

CHEAP STRIPPABLE POLYMER FILM TO DECONTAMINATE OR TO PREVENT CONTAMINATION

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ABSTRACT

The use of a rubber film directly formed on a metallic surface from an aqueous emulsion is able to protect it very effectively against contamination by cesium in water solution. This protection is effective for a long period of time. The film remains 100 % waterproof and impermeable in all environmental conditions (humidity, irradiation). When used as a decontamination process, the implementation of this film is able to remove about 90% of the surface contamination. This film can be easily recycled, and the different products can be separated or treated. The mechanical properties of this film (adhesion, extension, resistance) make it strippable. However, the composition of the rubber emulsions has also been optimized to comply with other requirements, such as removing the film without contact by applying high pressure hot water in areas where human intervention is not permitted.

BACKGROUND

A decrease in the efficiency of some decontamination processes may occur after several implementations on the same surface, as recontamination between each implementation can occur. In some situations, achieving decontamination to acceptable levels can become difficult. The origin of this problem has been highlighted and solutions have been found. In fact, by thoroughly cleaning the surface, the decontamination process may lead to an increase of the adhesion of subsequent contaminants, thus making them much more difficult to remove. In concrete terms, some chemical functional groups, such as hydroxides make possible the chemical sorption of metal ions. Simply removing grease or natural pollutants from the surface allows direct contact between the contaminants and these reactive sites, increasing adhesion. If the cleaning process is badly suited to the material to be decontaminated, a modification of the chemical composition of the surface can occur, possibly increasing the density of reactive sites, making the problem worse. Predicting the evolution of the surface chemical properties with time is a challenge. Prevention of surface contamination appears to be a wiser approach. The principle is to prevent strong adhesion of the contaminants by masking the reactive groups likely to chemically bind the contaminants to the surface. With this aim in view, different methods of surface treatments offering such barrier effects have been developed at the French atomic Energy Commission (CEA). One possibility is the use of a removable protective polymer film, which can be used also for decontamination purposes. The other possibility is the vapour phase deposition of inert mineral layers on the surface.

In this paper, we will describe both the studies and results that lead us to this prevention approach to the surface contamination problem, and the improvements obtained in terms of decontamination efficiency with this new approach. We demonstrated that by thoroughly cleaning the surface, the decontamination processes increase the adhesion of subsequent contaminants. In fact, the first decontamination is often efficient because it simply removes the surface pollutants (like grease) in which the radioactive contaminants are embedded. Removing pollutants (like this grease) automatically removes the contamination. Therefore, subsequent contaminants will be in direct contact with the material surface. This surface can't be removed and mustn't be damaged. The decontamination process must be able to reduce the adhesion of the contaminants to the surface. This is more difficult to achieve and demands

knowledge of the interactions between the contaminants and the surface. Developing a well suited decontamination process is hence difficult since this knowledge is rarely accessible.

OBJECTIVES

The goal of our research program is to find a way to ensure the ability to decontaminate surfaces easily during their whole lifetime using well-known and well-accepted industrial decontamination processes. To fulfill these requirements, it is necessary to prevent strong bondage of the contaminants to the surface of the equipment.

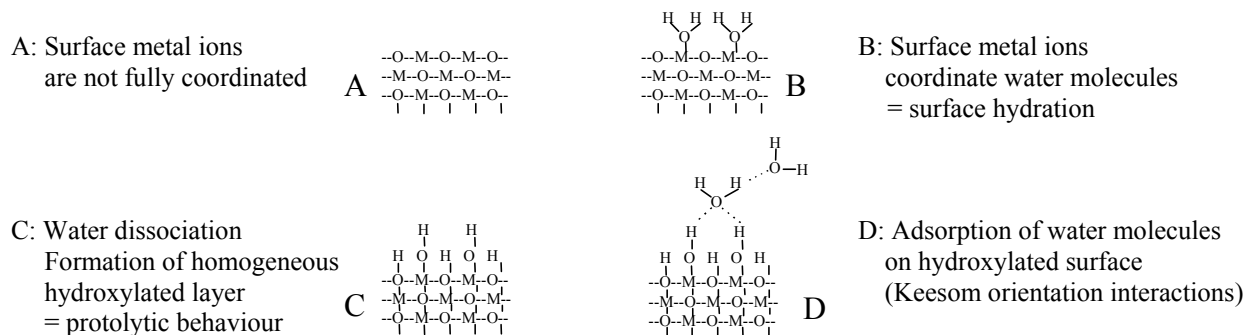
METHODOLOGY

CEA 's concept is to place an interface material between the surface and the contaminated environment to prevent any direct contact between the contaminants and the reactive sites at the surface. There are two competitive possibilities that may allow us to reach this objective:

