

PREVENTION : A NEW AND MAYBE WISER APPROACH TO THE SURFACE CONTAMINATION ISSUES

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ABSTRACT

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 vapor 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.

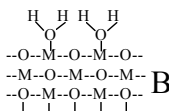
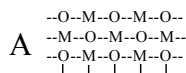
BACKGROUND

It has been observed that many decontamination processes decrease in efficiency after several implementations on the same equipment. 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

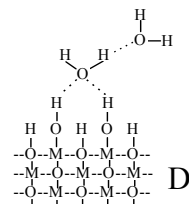
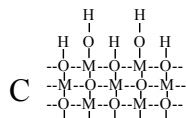
The goal of our research program is to find a way to ensure the ability to decontaminate surfaces easily during their whole lifetime using well-known and well-accepted industrial decontamination processes. To fulfill these requirements, it is necessary to prevent strong bondage of the contaminants to the surface of the equipment. The surface of metals is very reactive, especially in presence of water vapor. The following processes may occur [1, 2]:

**A: Surface metal ions
are not fully coordinated**



**B: Surface metal ions
coordinate water molecules
= surface hydration**

**C: Water dissociation
Formation of homogeneous
hydroxylated layer
= protolytic behaviour**



**D: Adsorption of water molecules
on hydroxylated surface
(Keesom orientation interactions)**

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



The contaminant is then chemically bonded to the surface. Its removal 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.

CEA 'S APPROACH

Our 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:

1. Utilize a fixed interface (which can be a Physical or Chemical Vapor 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.
2. 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.

First Axis Explored: The Removable Polymer Film

We decided to start our research program by investigating what is now referred to as the "polymer way". The main reason for this choice 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.1). 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 humidities 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. 2). A way to remove the film without hands-on contact (by simply applying hot water or water vapor) is currently being studied. This would allow the film to be used even in hot cells.

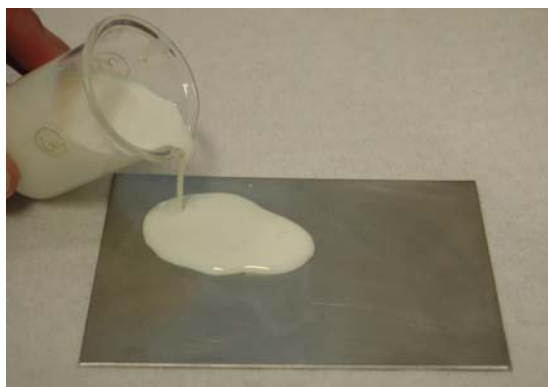


Fig. 1. Application of the stock, on the surface



Fig. 2. 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:

1. *As a decontamination process where the film is formed on a dirty surface and then removed.*

2. *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 using the method shown in Fig. 3. [3, 4, 5]

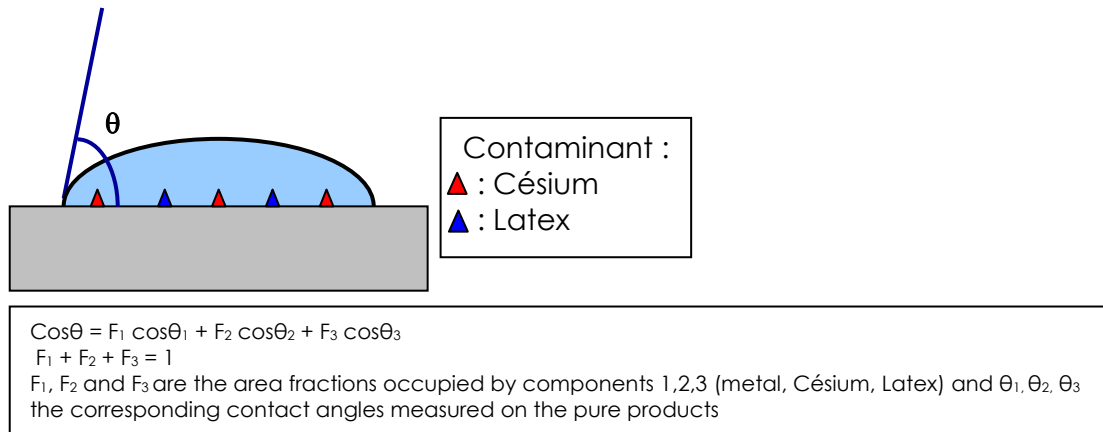


Fig. 3. Method to Determine Percentage of Surface Contaminated

The FTIR spectra shown in Fig. 4 have been recorded on stainless steel samples contaminated with CsOH, before and after application and removal of the polymer on the contaminated surface.

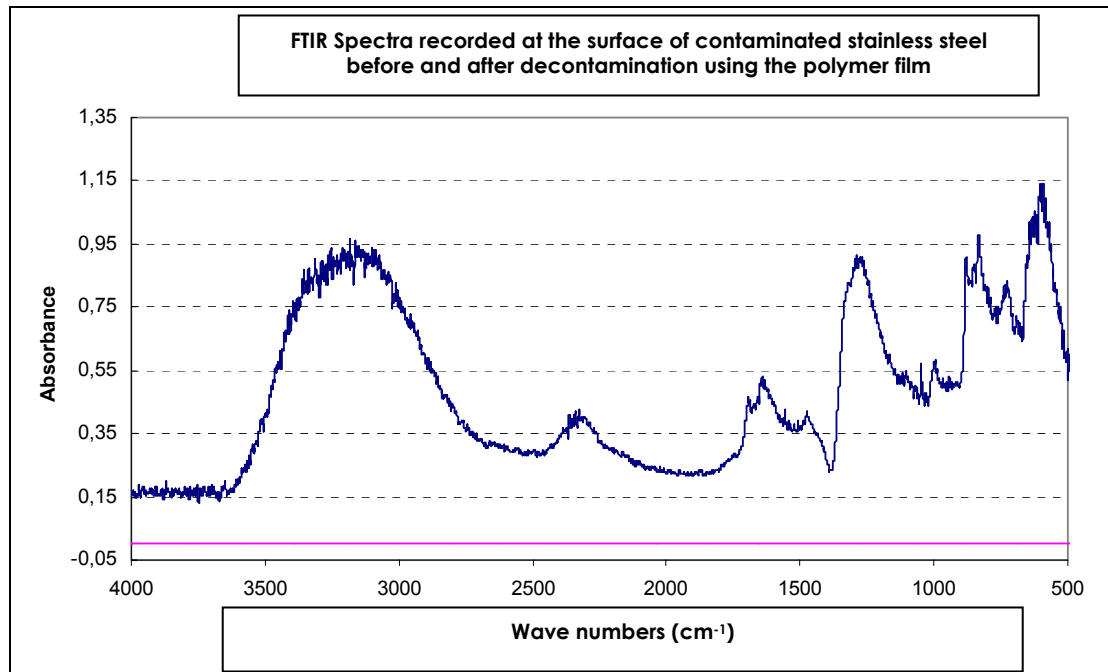


Fig. 4. FTIR Spectra Using Polymer Film

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:

- 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.

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 flat, and the contacts angles are identical, on the clean samples and on the samples contaminated after protection by the film. 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.

CONCLUSIONS AND PROSPECTS

The use of a rubber film directly formed on a metallic surface is able to protect it very effectively against contamination by cesium in water solution. This protection is effective for a long period of time 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 contamination. This film can be easily recycled, and the different products can be separated or treated. The mechanical behaviour of this film is good but can still be improved (resistance to perforation, adhesion...). The composition of the rubber emulsions has also been optimized to comply with other requirements, such as removing the film without contact by applying hot water or water vapor.

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