



Italian National Agency for New Technologies,  
Energy and Sustainable Economic Development ▶

# Experimental investigation of corrosion of nuclear materials and radioisotopes release under aggressive leaching conditions

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**A. Ubaldini, F. Cicconi, G. Pintilei, C. Telloi, A. Gessi, G. Marghella, A. Rizzo**



# Introduction

- ENEA general activities
- General aspects of corrosion
- Water radiolysis
- Leaching under aggressive conditions
- Metals and steel behaviour
- Conclusions

# General aspects: ENEA



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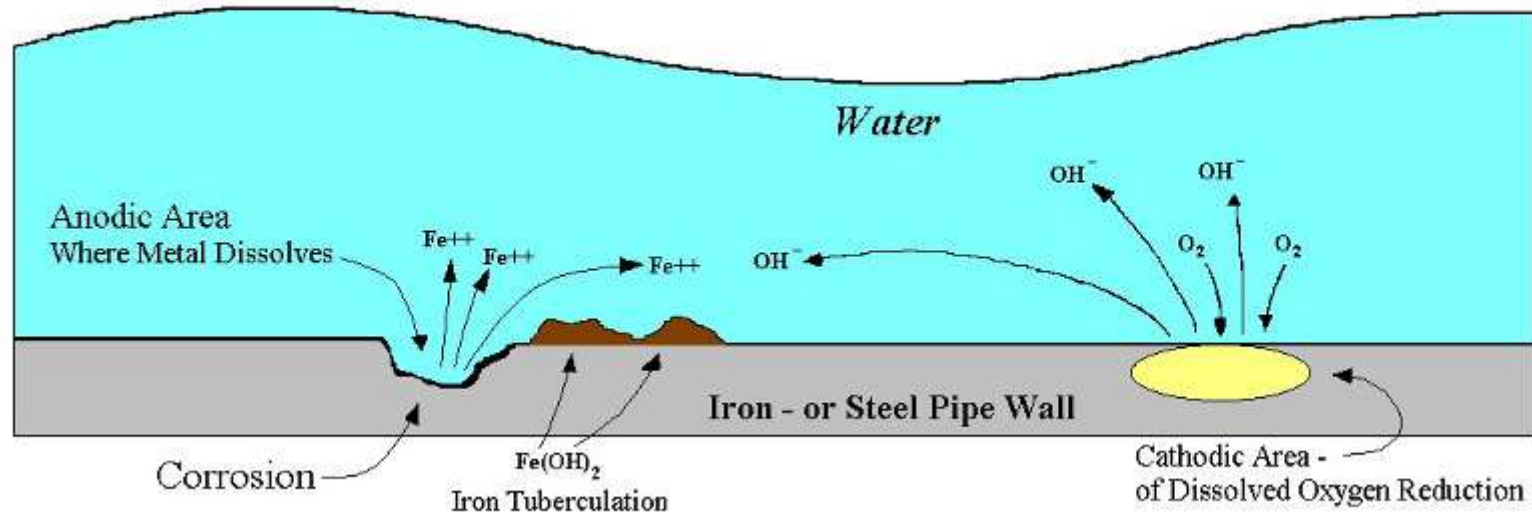
# Corrosion

- The term “**Corrosion**” indicates a natural and irreversible process of slow and continuous consumption of a material, which has the consequences of worsening the characteristics or physical properties of that materia.
- Corrosion can be defined as a process of degradation and transformation of some materials with high energy content into systems and other compounds with a lower energy content and therefore more stable.
- It depends on the external conditions and strongly on the environment in which it occurs (dry, humid, with high or low concentration of oxygen, due to microbiological action...)
- In general, corrosion is a complex set of different chemical-physical processes, each with its own peculiarities and different microscopic mechanisms and macroscopic consequences.
- Corrosion in aqueous environments is one of the most important

# Water radiolysis

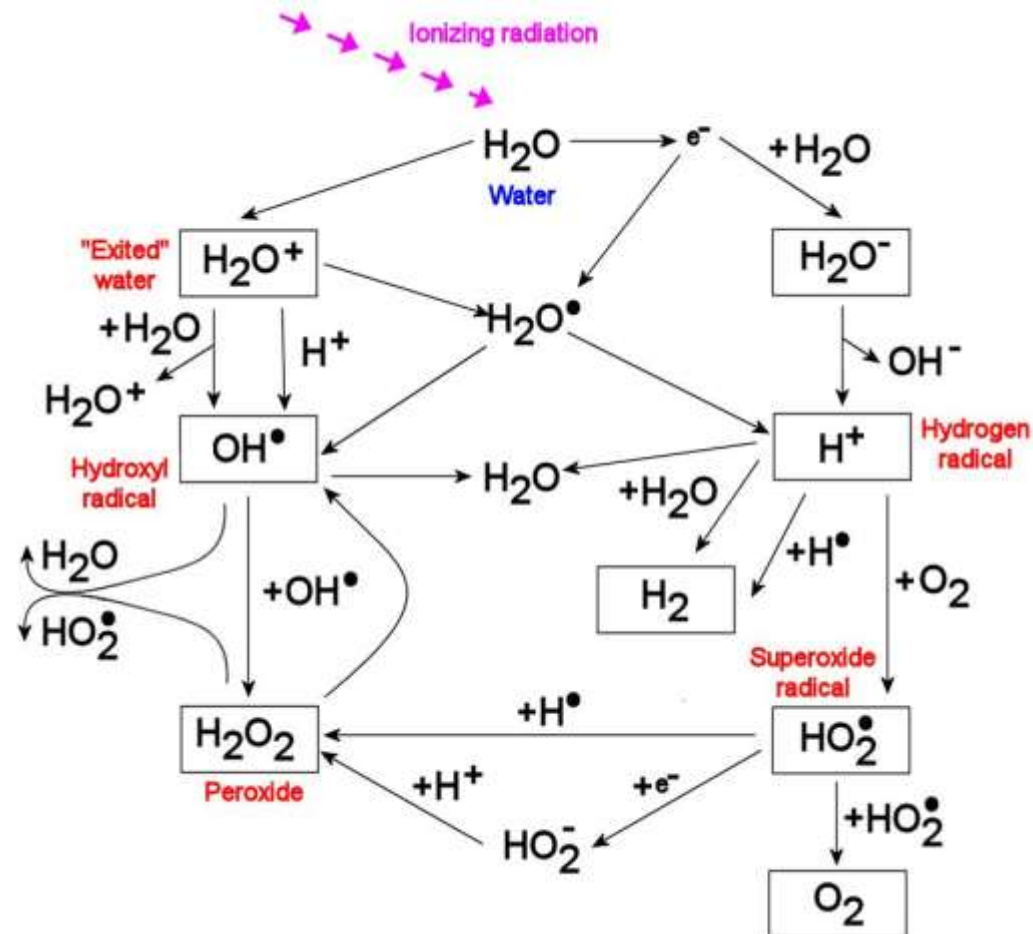
- Water is a very good solvent for a huge number of materials and compounds and it can lead, especially in case of saline solutions, even to corrosion of metals in steels albeit over a very long time.
- In presence of oxygen several galvanic processes can take place