- Utilize a fixed interface (which can be a Physical or Chemical Vapour Deposit). The interface material must be non-reactive with the contaminant and non-porous to avoid penetration. It must have a very long lifetime, therefore it can't be organic.
- Utilize a removable interface. The interface material can be reactive or porous since these properties can help to prevent the dispersal of the contaminants or even allow trapping and treating it. It can be a polymer film provided it's easy to peel off the surface and easy to treat as a waste.

INTERACTIONS SURFACE / CONTAMINANTS: STATE OF THE KNOWLEDGE

The surface of metals is very reactive, especially in presence of water vapour. The following processes may occur [1, 2]:



Once hydroxylated, such surfaces are likely to bond ionic contaminants like Cesium or Cobalt or Ruthenium according to the following ion exchange process:



CONSISTENCY OF SURFACE / CONTAMINANT INTERACTIONS

Fourier Transform Infra Red Spectrometry (FTIR), was applied to the study of surface contamination in the nuclear industry for the first time by Rouppert et Al.[3] quite recently.

In situ observations give relevant indications on the chemical forms and on the sorption modes of the contaminants and their evolution with environmental conditions.

We will see hereafter, that these chemical forms of the contaminants and the chemical bonds with the surface are likely to evolve greatly through time, depending on the storage conditions of the contaminated samples.

FTIR Spectra of CsOH surface contaminated Stainless Steel have been recorded before and after water vapour treatment [3].

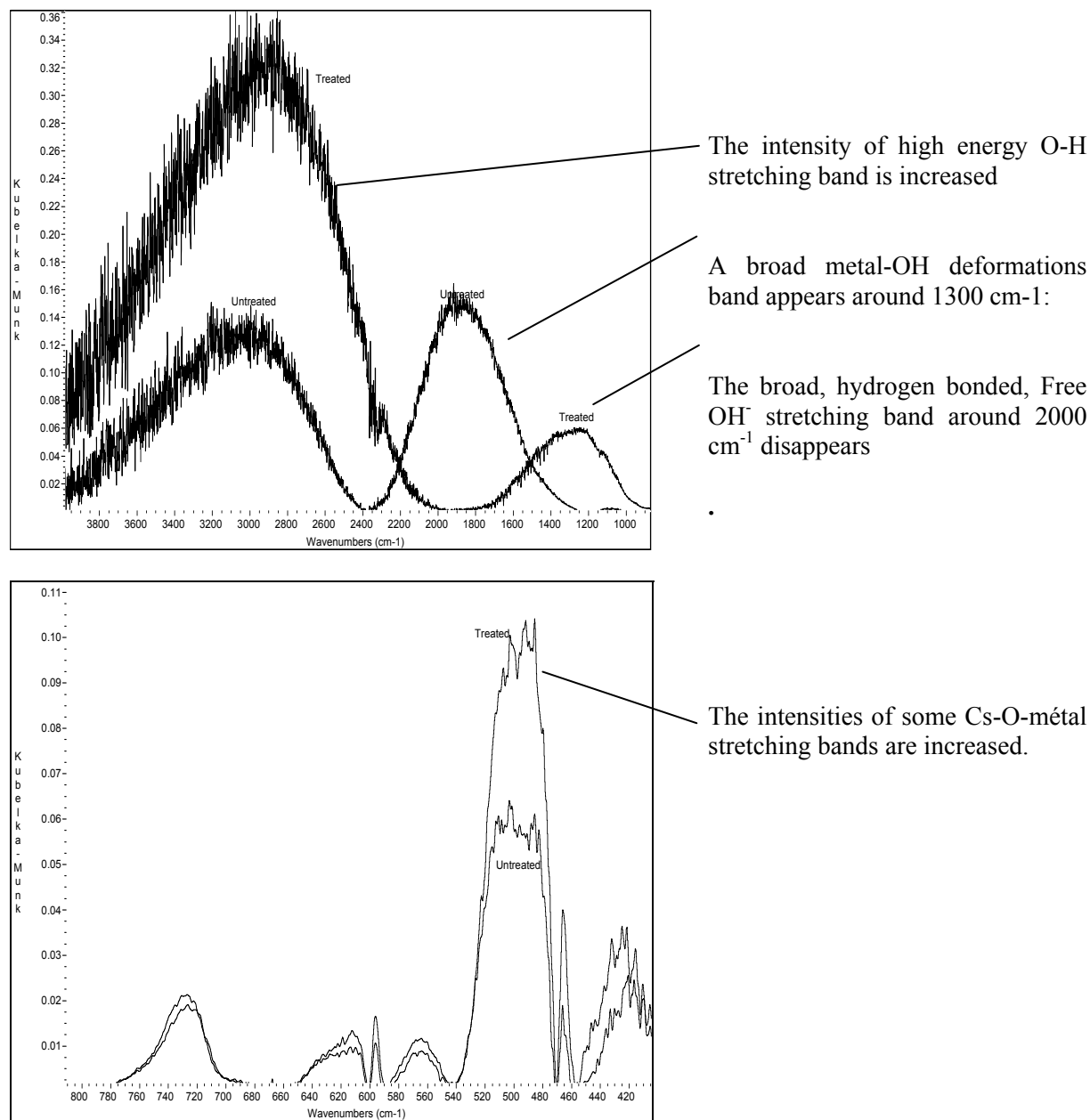
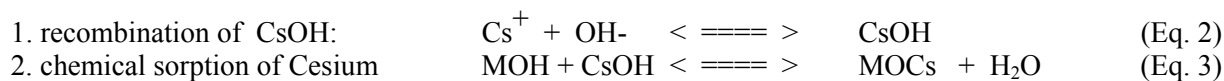


