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Study of the occurrence of hidden corrosion in packaging steels, exposed to potentially corrosive materials such as resin, compound, or foam, in transport conservative temperature/humidity conditions

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Abstract

In application of article 614 of IAEA SSR-6 2012 edition, the packaging materials and any components shall be chemically compatible with each other. However, designers may use different potentially corrosive materials (phenolic foam, mortar-type compound, borated resin) as shock absorbers, thermal or radiological protection, set between steel casings susceptible to corrosion. Could a corrosion process occur between this combination of materials and how would it affect the safety of the packages through their lifetime?

These components often contain halogenides, initiator of steel corrosion under specific conditions of temperature and humidity, which can be reached:

- throughout the packaging manufacturing process if not enough precautions regarding humidity are taken before the operation of closure,
- during the package exploitation if a leak occurs in the outer casing (missing fusible plug, defectory safety valve or weld),

knowing that the temperature inside the packages in normal conditions of transport can exceed 100°Celsius due to the content's inner thermal power and sunshine conditions. This potential corrosion, neither visible from the outside nor from the internal cavity, can be a slow process impairing the mechanical strength of the package within an average 30 years lifespan (i.e. containment and anti-puncture envelopes, gussets).

A test program has been established, and submitted for approval to the French Authority, to expose the materials used in CEA type B packages to laboratory conditions, representative of the conditions described above. Black and stainless steel test coupons (plain, welded, scratched) have been set in the presence of resin/compound/foam blocks in thermal reactors. These reactors have been submitted to several thermal cycles in ovens, with temperature/humidity being monitored. Afterwards, several examinations (weighing, SEM/EDS; Raman spectroscopy) have been performed to assess the corrosion damage and conclude if some configurations present a risk, implying further assessment or precautionary measures. This paper will present the chosen methodology, the test set-up and the most relevant results.

1 - Introduction

As part of the package design approval by its competent Authority, CEA (the French Alternative Energies and Atomic Energy Commission) was questionned about potential corrosion occurring inside the protective structures of the packagings. This phenomenon would not be visible from the outside, nor from the inner cavity, but, during the lifespan of a container, could impair safety by damaging the protective steel shells.

The Radioactive Material Transport Unit (STMR, Cadarache, France) decided to conduct a study, in collaboration with the Physical Chemistry Department (DPC, Saclay, France). From a catalogue of 20 different models of type B packagings, STMR selected a combination of potentially Corrosive Materials (CM) such as phenolic foam, mortar-type compound and borated resin in contact with Metallic Materials (MM), such as black or stainless steel of different grades. The temperatures in normal and accident conditions of transport were identified for each packaging. On this basis, CEA submitted for approval a test program to the French Authorities in 2014, and the experimentations have been conducted since then. This paper describes the different steps of this program:

- Program outline,
- MM and CM supply,
- Experimentation equipment,
- Analysis of the results.

2- Program outline

The CM are set in contact with the MM, in a leak-tight reactor, in which the atmosphere is air with a starting humidity of 85% (representative of the humidity found in Paris area). Temperature cycles are applied on a 2 weeks basis (2 weeks at ambient temperature, alternatively with 2 weeks at maximum temperature[1]). These cycles have been selected because they are in the same number of magnitude as the duration of a type B transport (including provisions for normal conditions of transport delay). Two trial durations have been chosen: 3 months and 1 year.

Afterwards, a 3 months trial with 100% humidity has been conducted on the coupons with the maximum corrosion impact, in parallel with a 3 months trial without CM in order to discriminate the humidity effect on the corrosion phenomenon.

At the end, coupons are submitted to several examinations:

- Gravimetric measurements (weighing), in order to assess the average rate of corrosion,
- Surface examination with an optical microscope, in order to detect potential localized corrosion,
- SEM/EDS or Raman spectroscopy enabling to characterize the corrosion products and the depth of localized corrosion.

This program is summed up in figure 1.

