

RELIABILITY AND CONSISTENCY OF SURFACE CONTAMINATION MEASUREMENTS

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ABSTRACT

Surface contamination evaluation is a tough problem since it is difficult to isolate the radiations emitted by the surface, especially in a highly irradiating atmosphere.

In that case the only possibility is to evaluate smearable (removeable) contamination since ex-situ countings are possible. Unfortunately, according to our experience at CEA, these values are not consistent and thus non relevant.

In this study, we show, using in-situ Fourier Transform Infra Red spectrometry on contaminated metal samples, that fixed contamination seems to be chemisorbed and removeable contamination seems to be physisorbed. The distribution between fixed and removeable contamination appears to be variable.

Chemical equilibria and reversible ion exchange mechanisms are involved and are closely linked to environmental conditions such as humidity and temperature.

Measurements of smearable contamination only give an indication of the state of these equilibria between fixed and removeable contamination at the time and in the environmental conditions the measurements were made .

INTRODUCTION

Experiments carried on by Chambers et Al. [1-5] have shown that radionuclides on stainless steel may evaluate from a fixed to a removable form depending on environmental conditions. Surface ion exchange and complexation phenomena are involved.

In the current study, we shed light on this point and highlight what are the effects of different environmental conditions upon the contamination behaviour.

We show through the precise example of stainless steel contaminated at high temperature by cesium compounds that the contaminant is present in several different chemical forms. Several chemical equilibria involving Cesium, metals, metal oxides and hydroxides at the surface of stainless steel have actually been determined using Fourier Transform Infrared Spectrometry (FTIR) in diffuse reflectance. The distribution between these forms can evaluate with time and storage conditions.

We demonstrate that these rearrangements (that can be predicted using the General Law of Equilibrium enunciated by Le Chatelier) may explain the adhesive behaviour of contaminants

and hereby the possible reversible transformation of fixed radioactive components to removable forms.

This phenomenon modifies the results of contamination measurement performed using smear methods and has the potential to explain the occasional inconsistency of smearable surface contamination on stainless steel noticed by Bennett et Al. [1] and Chambers et Al. [2; 3; 4; 5].

INCONSISTENCY OF SMEARABLE SURFACE CONTAMINATION : STATE OF THE KNOWLEDGE

Bennett et Al. [1] and Chambers et Al. [2; 3; 4; 5] have noticed occasional inconsistency of smearable surface contamination on stainless steel. In order to clarify this phenomenon these authors have studied the mechanisms of contamination of stainless steel at molecular scale. 2 phenomena seem to be involved : sorption and diffusion.

A review of these transport and sorption phenomena of radio-contaminants has been published recently [6]. Sorption can be divided in 4 different categories : adsorption, ion exchange, complexation and precipitation.

These mechanisms appear to be intimately connected and it is impossible to separate completely their individual influence. However, it has been hypothesized that each phenomenon may be described as a system in equilibrium using chemical reactions. It thus becomes possible to predict the direction of displacement of these equilibria under the influence of environmental strains using Le Chatelier principle [7].

In the framework of this project, we have attempted to deconvolute experimentally the influence of transport and the influence of sorption in the apparent inconsistency of smearable contamination measurements.

EXPERIMENTAL

Sample Contamination

High temperature contamination was simulated by placing 17*17*5 mm 304 L Stainless Steel plates in sealed metallic boxes containing 100 mg CsOH. These boxes were then placed in an oven programmed to follow a specific thermal cycle culminating at 850°C for 24 hours.

Sample Treatment

- decontamination treatment using high pressure water for 5 minutes
- ... or exposure to distilled water for 1 month
- ... or exposure to water vapour for 2 hours in a stew pot
- ... and thermal ageing at 170° or 350° in an oven

Characterisation Methods Used

Secondary Ion Mass Spectrometry (SIMS) has been used to evaluate the distribution of the contaminant below the steel surface and its evolution due to decontamination treatments and thermal ageing. Due to the high temperature contamination method, cesium is included in a 1

micrometer thick oxide layer at the steel surface. SIMS method allows to study the z distribution of cesium in this layer that could evolve with time and sample treatments.