## *The Corrosion Cell :*



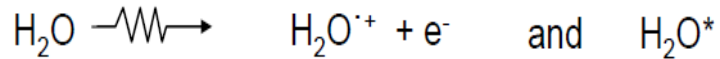
# Water radiolysis

- In presence of ionizing radiation a series of chemical physical process occurs lead to the formation of extremely active species: active ions, free hydroxyl radicals, free hydrogen atoms and solvated electrons including  $\cdot\text{OH}$ ,  $\text{O}\cdot$ ,  $\text{H}\cdot$ ,  $\text{HO}_2\cdot$ ,  $\text{O}_2\cdot^-$ ,  $\text{H}_2$ ,  $\text{O}_2$ ,  $\text{H}_2\text{O}_2$ , making water more aggressive medium



# Water radiolysis

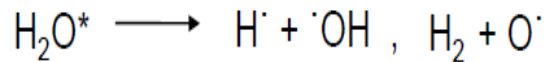
a) Ionization and activation of water molecules



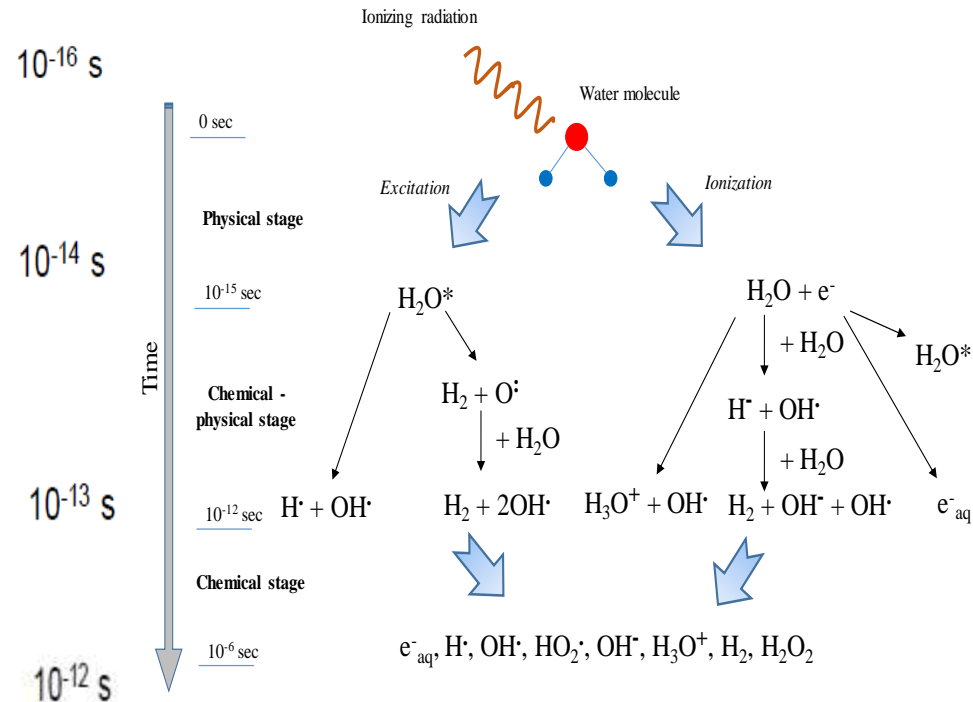
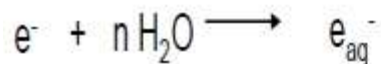
b) Ion-molecule reactions