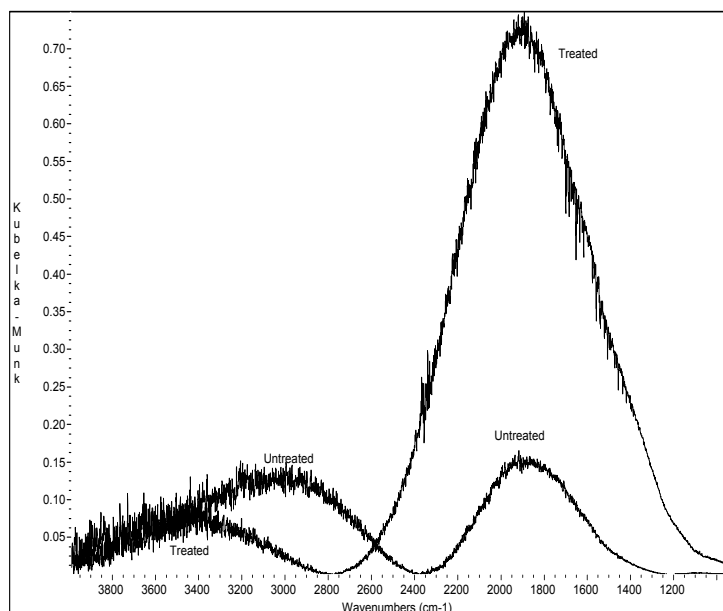
Fig. 1. FTIR Spectra of CsOH contaminated Stainless Steel before and after water vapour treatment

After exposure to water vapour a reorganization occurs leading to the disappearance of free Cs⁺ and OH⁻, these ions being apparently involved in 2 competing reactions [3]:



