SEAWATER CORROSION OF RADIOACTIVE MATERIAL TRANSPORT PACKAGES

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ABSTRACT

The transport of radioactive materials by sea is estimated to 255 shipments on average each year in France. To these movements may be associated the risk of immersion of a ship's cargo by accident. In this case, the packages of radioactive materials immersed in this way can lie at different depths and suffer seawater corrosion.

This study estimates in a conservative manner the minimum time for the loss, due to corrosion, of watertightness or strength of the constituents of the packages. The recovery of packages immersed may thus be organised and carried out in satisfactory conditions, as regards contamination problems, if within this minimum time.

The most toxic radioactive materials likely to be involved include : PuO_2, high-activity vitrified waste, UF_6 and irradiated fuel. The types of packaging studied, are those most frequently used for the maritime transport of the materials dispatched or received by France.

Seawater is a particularly aggressive environment for the majority of metallic materials which constitute these packages and their immersion in a marine environment can set up strong galvanic interaction between the different materials, which accelerates corrosion.

Two types of phenomena can be identified :

- phenomena of **generalised corrosion**, which are slow-acting and involve the overall weakening of the structure, culminating in large leaks and contamination, either in solution or in suspension,
- phenomena of **localised corrosion**, quick-acting but not accompanied by loss of strength, and culminating in a large number of minor leaks and thus the rapid entry of water, but without any serious transfer outside of the package. The dispersed contamination should thus be low.

Three phases may thus be defined :

- a destruction phase : at the end of this phase, destruction of the package caused by generalised corrosion will occur, implying the probable ejection of the materials,
- a shorter, penetration phase : at the end of this phase, penetration of water caused by localised corrosion of the structure of package will probably occur,
- a phase of loss of watertightness, also shorter : at the end of this phase, a loss of watertightness caused by localised corrosion of the sealing surfaces will occur.

Thus, the estimated destruction time of the packages in the sea varies from 80 years to several thousand years. The time for the penetration of a package is, on average, 10 years. But the loss of watertightness may be much more rapid, about two years.

INTRODUCTION

This survey allows conducting a conservative assessment of the minimum time for tightness or mechanical resistance loss, due to corrosion, of radioactive material package components immersed after a maritime accident.

The types of packagings studied are those most frequently used for sea transport of the most toxic or most frequently transported materials, PuO2, irradiated fuels, highly active vitrified waste and UF6.

Seawater is a specially aggressive environment for most of metal materials composing such packagings, and may generate high galvanic couplings between the various materials, thus accelerating corrosion.

Two types of phenomena can be considered : generalized corrosion phenomena and selective corrosion phenomena, from which three periods can be defined: a destruction time, a perforation time and a tightness loss time.

DESCRIPTION OF THE SELECTED PACKAGES

Five packaging families were selected :

- Irradiated fuel transport casks : TN 12/1, TN 12/2 and TN 17/2, which may also be used for transporting MOX type new fuels
- Highly active vitrified waste transport casks : TN 28 VT, TS 28 V
- Plutonium oxide powder transport packagings : FS 47
- Natural uranium hexafluoride transport cylinders : 48 Y
- Enriched uranium hexafluoride transport cylinders 30 B in their protective overpack.

These packages are made of different materials, namely: carbon steel, stainless steel, copper, aluminum alloys, etc., generating galvanic couplings.

TYPE OF CORROSION

By definition [ISO 1986], corrosion corresponds to the physico-chemical interaction between a metal and its environment, generating modifications in the metal properties and often a functional degradation of the metal itself or its environment, or the technical system formed by both factors. Corrosion thus represents any degradation process of metal materials, or their properties, due to a reaction with the environment.

Seawater is a specially aggressive environment for most metal materials. Various types of corrosion can be met.

Generalized corrosion

This is a nearly uniform attack on all points of the material surface. It appears as a more or less regular dissolution of a metal placed in an aggressive environment [Alechine et al. 1993].