c) Dissociation of excited molecules



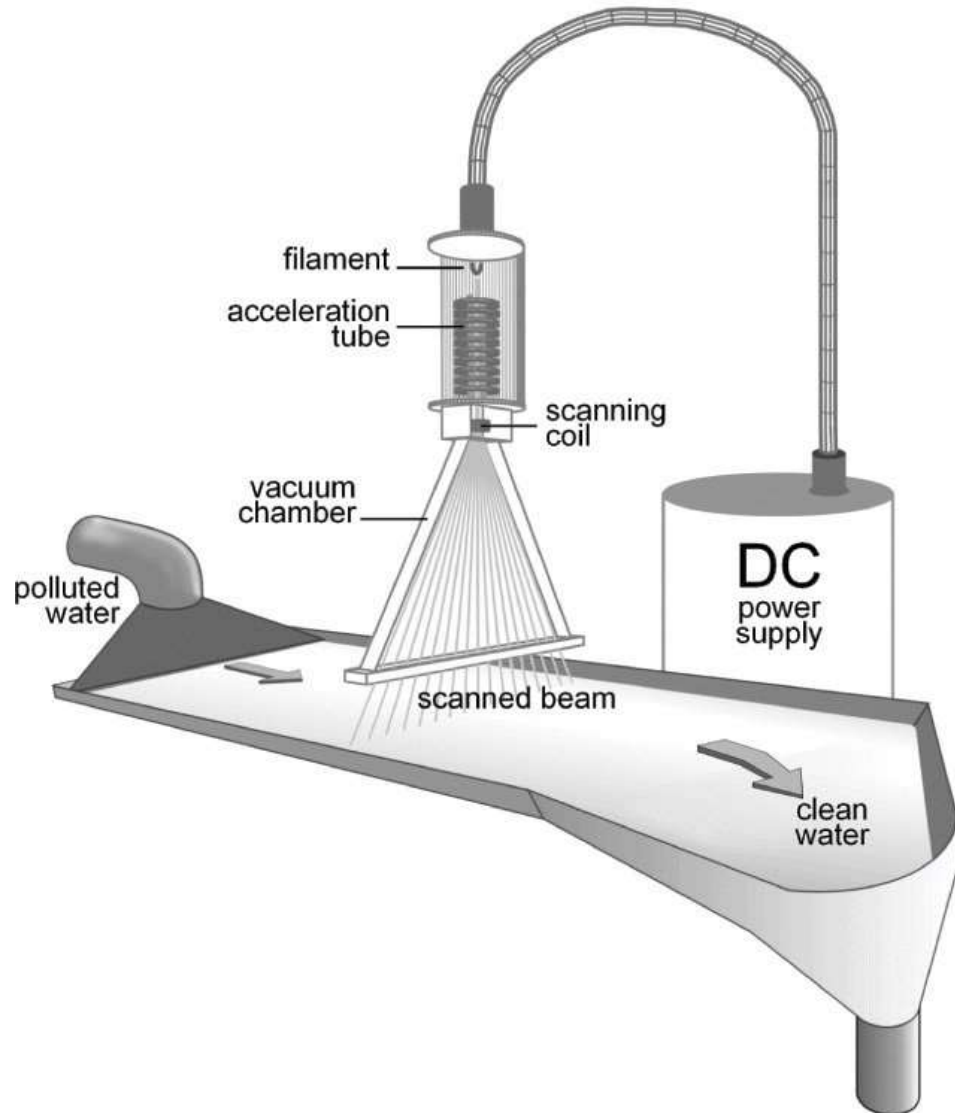
d) Free electron solvation



➤ Radicals and ions can be extremely aggressive and they can induce new reactions

# Water radiolysis

There are industrial wastewater treatment plants that use beams of ionizing radiation, particularly electrons, to remove pollutants that cannot be destroyed in any other way. They are very effective





# Metals corrosion

- Some of these species, such as hydrated electrons and hydrogen atoms are strong reducing agents, whereas hydroxyl radicals are very strong oxidative ones. Under such conditions, even low reactive metals, as molybdenum or some steels, can undergo to much more severe corrosion than what could be expected during a typical use, reducing the life time of certain components.
- Radiolysis of water and its effects are difficult to study at laboratory scale and in reasonable time.
- It is possible to emulate such conditions using highly concentrated  $\text{H}_2\text{O}_2$  at a high temperature and different pH.

# Metals corrosion

- The behavior of some metals and steels under these conditions has been studied.
- Samples of various metals with masses of the order of a few hundred milligrams were subjected to the action of hydrogen peroxide at 70 °C, (40 % w/w) with or without addition of hydrochloric acid at different concentrations, to conduct an accelerated study of their corrosion. H<sub>2</sub>O<sub>2</sub>

Metallic system	HCl added	Time [min]				
		5	10	15	30	60
Molybdenum	0	5	10	15	30	60
Tungsten	0	5	10	15	30	60
Niobium	10 %	60	120	180	240	360
Iron	0			15	30	60
Iron	1 %			15	30	60
Iron	5 %			15	30	60
Steel 616	0	60	120	180	240	360
Steel 616	1 %	60	120	180	240	360
Steel 616	5 %	60	120	180	240	360
Steel 616	10 %	60	120	180	240	360
Steel 616L	0	60	120	180	240	360
Steel 616L	1 %	60	120	180	240	360
Steel 616L	5 %	60	120	180	240	360
Steel 616L	10 %	60	120	180	240	360
Steel 616Ti	0	60	120	180	240	360
Steel 616Ti	1 %	60	120	180	240	360
Steel 616Ti	5 %	60	120	180	240	360
Steel 616Ti	10 %	60	120	180	240	360
Steel 321	0	60	120	180	240	360
Steel 321	1 %	60	120	180	240	360
Steel 321	5 %	60	120	180	240	360
Steel 321	10 %	60	120	180	240	360
Steel 347	0	60	120	180	240	360
Steel 347	1 %	60	120	180	240	360
Steel 347	5 %	60	120	180	240	360
Steel 347	10 %	60	120	180	240	360

# Metals corrosion

Molybdenum, tungsten and few other metals react quickly with hydrogen peroxide, cast iron can be corroded or altered, while other metals, such as niobium, are practically not corroded. Steels usually are resistant to pure peroxide, but undergo to corrosion when pH is lower than 7.