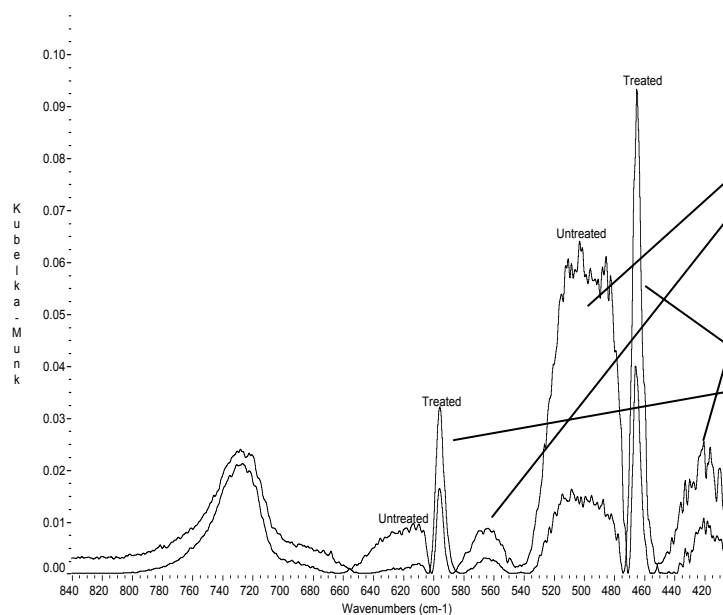
The exposure of contaminated stainless steel to water vapour leads to the chemical sorption of CsOH making this contaminant nearly unremovable from the surface.

The same trials have been performed after having dipped the contaminated steel in liquid water at ambient temperature for 1 month. It is obvious that the chemical forms of Cs are totally different in that case [3]:



A big part of the CsOH is dissociated:

- the intensity of the broad absorption band around 2000 cm^{-1} is increased indicating the presence of a higher amount of free hydrogen bonded OH-groups in the oxide layer and of a corresponding amount of Cs^+ ions.
- the intensity of the broad O-H stretching band between 2500 and 4000 cm^{-1} is diminished, especially in the low energy portion of the band, indicating the presence of isolated (not hydrogen bonded) hydroxyl groups: newly restored metal hydroxides and isolated residues of CsOH for example.



A part of the initially chemisorbed Cesium is released in the distilled water since the intensity of some of the Cs-O-M stretching bands is diminished.

A reorganization seems to occur, since the intensity of other Cs-O-M bands is increased.

Fig. 2. FTIR Spectra of contaminated Stainless Steel before and after a 1 month exposure to distilled water

The following chemical systems are involved:

1. $\text{CsOH} \rightleftharpoons \text{Cs}^+ + \text{OH}^-$ (Eq. 4) Dissociation of CsOH in water
2. $\text{CrO}^- + \text{H}^+ \rightleftharpoons \text{CrOH}$ (Eq. 5) Acidic behaviour of hydroxyl groups
3. $\text{CrOCs} + \text{H}^+ \rightleftharpoons \text{CrOH} + \text{Cs}^+$ (Eq. 6) Desorption of chemisorbed Cesium

The exposure of contaminated stainless steel to liquid water, unlike exposure to water vapour, leads to the desorption of Cs making this contaminant much easier to remove from the surface.

EXPLANATION

According to Le Chatelier [4], if the value of factors modifying the chemical equilibria such as H^+ and Cs^+ concentrations is changed, a rearrangement of the system will be occasioned to nullify these changes:

- the presence of water dilutes Cs^+ hence displaces equilibria 4 & 6 to the right.
- the increase of acidity displaces equilibria 5 & 6 to the right as well.

Experimental results appear to be in good agreement with this theory.

Three different forms of Cesium contaminants have been identified [3]:

- chemically sorbed: chemical bonds develop through ion exchange/complexation mechanisms with hydroxides
- physically sorbed: electrostatic, Van Der Waals or Hydrogen bond forces link undissociated Cesium compounds to the surface, especially oxides and hydroxides
- "free" Cs^+ ions: they result from the dissociation of Cesium compounds with no further reaction. The existence of this form has been demonstrated by the discovery of Hydrogen bonded "free" OH^- groups in the oxide layer when CsOH contaminant is used, meaning correlatively that "free" Cs^+ ions are present as well.

Water or high humidity allow dissociation of molecules into ions and increase their mobility. This leads to rearrangements such as recombination of ions in molecules or further chemical sorption reactions through chemical ion exchange processes during subsequent drying.