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[1] depending on the package thermal studies, in normal or accident conditions of transport, this maximum temperature is set either at 60°C or 85°C or 160°C

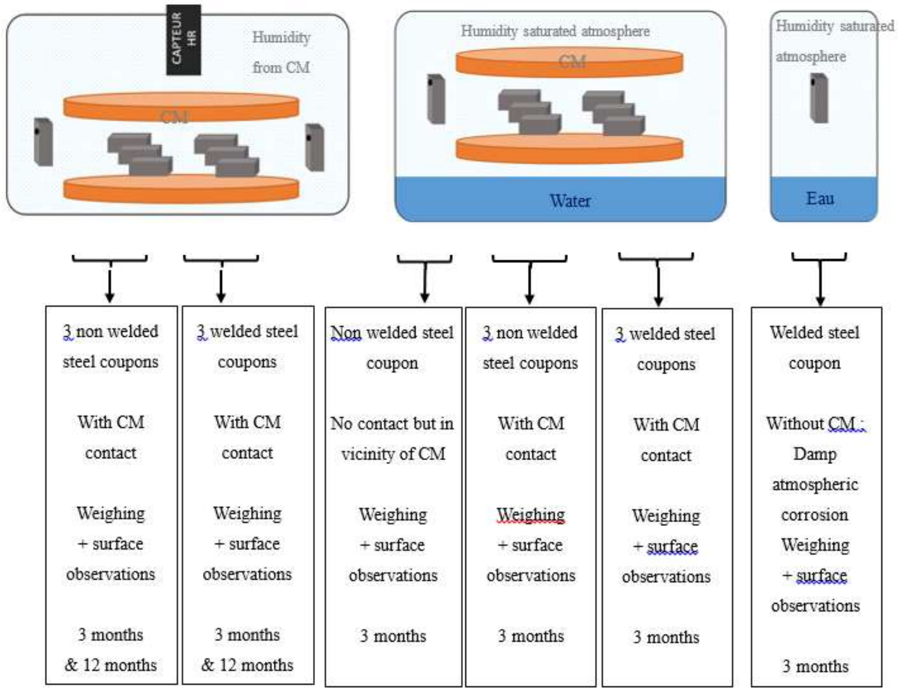

Figure 1 : Program outline

3 – MM an CM supply

3.1 – MM supply

MM, representative of the steel used in packagings, were supplied according to the following steps:

- Black steel and stainless steel were supplied in accordance to a quality assurance plan, in order to guarantee the traceability and the conformity to steel sheets supply norms (mainly to the chemical and mechanical characteristics).
- The steel sheets were welded according to the Welding Procedure Specification of each packaging (supported by the adequate Procedure Qualification Record).
- Coupons (25 mm x 15 mm x 11 mm) were machined out of the sheets on a welded or non welded area (see figure 2).
- On the request of the French Authority, 0,3 mm deep scratches were added on the surface of the coupons.

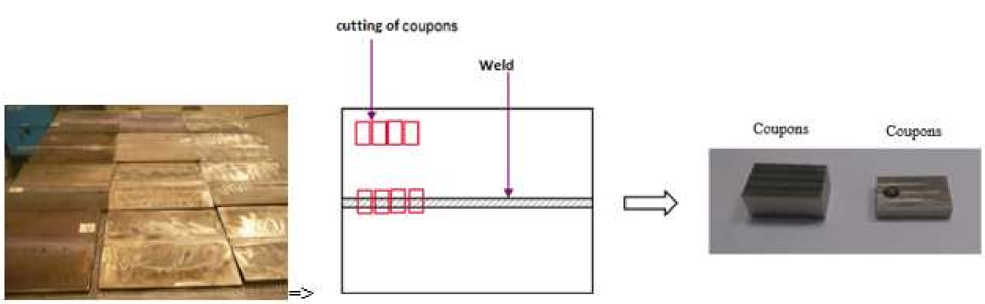

Figure 2 : Localisation for the cutting of coupons on the welded steel sheets

3.2 – CM supply

Many potentially corrosive materials could be found in the 20 CEA type B packagings. On the basis of a preliminary characterization focused on the porosity, the hydric behavior, the rate of halogen and the pH, the materials presenting the most important risk of corrosion were selected for each of the 3 families: 200h phenolic foam (see fig.3), PNT7 compound (see fig.4) and HETRON resin (see fig.5). From raw blocks, supplied under quality assurance plan, they were cut, without using water, into their trial shapes (80 mm diameter disks, 5 mm thickness).