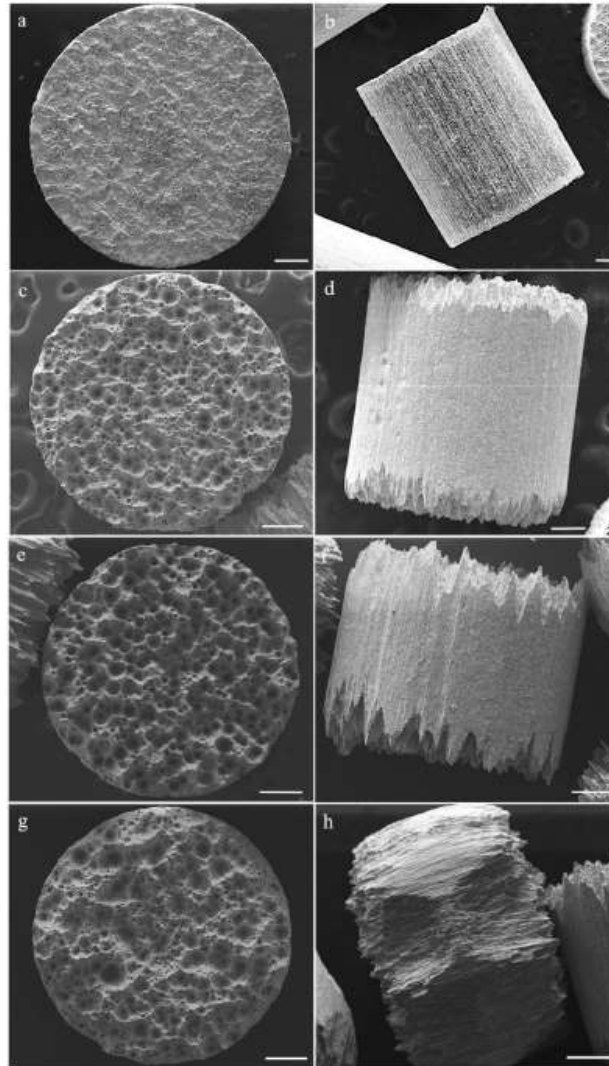
The case of pure molybdenum is interesting and it has been studied in details

This metal has normally high resistance versus corrosion much slower than steel, low linear expansion coefficient, relatively high thermal and electrical conductivity and excellent mechanical characteristics, even at very high temperature, such as high tensile strength and stiffness.

However it reacts with pure hydrogen peroxide with a reaction rate that depends on the concentration. molybdic acid  $H_2MoO_4$  forms

# Metal corrosion

The temporal evolution of molybdenum pieces surface that have been in contact with hydrogen peroxide 30% and the appearance of corrosion can be observed



time

SEM images of some molybdenum pieces from top row to bottom row:

**0 min ((a) basal view, (b) lateral view)**

**30 min ((c) basal view, (d) lateral view),**

**60 min ((e) basal view, (f) lateral view),**

**120 min ((g) basal view, (h) lateral view).**

# Metal corrosion

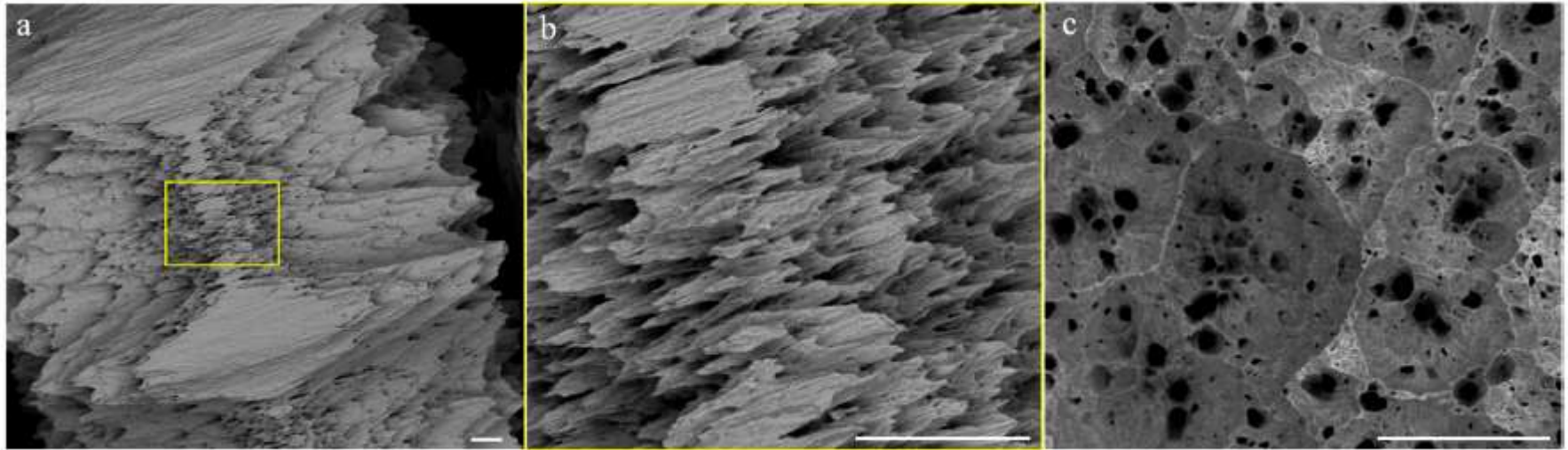
Mean dimensions of the diameter and the lengths of the pellets at various dissolution times in peroxide solution 30%.