Fourier Transform Infra Red Spectrometry (FTIR), to the best of our knowledge, was applied to the study of surface contamination in the nuclear industry for the first time by Rouppert et Al.[6] quite recently. In situ observations give relevant indications on the chemical forms and on the sorption modes of the contaminants. A Mattson Infinity spectrometer has been used with the diffuse reflectance device. The sample cell was placed under a dry air flow. All background spectra were recorded at 0.5 cm⁻¹ resolution over the complete medium Infrared range (400 - 4000 cm⁻¹). 304 L stainless steel treated at 850° for 24 hours without Cesium was used as reference material.

RESULTS AND DISCUSSION

Cesium Distribution Below the Surface of Stainless Steel

The first step was to determine the distribution of cesium below the surface. It is obviously easy to understand that contamination measurements made using smears are very dependent on cesium surface concentration and cesium distribution below the surface. Cesium distribution was evaluated using Secondary Ion Mass Spectrometry (SIMS) after contamination, after decontamination and finally after decontamination and thermal ageing of the samples for 1 month at 350°C. Results reported below only give a general tendency. We do not show here the real data recorded using the SIMS spectrometer.

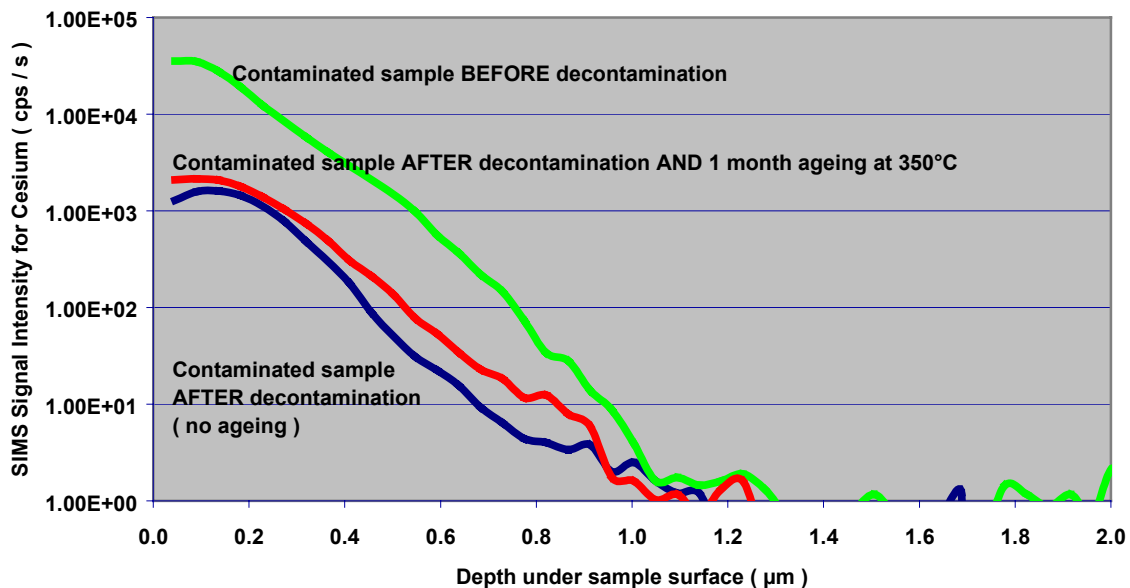


Fig. 1 : Cesium distribution below the surface of stainless steel

- Cesium concentration is a maximum one near the surface and regularly decreases to reach a concentration close to zero about 1 µm below the surface. 1 µm is the mean thickness of the oxide layer at the surface after the standard contamination cycle applied.

- We can see that the decontamination treatment using high pressure water for 5 minutes strongly reduces Cesium concentration near the surface, but does not affect cesium concentration deeper than 0.5 μm below the surface.
- after a 1 month ageing of the samples at 350° in a dry atmosphere, the distribution of cesium is not affected. There is no noticeable diffusion phenomenon.

According to Fick's equation (Rivoallan et Al. [8]), diffusion of metal ions at low temperature in oxide layers is very slow, except in grain joints and boundaries (Fehlner et Al. [9]; Revesz et Al. [10]; Jarawani et Al. [11]).

The current results seem to show that the distribution and the surface net concentration of volatile contaminants are quite stable with time at common operating temperatures.

Though, we do not believe that diffusion is a key mechanism to explain the evolution of smearable surface contamination.

Cesium Chemical Forms and Modes of Sorption at the Surface of Stainless Steel

The first step was to characterise the surface of stainless steel contaminated with CsOH at 850°. The reference material used to record background spectra is stainless steel treated at 850° without Cesium.