Figure 3 : 200h phenolic foam

Figure 4 : borated mortar-type PNT 7 compound

Figure 5 : HETRON resin

4 – Experimentation equipment

4.1 – Chemical reactor

The function of this reactor is to be inert chemically, to resist trial temperatures, to enable a view of the reactions inside throughout the trial. It must ensure a good level of leak-tightness and guarantee that the contact between CM and MM is maintained. Therefore, the following structure described in figure 6 was specifically designed (see also photos in fig.7).

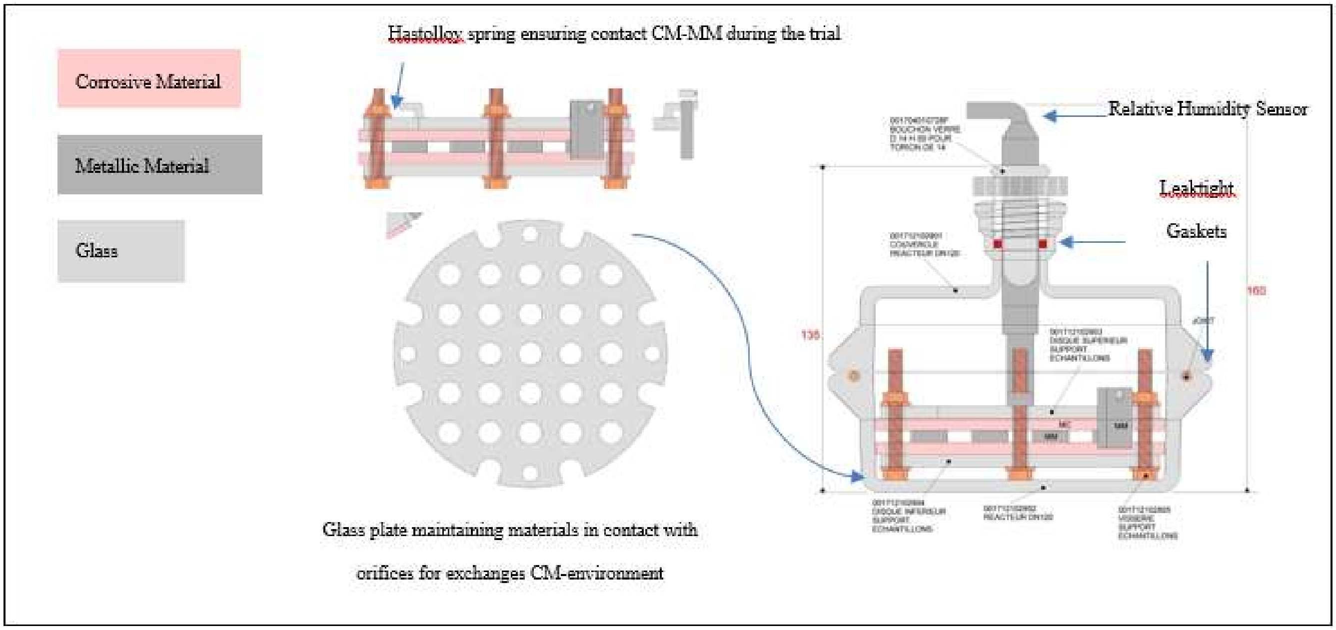

Figure 6 : Layout of the glass cells

(a) *(b)* *(c)*

Figure 7 :Experimental setting, (a) metallic coupons inserted between CM, (b) device maintaining contact between CM and MM , (c) cells equipped with Relative Humidity sensor, set in oven

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4.2 – Humidity sensor

The model reference is ROTRONIC HC-2S up to 85°C and HC-2 IC102 up to 160°C. It is connected to a PC for continuous recording. The sensor was tested in an empty cell and a cell with 200h foam with 25°C/60°C cycles before the official trial and it shows the capacity of the foam to release humidity gradually, and the fact that there is a loss of humidity due to an insufficient leak-tightness level of the reactor at high temperature (see the slow downward curves in fig.8 each time the cycle temperature is high). This is the reason why 3 months trial with permanent 100% humidity were added to the program.