The rearrangements observed lead to changes in contaminant sorption modes thus modifies the adhesive behaviour of the contaminants. The distribution of Cs compounds between measurable and not measurable chemical forms is represented below [3]:

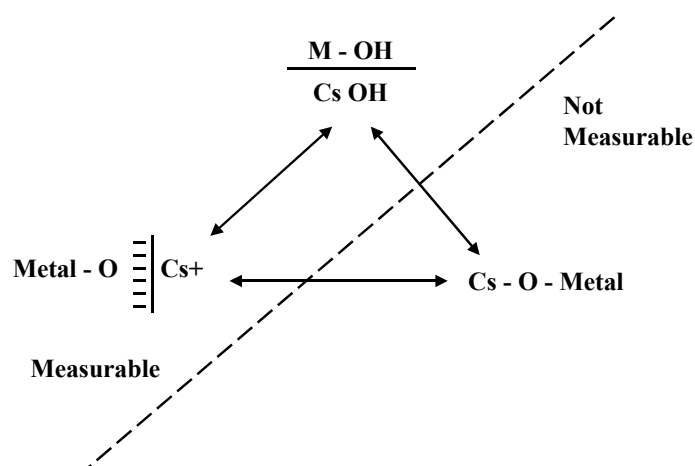


Fig. 3

CONCLUSIONS

Depending on the environmental conditions (exposure to liquid water or water vapour) the contaminant can become chemically bonded to the surface or desorbed. The chemical forms of the contaminants and the chemical bonds involved between the contaminant and the surface are not consistent at all and their evolution appears to be rather unpredictable. The removal of the contaminants will require a good understanding of the sorption reactions and will possibly demand the use of specific reagents. However, modification of decontamination processes may create other problems, in part because new chemicals may impair plant waste processes. Therefore, it was decided to focus our study on the modification of the materials surface. The aim of our work is to specify surface treatments making impossible the bondage of the contaminants to the surface, or treatments favouring weak adhesion of the contaminants to the surface. These treatments should improve the efficiency of existing decontamination processes.

EXPERIMENTAL: FORMULATION OF A STRIPPABLE POLYMER FILM

The main reason we decided to start our research program by investigating what is now referred to as the "polymer way" is that a polymer film can be applied on existing equipment or even on contaminated equipment as a cleaning process.

Equipment in contaminated environments in nuclear plants may be extremely diverse: size, shape, kind of materials. It is thus nearly impossible to implement an already built polymer film on such surfaces. The coverage of the surface and the adhesion of the film would be very poor, impairing the expected protective effect. Therefore, we decided to build up a polymer film directly on the surface. A liquid polymer, that will wet and cover the surface thoroughly, is required to build up this polymer film. We used a commercial emulsion of rubber in water.

The film formulation includes two different types of rubber in emulsion (50% by weight in water) to adjust the hardness and the adhesion properties of the film. A specific granulated complexant for Cesium was added along with a thickener to adjust the thickness of the film and the cover qualities. The mixture was simply homogenized with a magnetic stirrer.

This film stock was applied with a brush or poured onto the surface to form a protective film about 200 μm thick (Fig.4). Objects can also be covered by dipping them directly in the stock. The film forms and dries in about two hours depending on temperature and humidity. The film still forms at relative humidity's as high as 75 %. Once dried, the film remains a solid coat even if hot water is applied for several hours. The film remains in good state even after ageing in a radioactive environment. It has been tested at up to 50 kGy so far.

After complete drying, the film can be peeled off the surface very easily in once piece, or in a finite number of pieces (Fig. 4). A way to remove the film without hands-on contact (by simply applying hot water or water vapour) is currently being studied. This would allow the film to be used even in hot cells.

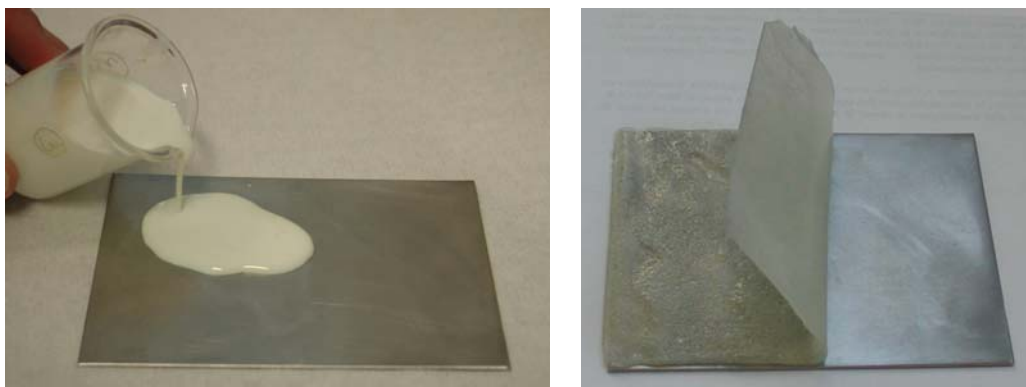


Fig. 4 Application of the stock, on the surface and peeling of the film

After removal, the film can be dissolved in a 0.5 M nitric acid and surfactant solution. The different products can be separated by filtration, centrifugation, and flocculation of the organic matter. The polymer is not contaminated allowing its treatment by incineration.