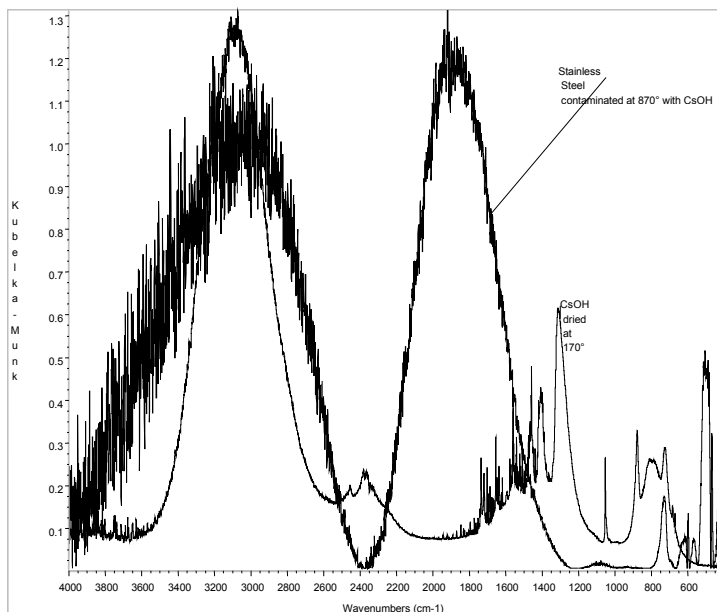


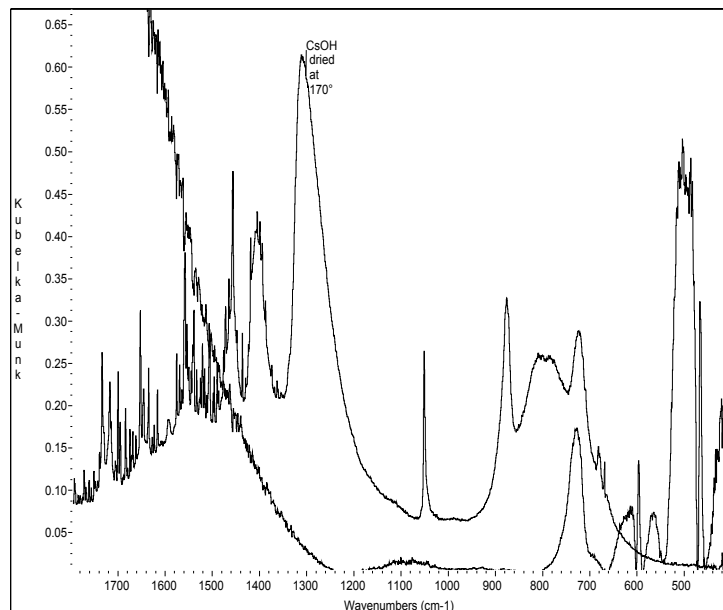
Fig.2: FTIR Spectra of CsOH and stainless Steel contaminated with CsOH at 850°C

Normalized Spectra

The spectra of the initial CsOH contaminant and of the contaminated stainless steel surface are quite different, indicating a change in the chemical form of the contaminant.

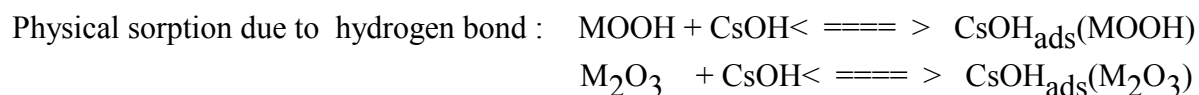
The broad O-H stretching band (2200-1500 cm^{-1}), shifted towards low vibration energies, indicates the presence of free, OH- groups in the oxide layer, hence the presence of free Cs+ as well. The negative shift of this absorption band reveals the existence of strong Hydrogen bonds between these free OH- and the metal oxides at the surface.

The broad O-H stretching band of higher energy around 4000-2500 cm^{-1} reveals that undissociated CsOH molecules are still present. The broadness of this band is due to hydrogen interactions between the contaminant and the metal oxides.

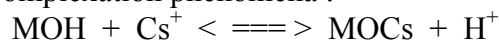


Mixed Cesium and Metal oxides seem to be present as well (presence of new absorption bands below 800 cm-1). This bands are significantly different from those of pure CsOH indicating that, in all likelihood, chemisorption reactions have occurred.

