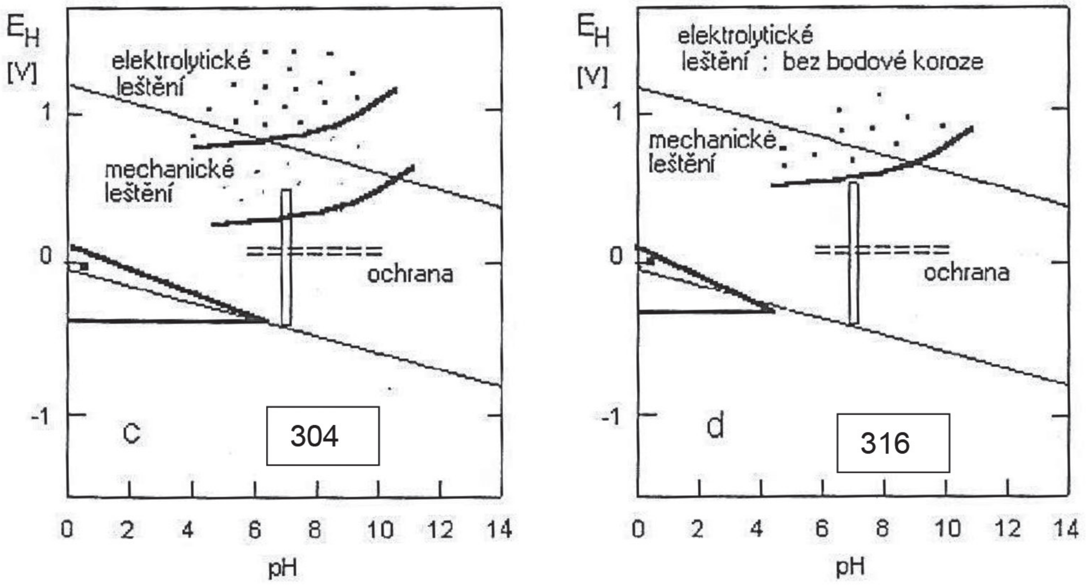

***Figure** 7 The E-pH diagram for steel 304 and 316 in the aqueous solution of 0.1 mol/l NaCl (Key: electrolytic polishing/elektrolyticke lesteni, mechanical polishing/mechanicke lesteni, protection/ochrana, electrolytic polishing: without pit corrosion/elektrolyticke lesteni: bez bodove koroze, mechanical polishing/mechanicke lesteni, protection/ochrana)*

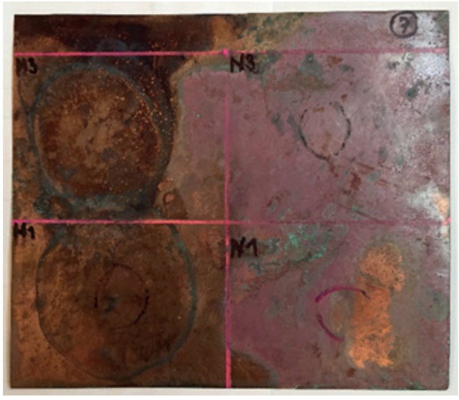

***Figure** 8 The K7 sample after the passive decontamination*

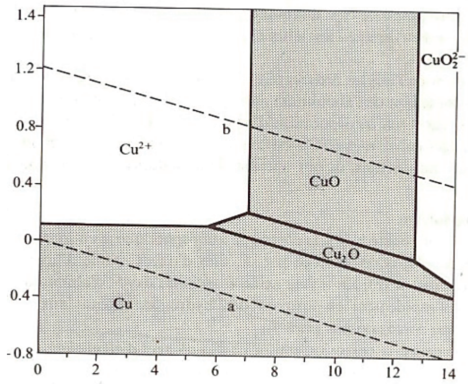

***Figure** 9 The E-pH diagram for copper in water, area "Cu" - Immunity region, area "CuO and Cu_2O"- Corrosion region, area "Cu^{2+} and CuO_2^{2+}"- Passive region*

and passivity of steel AISI 304 and 316 in the aqueous solution of 0.1 mol/l NaCl (3.5g/l Cl) at the temperature of 25 °C were experimentally determined. Under the protective potential (protection in the diagram), the perfect passivity occurred; above this potential, passivity was imperfect. The areas of uniform, as well as pit corrosion, are more extensive in the case of AISI 304 steel. The pit corrosion is also affected by the surface treatment (such as polishing) [3]. Steel Cr12 has the point of occurrence of the point corrosion slightly shifted to the lower values of breakdown potential compared to CrNi18-10 even in alkaline region. In alkaline environments, all the aforementioned steel materials are subject to an increased potential of pit corrosion (pitting) breakdown with increasing pH values.