RESULTS

The process has been tested in 2 different ways:

- As a decontamination process where the film is formed on a dirty surface and then removed.
- As a surface protection process where, the film is formed on a clean surface, then the surface is contaminated.

Cesium contamination was simulated by using a solution of CsOH in water. A calibrated drop was deposited on the surface and allowed to dry naturally at ambient temperature. Two different methods were used to characterize the amount of contaminants on the surface of the metal samples. Fourier Transform Infrared Spectrometry (FTIR) was used for qualitative and quantitative measurements and wettability measurements were used to determine the percentage of the surface covered by the contaminant [5, 6, 7].

DECONTAMINATION

The FTIR spectra shown in Fig. 5 have been recorded on stainless steel samples contaminated with CsOH, before and after application and removal of the polymer on the contaminated surface.

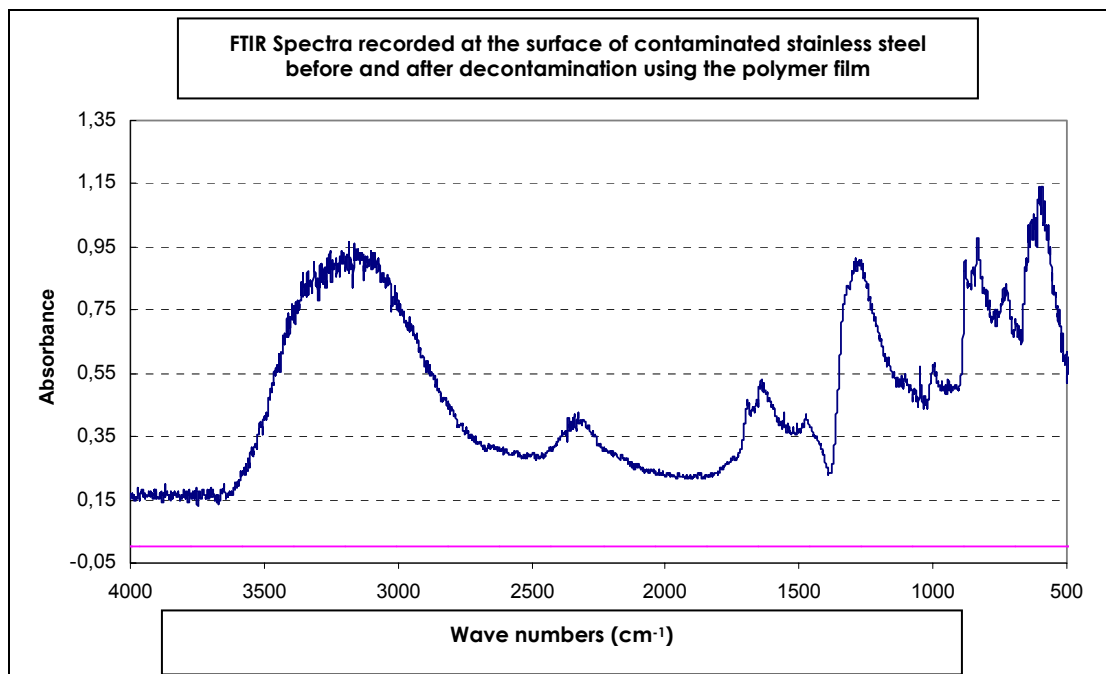


Fig. 5 FTIR spectra of the surface decontaminated using the polymer film

These spectra show that after application and removal of the polymer film on the contaminated surface, the CsOH contaminant is no longer detectable. Since the sensitivity of the FTIR technique may not be sufficient to detect trace amounts of CsOH on the surface, the wettability technique described above was used to confirm the results obtained with the FTIR technique.