Fig.3: FTIR Spectra of CsOH and stainless Steel contaminated with CsOH at 850°C



Chemical sorption due to ion exchange or complexation phenomena :



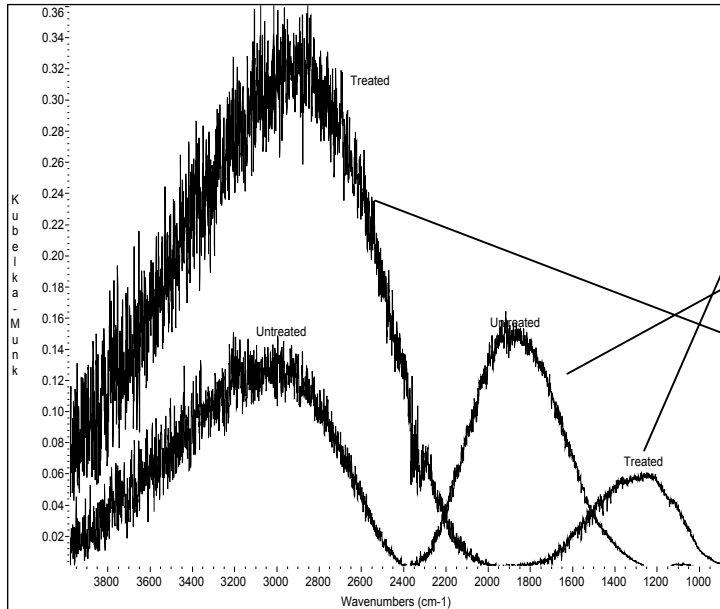
This ion exchange process is linked to the presence of metal hydroxides and oxyhydroxides (Grandstaff et Al. [3; 4])

This mechanism is also hypothesized in the studies of Chambers et Al. [2; 5]. In that case this reaction only involves available free Cs⁺ ions present in the oxide layer.

A direct reaction between hydroxides and CsOH is unlikely since it would request the presence of an electrolyte allowing the dissociation of CsOH.

The contaminated material has been treated for 2 hours in water vapour at 100° C in order to evaluate the influence of extreme humidity or water on hot contaminated stainless steel surface, as regards the behaviour of the contaminant.

After a 1 day drying of this sample in an oven at 170° C, the following FTIR spectra are obtained :



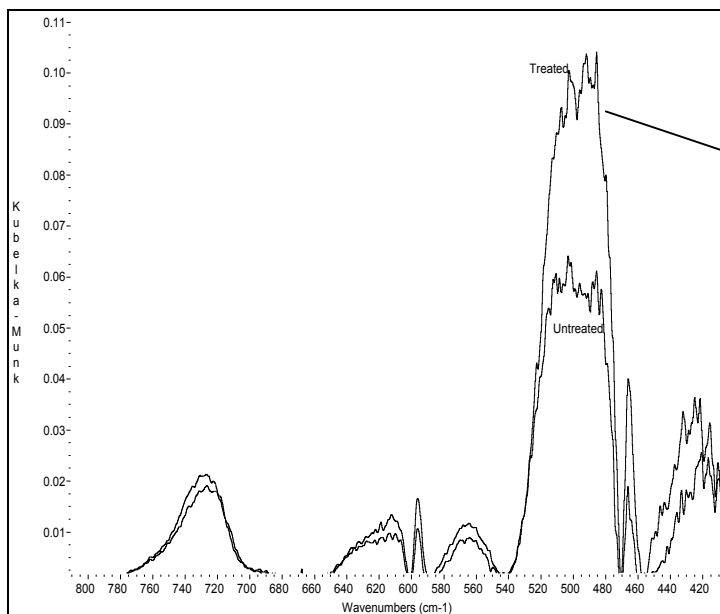
Regular intensities

A broad metal-OH deformations band appears around 1300 cm⁻¹ :

The broad, hydrogen bonded, Free OH⁻ stretching band around 2000 cm⁻¹ disappears

The intensity of high energy O-H stretching band is increased.

Fig.4 : FTIR Spectra of CsOH contaminated Stainless Steel before and after water vapour treatment Sample dried at 170° for 1 day

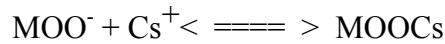
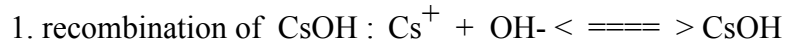


Regular intensities

The intensities of some Cs-O-métal stretching bands are increased.