Reaction Time	Mean Pellet Diameter ( $\mu\text{m}$ )	Mean Pellet Length ( $\mu\text{m}$ )
0 min	$1490 \pm 10$	$1710 \pm 10$
30 min	$1253 \pm 10$	$1113 \pm 10$
60 min	$1265 \pm 10$	$935 \pm 10$
120 min	$1210 \pm 10$	$626 \pm 10$

Mean dimensions of the diameter and the lengths of the pellets and maximum values for diameter and length of corrosion lines as obtained by SEM image analysis at various dissolution times in peroxide solution 30%.

Reaction Time	Mean Corrosion Lines Diameter ( $\mu\text{m}$ )	Mean Corrosion Lines Length ( $\mu\text{m}$ )	Max Value of Corrosion Lines Diameter ( $\mu\text{m}$ )	Max Value Corrosion Lines Length ( $\mu\text{m}$ )
30 min	$1253 \pm 10$	$1113 \pm 10$	118	271
60 min	$1265 \pm 10$	$935 \pm 10$	108	408
120 min	$1210 \pm 10$	$626 \pm 10$	126	626

# Metal corrosion



Backscattered SEM images of Mo pellet as obtained after 120 min of reaction time.  
Lateral  
All scale bars are of 50  $\mu\text{m}$ .

The corrosion lines run along the lateral surface until reaching the middle of the barrel-shaped pellet.



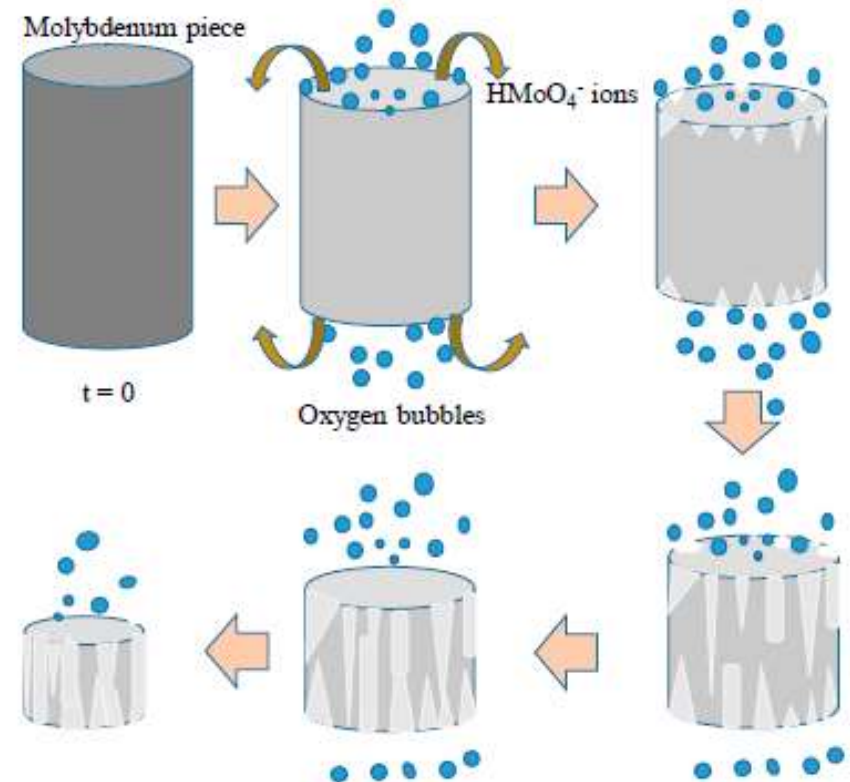
# Metal corrosion

Dissolution on the planar faces starts at the beginning uniformly over the entire surface

and on both sides in a similar manner. However very soon, there is formation of some deep corrosion points on these surfaces, with morphology that is quite reminiscent of pitting.

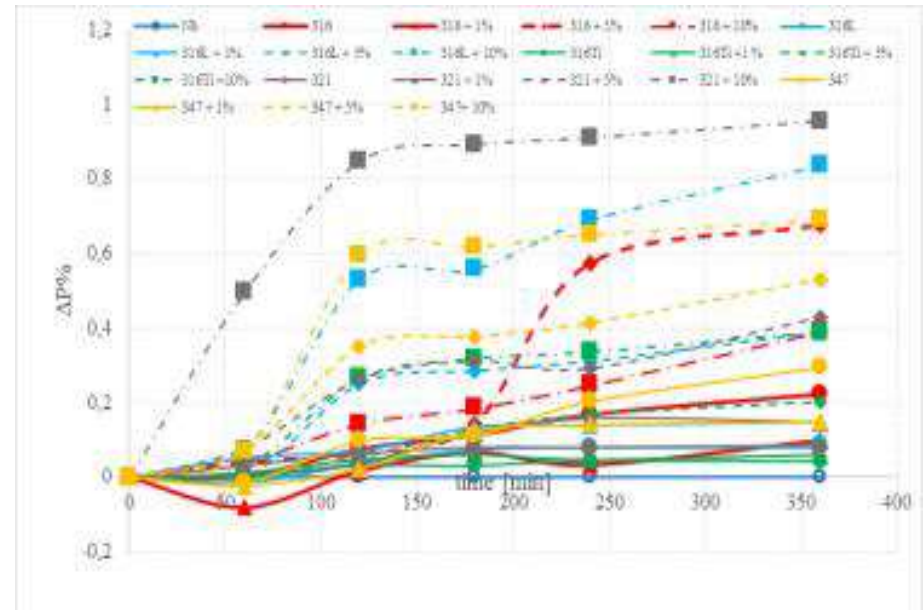
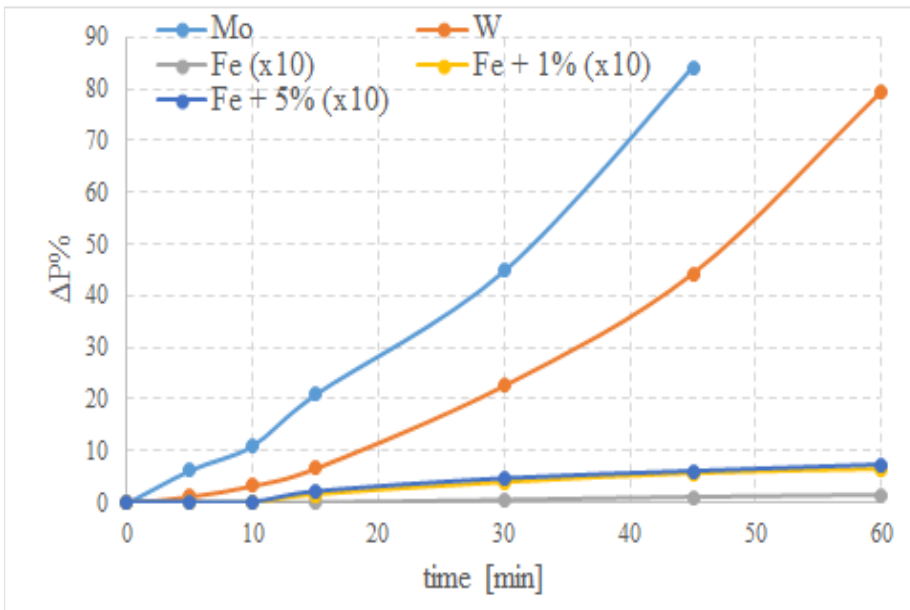
These corrosion marks, especially the larger ones, are often separated by thin walls that meet at angles of about  $120^\circ$