In seawater, generalized corrosion rates are sometimes high, but selective corrosions are more insidious, more difficult to control and sometimes to detect.

Selective corrosion

It is due to the location of anodic areas at certain parts of the interface, due to inconsistencies in metal or electrolyte [Alechine et al. 1993].

- **Galvanic corrosion**, or bimetallic corrosion, due to electrical coupling, in an electrolyte, between the corroded metal and a more noble metal, or between any adjacent anodic and cathodic areas. This is an electrochemical process which may generate various forms of corrosion, and more specially pitting corrosion. It consists of highly localised attacks, usually relating to the creation of small anodes adjacent to a large cathode, due to local destruction of the protective film. Stainless steels are specially sensitive to this type of corrosion in presence of chloride ions. Presence of oxygen or of an oxidizer is necessary and the pitting risks are all the more important as the steel corrosion potential is high.

- **Crevice corrosion**: this corrosion is due to a modification in chemical conditions within a confined area with respect to the environment; it is characterized by :
    - an oxygen depletion generating corrosion by differential airing.
    - acidification of the solution inside the crevice.

This corrosion develops in confined environments, under seals or under deposits, for example; this is why it is also known as interstitial corrosion and corrosion under deposit.

Other types of corrosion :
- blister, propagating through local cavity enlarging
- intergranular, between the metal crystalline grains, accelerated by precipitation phenomena at grain joints due, for example, to high temperature sensitizing or mechanical stresses.

RESISTANCE OF PACKAGE MATERIALS IN SEAWATER

Carbon steel

Carbon steel in seawater may undergo various types of corrosion: generalized corrosion [Mathieu 1981] , galvanic corrosion [Plante and Cojan 1981] due to carbon steel/stainless steel coupling or to carbon steel/copper coupling which may appear as extended corroded surfaces or pitting [Mathieu 1981]. Table 1 below summarizes the various corrosions.

Table 1 : Corrosion rates for carbon steel

Types of corrosion	Carbon steel corrosion rate (mm.year^{-1})
Generalized corrosion	0.1-0.2
Pitting corrosion	2-3
Extended galvanic corrosion : (anode and cathode surface ratio)	
Fe/Cu minimum coupling (1/1)	0.2
Fe/Cu maximum coupling (1/25)	10
carbon steel/stainless steel coupling (1/5)	5
carbon steel/stainless steel coupling(1/100)	10

Austenitic stainless steels

The stainless steel resistance to corrosion is basically due to the presence of chromium.
In chlorinated environment, austenitic stainless steels have a good resistance to generalized corrosion but may undergo important selective corrosion, by pitting [Barnier et al. 1980], [Grolleau and Leguyader 1996], [Mathieu 1981] and by crevice effect. In certain cases, they are also sensitive to stress corrosion. Table 2 below summarizes the various corrosions.

Table 2 : Corrosion rates for stainless steel

Types of corrosion	Stainless steel corrosion rate (mm.year^{-1})
Generalized corrosion	0.0004
Pitting corrosion (304 L steel)	12
Crevice corrosion (304 L steel)	12
Stainless steel/copper galvanic corrosion:	
surface ratio 1	0.5
surface ratio 10	5

Aluminum alloy

The aluminum resistance to corrosion is due to the development of a 50 to 100 angström oxide film (alumina) isolating the material from the environment. Like for steels, selective corrosions are the most critical: pitting corrosion, blister corrosion [Schumacher 1979], galvanic corrosion [Schumacher 1979], intergranular corrosion. Table 3 below summarizes the various corrosions.

Table 3 : Corrosion rates for aluminum

Types of corrosion	Aluminum corrosion rate (mm.year^{-1})
Generalized corrosion	0.05
Pitting corrosion	5
Crevice corrosion	5
Galvanic corrosion : aluminum / carbon steel aluminum / stainless steel aluminum / copper	 0.1 1 10

Zircaloy

The resistance of the zircaloy cladding of the fuel pellets appears to depend on the immersion depth [Groupe permanent 1984] :

- at less than 1500 m depth, the cladding remains tight; all surveys demonstrate that hundreds of years are necessary for the corrosion to become such that the cladding breaks, and thus the ultimate barrier to radioactivity scattering be destroyed ;
- at more than 1500 m depth, the fuel sheath breaks due to zircaloy buckling under pressure.