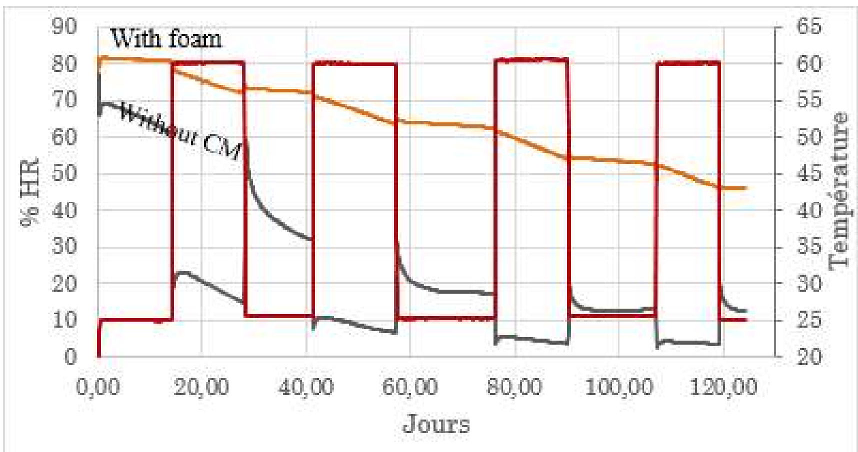


Figure 8 : Relative humidity evolution in an empty cell and a cell with 200H foam

4.3 – Post trial measurements

The optical microscope is an Olympus Bx51 (magnification x5 to x100).

The weighing is performed after desquamation of oxid layers under NF ISO 8407. The average corrosion speed is calculated with the formula $\frac{\Delta m.365}{\rho.S.ndays}.10^{-6}$ (Δm is the loss of mass; ρ is the density; S is the surface of exposure; n_{days} is the trial duration).

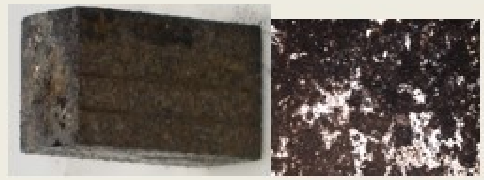
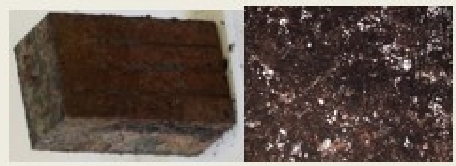
The Raman spectrometry (HORIBA XPLORA) enables the identification of the type of oxide involved in the corrosion.

The Energy Dispersive Spectrometry (X FLASH 6/30 BRUCKER) identifies the corroded zone and gives access to the depth of corrosion measurement.

5 – Analysis of the results

5-1 Observations

As per fig.9, stainless steel do not show evidences of corrosion. It is corroborated by weighing. Black steel, and especially E24-2, E36-4 and Mars 240 in contact with 200H foam, are corroded.

MC	max Temperature	MM grade	3 months trial typical optical observations
200H Foam	60°C	E24-2	
		E36-4	
		Mars 240	
	85°C	304L –8 mm thick	
		Uranus 45N	
PNT7 mortar	60°C	304L	
		Fe430D1	