Fig.5 : FTIR Spectra of CsOH contaminated Stainless Steel before and after water vapour treatment Sample dried at 170° for 1 day

Surprisingly, the mobility of free ions in the oxide layer seems to increase during the drying process. A reorganization occurs leading to the disappearance of free Cs⁺ and OH⁻, these ions being apparently involved in 2 competing reactions :



or ... similar reactions with MOH

The same trials have been performed in liquid water at ambient temperature :

The 17*17 mm sample were dipped in 10 ml of distilled water for 1 month. The concentration of Cs⁺ in residual water was measured using ICP-AES spectrometry : 6.4 mg/l.

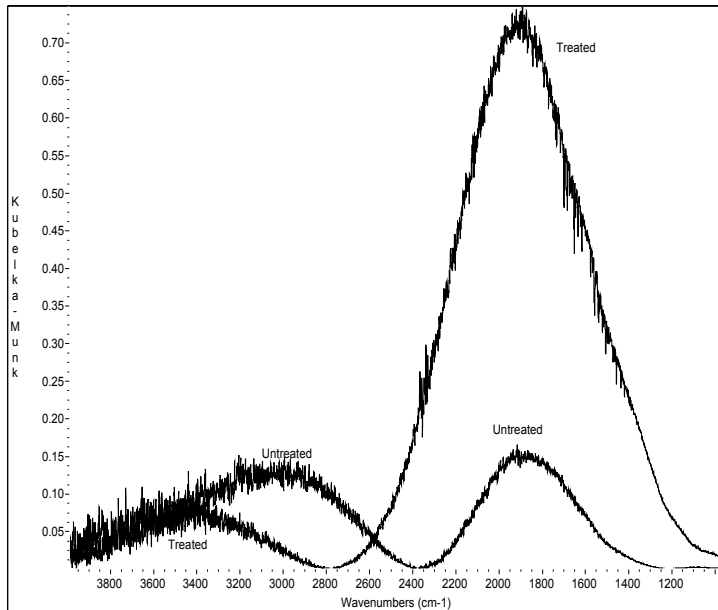


Fig.6 : FTIR Spectra of contaminated Stainless Steel before and after a 1 month exposure to distilled water and dried 1 day at 170°

Regular intensities

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.

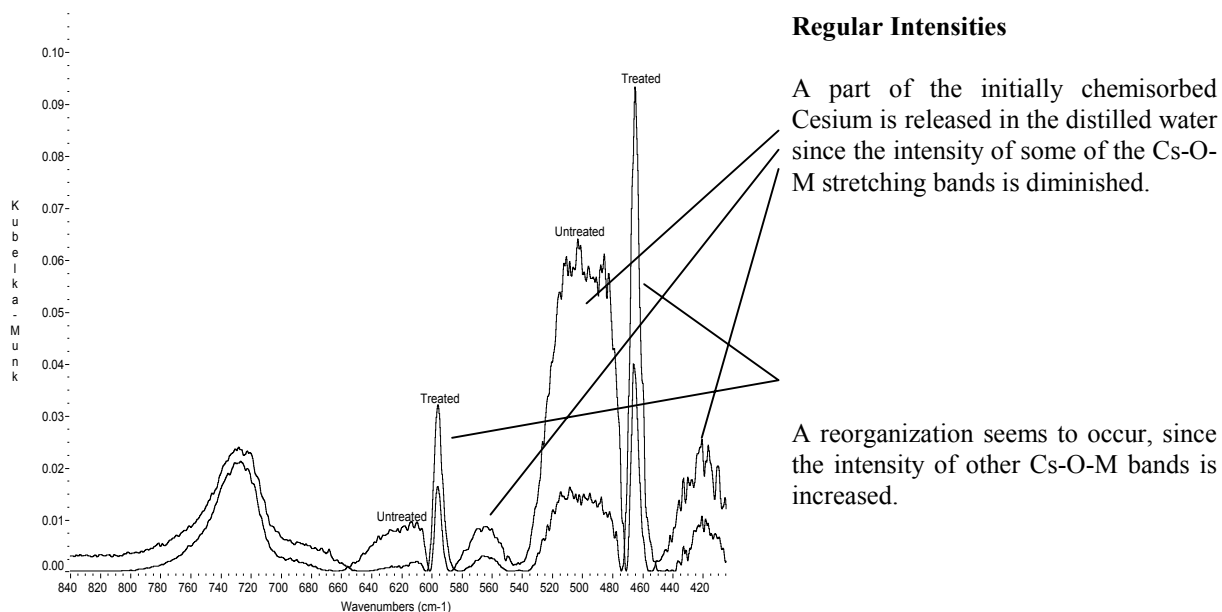


Fig.7 : FTIR Spectra of contaminated Stainless Steel before and after a 1 month exposure to distilled water and dried 1 day at 170°