In this case, as the signs of corrosion appear new, surface attackable by the peroxide is created, making the dissolution faster



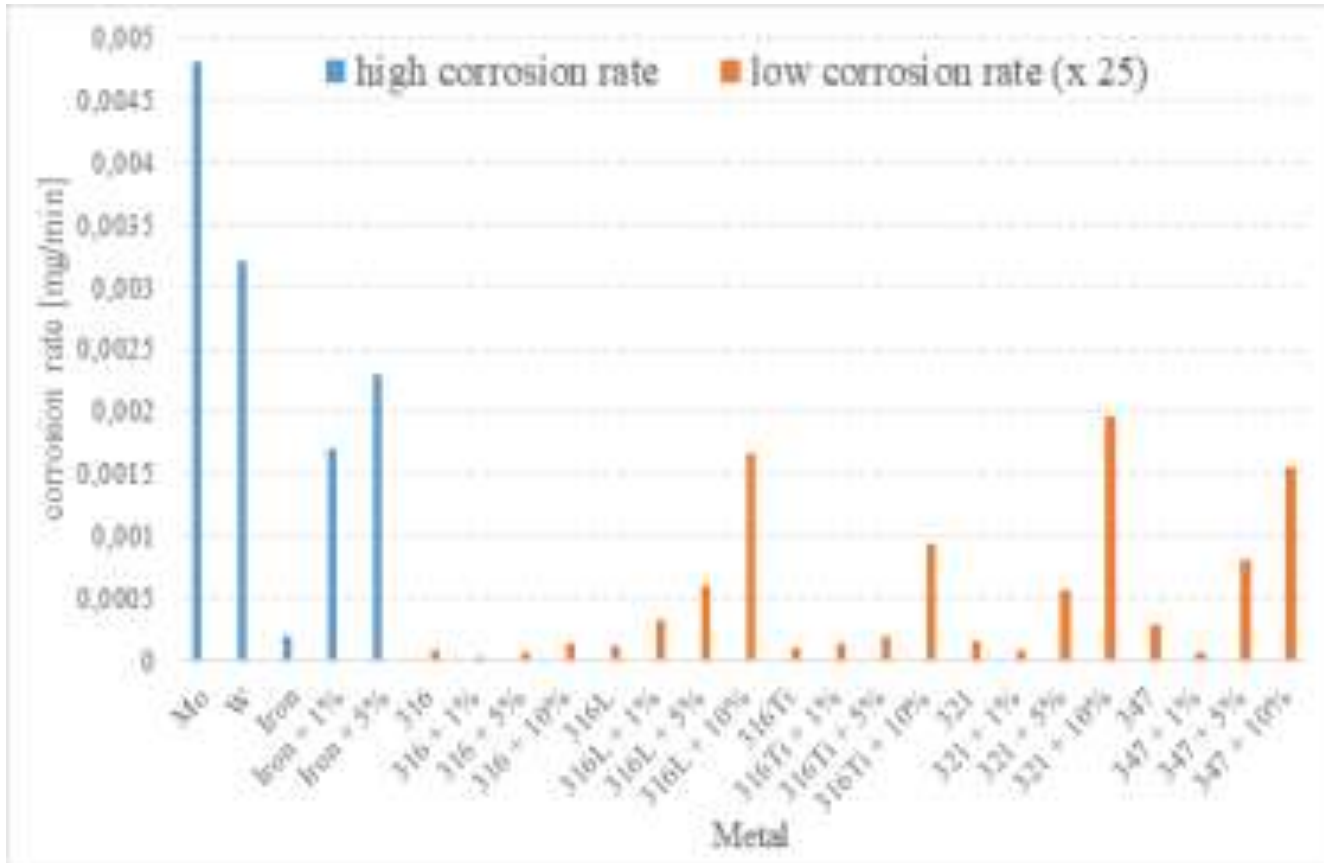
# Metal corrosion

The kinetics and mechanism of corrosion strongly depend on the type of material considered. The kinetics can be studied by the percentage weight change as a function of time.