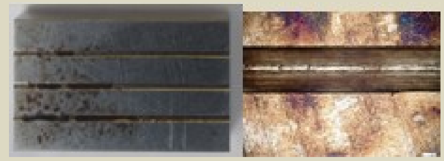
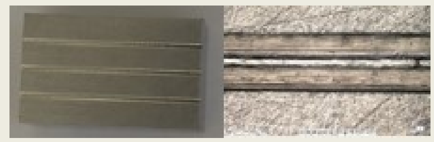
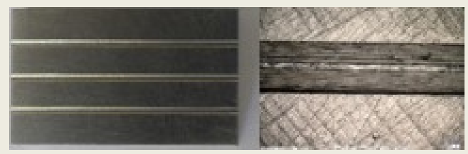
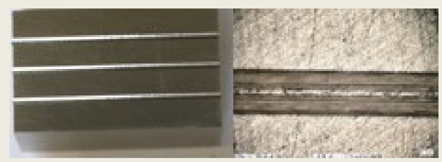
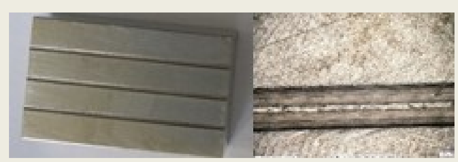
MC	max Temperature	MM grade	3 months trial typical optical observations
	85°C	304L	
HETRON Resin	85°C	Uranus 45N	
		304L	
	160°C	304L	
		Uranus 45N	
		A48FP	

Figure 9 : 3 months trial typical observations on coupons

5.2 – Focus on black steels with 200H foam

As shown in figure 10 and 11, the corrosion remains general and no evidence of localized corrosion was discovered. The average corrosion speed (see fig.12) in the worst condition of humidity is around 30 µm/year. It can be compared to a medium corrosivity in marine conditions (NF ISO 9223 and 9224: C3 class). In more realistic conditions of humidity, the corrosion rate would be qualified as low to very low (C1 or C2 class).