These wettability measurements gave the following results: if F_1 , F_2 and F_3 are the area fractions occupied by components 1,2,3 (metal, Césium, Latex) and if θ_1 , θ_2 , θ_3 are the corresponding contact angles measured on the pure products, then: $\cos\theta = F_1 \cos\theta_1 + F_2 \cos\theta_2 + F_3 \cos\theta_3$ and $F_1 + F_2 + F_3 = 1$.

- on a clean stainless steel surface, the contact angle measured was $(77\pm 3)^\circ$.
- on a stainless steel surface contaminated with CsOH, the contact angle is close to 0°
- after formation and removal of the film on the contaminated surface, the contact angle was $(54\pm 8)^\circ$

These values of contact angles show that about 90% of the contamination present at the surface was removed after implementation of this decontamination process. Only 10% of the surface is still covered by a monolayer of CsOH after removal of the film.

PROTECTION AGAINST CONTAMINATION

When testing the use of polymer film to protect against contamination, stainless steel samples were contaminated with CsOH after application of the polymer on the clean surface. The samples were then aged several days in different conditions of humidity. FTIR spectra were recorded on the surface of the steel after removal of the film. These samples were also characterized using the wettability technique. In all cases it was impossible to detect the presence of CsOH on the surface. The FTIR spectra are identical to the baseline (same as redline of Fig. 5), and the contact angles are identical on the clean samples $(77^\circ\pm 3^\circ)$ and on the samples contaminated after protection by the film. $(77^\circ\pm 3^\circ)$. Used as a protective

film, the polymer showed an efficiency of 100 % since the contamination never reaches the surface even after ageing in several environmental conditions.

FILM REMOVING

The polymer emulsion may be sprayed like paint onto the surface to form the film. Film mechanical properties are even enhanced when the polymer is applied this way.

Some trials have been made to insure that the film can be removed without direct human intervention in hot cells or other highly contaminated areas where access is prohibited or limited to a very short period of time. On the following photograph, we can see the film removed from a stainless steel surface using high pressure hot water:

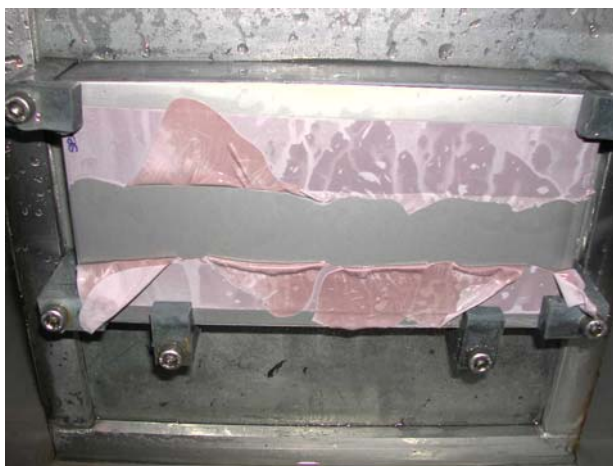


Fig. 6

The film is entirely removed from the surface in one piece and doesn't leave any residue on the surface, allowing you to get back and recycle the contaminants and the components of the film.

FILM RECYCLING

The film can be easily dissolved in a diluted HNO_3 + surfactant solution. The components can be separated by filtration of the complexant powder and flocculation of the polymer.

CONCLUSIONS AND PROSPECTS

Adhesion of contaminants on stainless steel, and probably on many other materials is completely unpredictable and changing with time, environmental conditions, and with the implementation of cleaning processes.

Therefore, it is very risky to anticipate how difficult it will be to decontaminate the surface. That's the reason why protection of the surface appears to be a wiser approach, by preventing direct contact between contaminants and reactive groups of the material.

The use of a rubber film directly formed on a metallic surface from an aqueous emulsion is able to protect it very effectively against contamination by cesium in water solution. This protection is effective for a long period of time. The film remains 100 % waterproof and impermeable in all environmental conditions

(humidity, irradiation). When used as a decontamination process, the implementation of this film is able to remove about 90% of the surface contamination.

This film can be easily recycled, and the different products may be separated or treated. The mechanical properties of this film (adhesion, extension, resistance) make it strippable. However, the composition of the rubber emulsions has also been optimized to comply with other requirements, such as removing the film without contact by applying high pressure hot water in areas where human intervention is not permitted.

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