# Metal corrosion

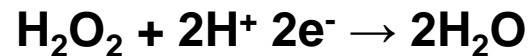


Corrosion rate for different metals exposed to  $H_2O_2$  at 70 °C, under different pH

# Metal corrosion

In general, a decrease in weight as a function of time is observed, in most of the cases it is very small, but still measurable.

Hydrogen peroxide under acidic pH is a good oxidant, according the semi reaction:



Many metals under these conditions are oxidized to higher valence states, normally more soluble in water.

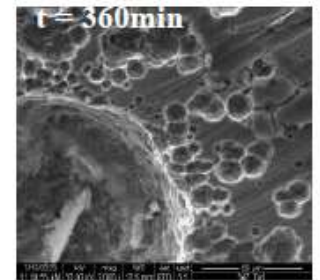
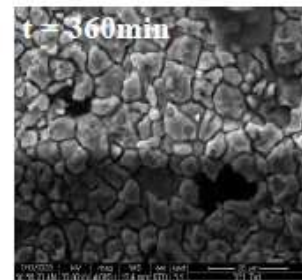
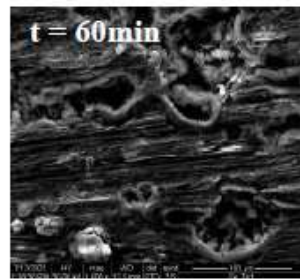
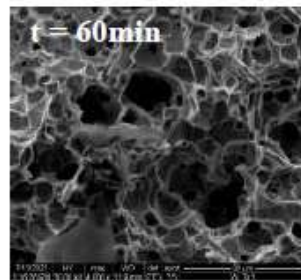
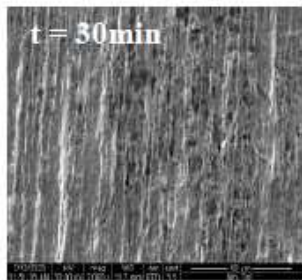
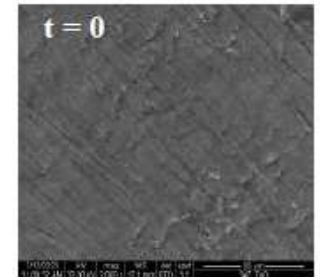
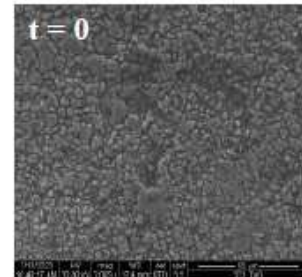
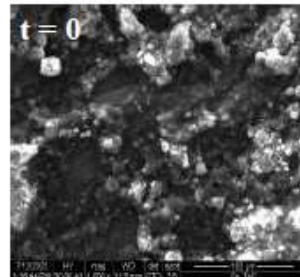
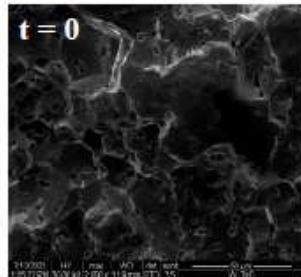
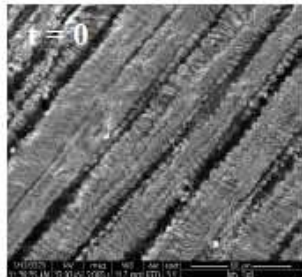
The lower the pH, the more aggressive is the environment.

However, it is observed that the dissolution is very rapid in the first moments, in all cases, then it slows down.

This may be due to the self-decomposition of hydrogen peroxide which especially that can be even be catalyzed by the metals themselves.

# Metal corrosion

SEM images of the surfaces of some samples at the beginning of the process ( $t = 0$ ) and their evolution as a function of the time can be a tool for studying behavior of these metallic systems



Mo

W

Fe + 5% HCl

Steel 321 + 10% HCl

Steel 347 + 10% HCl

# Metal corrosion

There are some common features as well and it seems realistic that these analogies depend mainly on the action of the peroxide.

In the early stages it is difficult to identify specific areas of corrosion on the surfaces.

On the contrary, after some time there are signs of very localized corrosion and it seems indeed that intergranular type is prevalent.

This is particularly evident in the case of Mo and W, but also for some steels.