Assessment of changes in the K7 sample - copper (99 %), Figure 8.

Three types of pit corrosion can develop on copper in aqueous solutions. The brown areas are likely to represent copper oxides, green copper chloride dihydrate.

Copper shows good resistance to atmospheric corrosion, cold as well as warm water, unless the flow rate exceeds several meters per second. The standard potential of copper (standard potential Eo = + 0.34 V, SHE) is higher than that of the hydrogen electrode. In the absence of oxidizing substances, copper therefore resists corrosion in acidic environments (non-oxidizing acids).

On the other hand, in the presence of oxidizing substances with a higher reduction potential, Cu dissolves (the Cu^{2+} region) such as in the aqueous solutions of HNO_3, in aerated H_2SO_4 acid, in the solution of $FeCl_3$ or in the solution containing peroxide, or where applicable hypochlorite NaClO (with oxidizing effects) depending on concentration. Corrosion also develops in strong alkaline solutions (pH 13-14) with oxidizing effects (E > 0.4 V, the area of CuO_2^{2-}), or where applicable copper oxides are formed (CuO) with protective effects (pH 10-12), Figure 9.

Assessment of changes in the K8 sample - zinc - iron, Figure 10.

The description is similar to K1. The N3 and N1 solutions acted on a smaller area (compared to the K1 sample); darker

Table 2 *Overview of changes on the surfaces of metals*

No.	Hvezda		Hypochlorite solution	
	H1	H3	N1	N3
K1	no changes	grey stains	dark grey areas and stains	dark grey and black stains
K2	no changes	no changes	no changes	no changes
K3	light grey and dull appearance, smaller area	light grey and dull appearance, larger area	light grey appearance	light grey appearance
K4	the rim of the area is green with brown dots inside	the rim of the area is greenish with more distinctive brown dots inside	large brown areas, light orange and pink stains	large brown areas, light orange and pink stains
K5	no changes	no changes	no changes	no changes
K6	grey area, light dots with residues of salt	grey area, light dots with residues of salt	dark grey area, light dots (with salt)	dark grey area, light dots (with salt)
K7	brown areas and light dots	darker brown areas and light dots	dark brown dots, turning pink	dark brown dots, turning pink
K8	minor changes, weak darkening	minor changes, weak darkening	dark grey areas, light as well as dark cells	sharp-cut grey (black) area, cells corroded to various extent

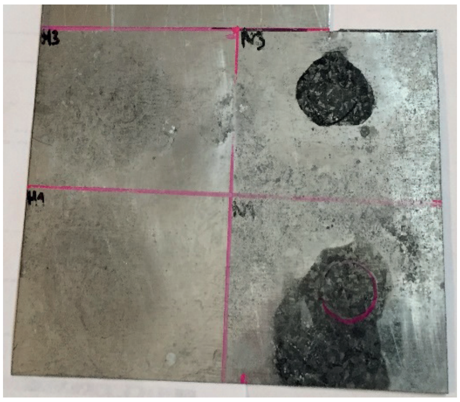

Figure 10 *The K8 sample after passive decontamination*

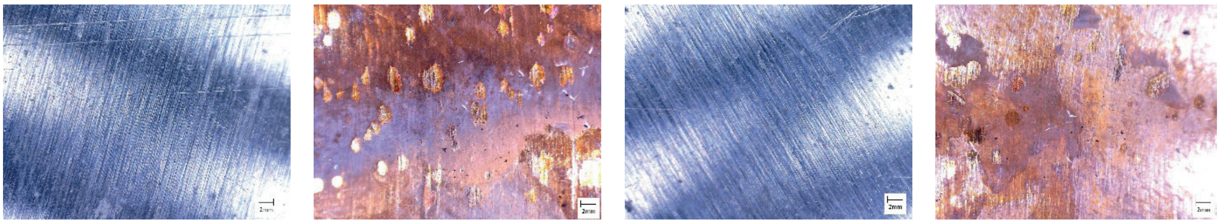

Figure 11 *An example of the scanned K7 sample (magnification 80 times), on the left is a photograph of the delimited area prior to the application of the N - hypochlorite mixture decontaminating solution and after exposure to the hypochlorite mixture after 1 hour (N1) and 3 hours (N3)*

appearance of exposed areas (using the same amount and concentration of solution on both plates K1 and K8).