The following chemical systems are involved :

1. $\text{CsOH} < \rightleftharpoons > \text{Cs}^+ + \text{OH}^-$ Dissociation of CsOH in water
2. $\text{CrOO}^- + \text{H}^+ < \rightleftharpoons > \text{CrOOH}$ Acidic behaviour of metal hydroxyl groups
3. $\text{CrOOCs} + \text{H}^+ < \rightleftharpoons > \text{CrOOH} + \text{Cs}^+$ Desorption of chemisorbed Cesium

According to Le Chatelier [7], if the value of factors of the equilibria such as H^+ and Cs^+ concentrations is modified, a rearrangement of the system will be occasioned to help nullify these changes :

- The presence of water dilutes Cs^+ hence displaces equilibria 1 & 3 to the right.
- The increase of acidity displaces equilibria 2 & 3 to the right as well.

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

CONCLUSION

Stainless Steel has been contaminated at high temperature using Cesium hydroxide.

Distribution, chemical forms and sorption modes of Cesium have been studied at Stainless Steel Surface before and after decontamination, and after exposure to different environmental conditions.

After contamination, the concentration of Cesium regularly decreases till a depth of $1\mu\text{m}$ below the surface, which is the thickness of the oxide layer that grows at the surface during the contamination treatment at 850°C .

Decontamination using high pressure water reduces surface concentration of Cesium till a depth of $0.5\mu\text{m}$ below the surface.

The distribution of Cesium does not evaluate afterwards even after thermal ageing for 1 month at 350°C .

These results show that inconsistency of contamination measurement are not linked to a potential evolution of the contaminant distribution.

Three different forms of Cesium contaminants have been identified :

1. chemically sorbed: chemical bonds develop through ion exchange/complexation mechanisms with hydroxides
2. physically sorbed: electrostatic, Van Der Waals or Hydrogen bond forces link undissociated Cesium compounds to the surface, especially oxides and hydroxides
3. "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.

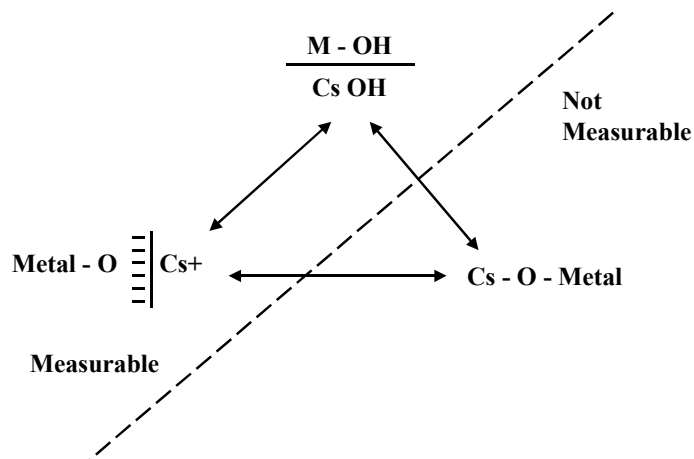


Fig.8: Distribution of Cs compounds between measurable and not measurable chemical forms

We hypothesize that the evolution of the distribution of the contaminant between these 3 chemical forms related to environmental conditions influence the level of smearable contamination measured using contact methods. This is the probable cause for the inconsistency of surface contamination measurements

ACKNOWLEDGEMENTS

This work has been performed at the French Atomic Energy Commission (CEA), Department of Materials Science and Engineering in Grenoble. Acknowledgements are due to the Cogema Company for its financial support and for the authorization given to present the results obtained in the framework of this project.

We also thank Yves Marechal (CEA - Department of Fundamental Research on Condensed Matter) for helpful discussions concerning the interpretation of FTIR spectra.

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