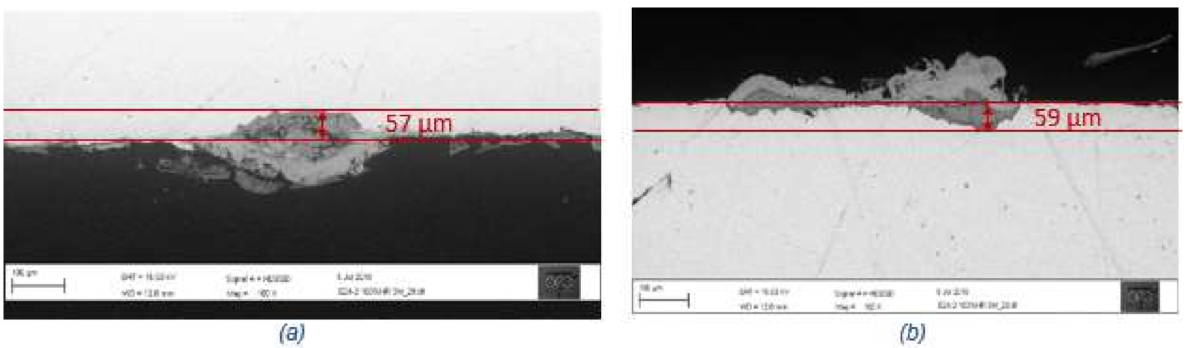


Figure 10 : Maximum corrosion depth measurements on SEM images (a) E24 (b) E36

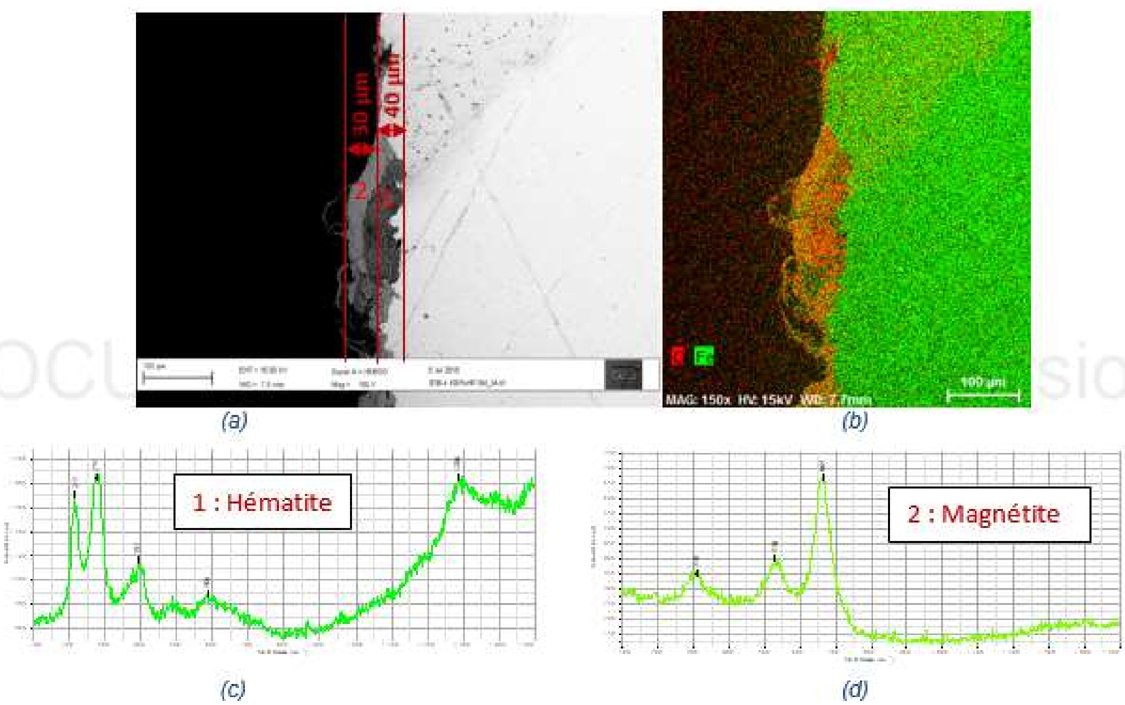


Figure 11 : (a) SEM image of steel coupon cross section (b) EDS cartography showing corrosion products (c) Raman analysis point 1 (d) Raman analysis point 2

Trial Duration – Steel aspect	E24-2				E36-4				Mars 240			
	85% RH		100% RH		85% RH		100% RH		85% RH		100% RH	
	Weight loss (mg)	Corrosion speed (µm/year)	Weight loss (mg)	Corrosion speed (µm/year)	Weight loss (mg)	Corrosion speed (µm/year)	Weight loss (mg)	Corrosion speed (µm/year)	Weight loss (mg)	Corrosion speed (µm/year)	Weight loss (mg)	Corrosion speed (µm/year)
3 months Non welded	4.9	**1.2**	101	**30**	4.8	**1.5**	100	**31**	0.8	**0.25**	102	**31**
3 months Welded	5.3	**1.6**	97	**29**	6.6	**2.0**	102	**31**	1.4	**0.43**	75	**23**
12 mois Non welded	6.2	**0.50**			0.7	**0.05**			0.7	**0.05**		
12 mois Welded	7.4	**0.58**			1.5	**0.12**			1.5	**0.12**		

Figure 12 : Average corrosion speeds for E24, E36 and Mars 240 (calculated with the hypothesis of homogeneous corrosion)

6 – Conclusion

As one could have anticipated, stainless steels are not exposed to a risk of corrosion from the selected materials present in CEA packagings, stated as potentially corrosive, such as resin, mortar or foam. As the preliminary characterization concluded, resins do not tend to present a corrosion risk in normal or accident conditions of transport because its capacity to retain humidity and the fact that the chlore it contains is chemically linked. Likewise, mortar type compounds do not easily release humidity and their pH are basic, which leads to the creation of a passive protective layer against corrosion.

As anticipated, the main corrosion phenomenon was detected on black steel in presence of phenolic foams. Several remarks could be highlighted:

- There are no aggravating effects from the scratches or the welded zones,
- The corrosion process is faster at the start and tends to stabilize after a few weeks,
- The corrosion phenomenon is not stronger than in saline environment and can be qualified as a low to very low corrosion process.

As regards CEA specific packagings, and even if the corrosion process has been stated as low, the corrosion detected on black steel plates would not be an issue because:

- The E24 or E36 plates are casings and do not contribute to any safety functions,
- The Mars 240 plate is coated by an anti-corrosion paint which prevents any corrosion from occurring.