Other surveys [Parfenov 1969] conducted in aqueous but non marine environments, provide interesting results:

- at a temperature of 315°C and with a pressure equal to 110 atm, the corrosion rate is 0.6 μm.year^{-1}. Considering the thickness of the zircaloy claddings which is about 600 μm, the life time (specific to corrosion) thus obtained is 1000 years. These figures correspond to the generalized corrosion of new zircaloy (non irradiated) ; for irradiated claddings sensitive to selective corrosion, life time is shorter.

BEHAVIOUR OF PACKAGES UNDER SEAWATER CORROSION

For the eight packages under study, two phenomena may be considered :

- generalized corrosion phenomena, slow phenomena resulting in an overall weakening of the structure creating a large sectional leakage thus allowing contamination transfers in solution or suspension,
- selective corrosion phenomena, fast phenomena not involving mechanical weakening and resulting in numerous small leakages, thus a quick water penetration, but with no important transfer outside the container. Contamination scattering should then be low.

It is thus possible to define three periods :

- a probable contamination discharge period, following a generalized corrosion, which will be noted as destruction time,
- a shorter probable water penetration period, following a selective corrosion on the packaging body, which will be noted as perforation time,
- a still shorter tightness loss time, following a selective corrosion under the cover or port element seals, which will be noted as tightness loss.

Table 4 below summarizes the life time of each package depending on various corrosion processes, keeping in mind that these values are reasonable envelopes, usually pessimistic, but involving high uncertainties in case of accelerating phenomena, like water local acidizing, more specially in case of crack development.

CONCLUSION

Based on a literature survey and on pessimistic assumptions, the perforation time of a packaging at sea is equal to 10 years as an average. But tightness loss may be faster. Indeed, some months may be enough for seawater to "wash away" the stainless steel layer under the seals and penetrate the packaging.

For more precise results on loss times of package leak tightness, it would be interesting to conduct specific corrosion tests using representative geometries of package components.

It should also be noted that the 304 L stainless steel which, under normal conditions, guarantees a good performance of package tightness systems, is seawater corrosion sensitive through pitting or crevices.

However, the results of this survey do not presume the mechanical effects of package immersion, which might also result in the immediate loss of package containment beyond certain depth thresholds, more specially through buckling of steel sheets or components under external pressure effect.

Table 4 : Summary of packaging life times (values corresponding to pessimistic hypotheses)

Packaging	Corrosion process	Destruction time, by generalized corrosion	Perforation time, by selective corrosion	Seal tightness loss time (seal bearing corrosion)
TN 12/1	radial/body	1300 years	30 years	
	axial/bottom	1700 years	35 years	
	axial/cover	400 years	10 years	16 months
TN 12/2 and TN 17/2	radial/body	1300 years	30 years	
	axial/bottom	1400 years	30 years	
	axial/cover	> 100 000 years	10 years	2.5 years
TN 28 VT and TS 28 V	radial/body	1500 years	130 years	
	axial/bottom	1800 years	130 years	
	axial/cover			
	TN 28 VT	> 100 000 years (stainless steel)	6 years	16 months
	TS 28 V	800 years (carbon steel)	15 years	16 months
FS 47	radial/body	62 000 years	60 years	
	axial/bottom	63 000 years	60 years	
	axial/cover	> 100 000 years	4 years	16 months
	radial / inner containers	40 000 years	16 months	
48 Y	cylinder	80 years	5 years	
30 B	overpack in stainless steel	7000 years	3 months	
	overpack in carbon steel	15 years	1 year	
	packaging in carbon steel			
	with overpack in stainless steel	7000 years	1 year	
	with overpack in carbon steel	70 years	5 years	

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