Figure 11 shows images of the K7 sample surfaces before and after exposure to the decontaminating solution. Significant changes on the surfaces due to exposure to the hypochlorite mixture and changes in colour with light or dark dots can be seen here.

4. Active decontamination

Surfaces of samples were scanned using digital microscopes. The surfaces were contaminated with HD and after 30 minutes the decontaminating solutions were applied with a manual sprayer. The contaminating substance in the place of "HD" application was removed only by using a paper pad. After 60 minutes from the beginning of the test, the liquid (mixture resulting from

Figure 12 *The effect of HD on the K4 sample (on the left, the surface prior to exposure to HD and after the exposure to HD)*

Table 3 *Overview of changes on the surfaces of each metal following the active decontamination*

No.	Type of metal	Effects on surface		
		HD	Hvezda	Hypochlorite mixture
K1	Zinc-plated metal sheet	no changes	no changes	blackening
K2	Titanium zinc (99 % Zn)	no changes	change, dulling stain	blackening
K3	Aluminium (99 %)	no changes	no changes	dulling
K4	Brass (CuZn30)	visible drops of HD	Change	change and visible drops of HD
K5	Stainless steel (18/8)	no changes	no changes	no changes
K6	Stainless ferritic steel	no changes	no changes	no changes
K7	Copper (99 %)	no changes	no changes	visible drops of HD
K8	CU anodised aluminium	no changes	disruption of the surface layer	destruction of the surface layer

decontamination) was removed, the surface washed with distilled water and dried; changes on the surfaces were visually assessed.

Samples with the dimensions 50×50 mm were used for the tests. The K2 - nickel sample was replaced by a titanium - zinc sample (the originally used sample was not affected by the decontaminating solutions) and the K8 sample - zinc - iron (which is almost identical with the K1 sample) was replaced by a sample of Cu anodised aluminium that is widely used in Prague's Metro.

The surface of the metal samples was divided into 4 regions: top left - the original surface, top right - contamination with HD, bottom left - Hvezda solution, bottom right hypochlorite solution.

Exposure to HD without subsequent decontamination resulted in no visual changes on the surfaces of the metal samples, with the exception of the K4 sample with traces remaining in the place of contact with applied HD drops, Figure 12.

The effects of HD and follow-up decontamination left visible changes on the surface of the K1 through K4, K7, and K8 samples. Considering the shorter time of exposure to the decontaminating solutions compared to the passive decontamination, those changes were less intense and affected smaller areas than in the case of the passive decontamination. The surface of the K2 sample, which remained unchanged after application of passive decontamination, visually changed after active decontamination, which can be ascribed to the concurrent effects of HD and decontaminating agents. Table 3 provides an overview of changes on surfaces of each metal following the active decontamination.

After the material has been decontaminated, the secondary contamination of the space may occur temporarily due to the delayed release of the contaminant (or decomposition products formed by the HD reaction with the decontaminant) sorbed on the surface or within the structure of the exposed material. Therefore, it is extremely important to know not only the effects of the contaminating substance and decontaminating agents on the surfaces of the materials, but also the efficiency of decontamination and the related potential of the secondary contamination.

Additional tests ascertained the efficiency of active decontamination and residual concentration of HD. The samples of metals were covered with a special paper reacting to HD released from the material or its surface by changes in colour. The changes were observed within a time interval of 15 minutes. No residual contamination was proven in any of the samples of metals.

5. Conclusion

The samples of metals made of nickel and stainless steel were not affected by the processes of decontamination. In the remaining samples, changes in colour of the surface following both passive and active decontamination appeared. Such changes do not always have a negative effect on the quality of the metal surface. Some components of the decontaminating solutions create a protective layer as well (such as metal oxides). On the other hand, the changes make the surface of metal look inaesthetic. The results of the tests imply that it is advisable to treat the surface of the metals prior to their use.

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