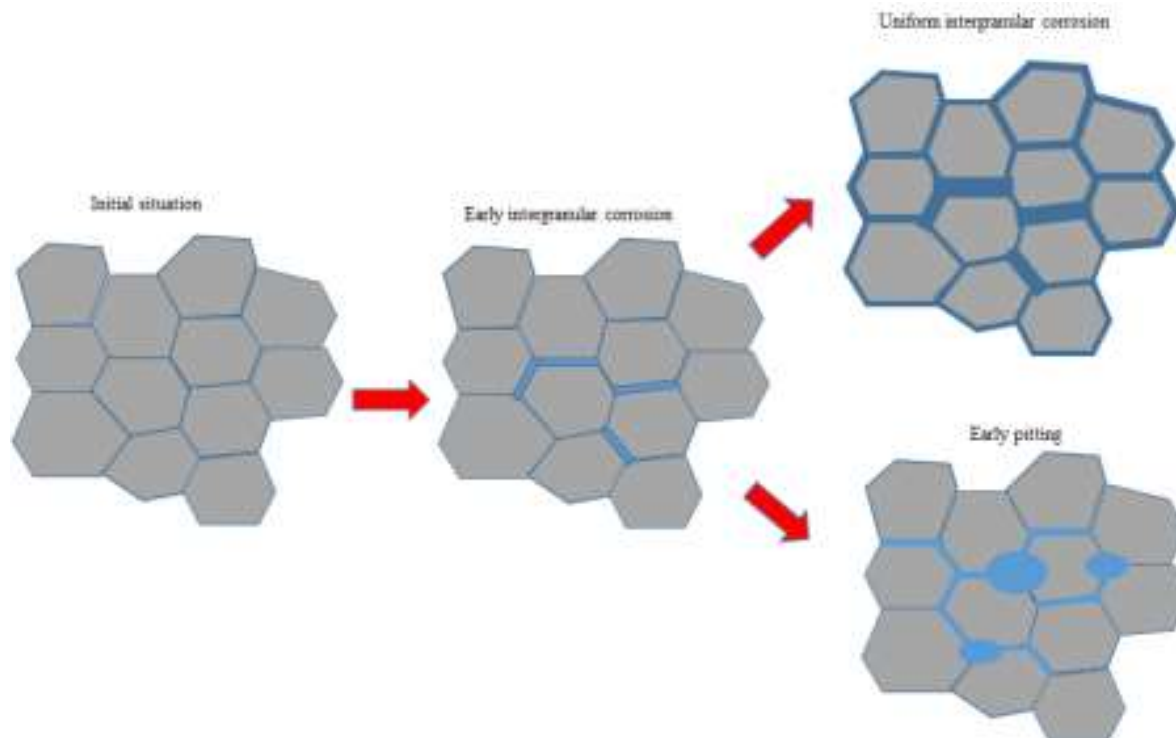
In general, after a sufficiently long time, on all metallic systems considered here, some deep corrosion points appear on the surfaces, with morphology that is quite reminiscent of pitting and some large craters form.

These corrosion marks, especially the larger ones, are often separated by thin walls that meet at angles of about  $120^\circ$ .

# Metal corrosion

The process begins in the parts of the surface with the highest energy and in the case of intergranular corrosion the driving force is the difference between the potentials of the grain boundary and the grain itself.

Once it has begun, it preferentially continues around those areas and the corrosion is faster where it has already started than on parts which have not yet been touched



# Other systems

Some concepts are general and can be applied to other types of materials, such as ceramics or even graphite, as well.

Again, corrosion very often acts preferentially from specific surface areas or points and the same reactive species acting on metallic systems can play a role for these materials in the same manner.

It should be kept in mind that in most cases, these compounds are sintered and therefore may have an intrinsic porosity (residues of air, of liquids from the processing can remain in these pores and eventually they can release the contents).

# Other systems

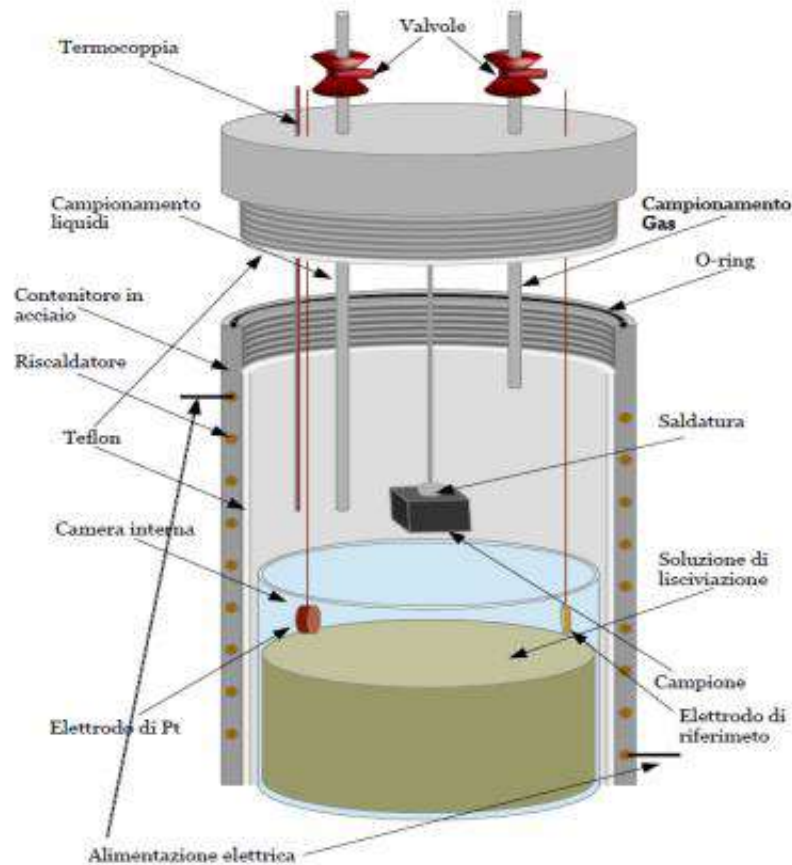
For instance, irradiated graphite constitutes a waste management challenge mainly owing to the presence of radionuclides such as  $^{14}\text{C}$  (half-life 5,730 years),  $^{36}\text{Cl}$  (half-life 308,000 years),  $^{60}\text{Co}$  (half-life 5.3 years), and  $^3\text{H}$  (tritium, half-life 12.3 years).

The water can therefore absorb long-lived radioisotopes therefore special attention must be paid those with great environmental mobility, like tritium, of the radiocarbon  $^{14}\text{C}$ , or the  $^{36}\text{Cl}$ . Each of these may easily enter the environmental cycle, in case of incident or because of small water leaks.

The resistance over time of these materials and the corrosion mechanisms that may occur in these conditions should be studied.

# Other systems

Preliminary leaching experiments were conducted to study release under aggressive conditions.



Graphite normally has good corrosion-resistance against most common acids and solvents, but lower resistance against oxidizing media (e.g. nitric acid). Actually, experiments have shown a great tendency to exfoliation of the graphite samples in high oxidizing solvent such as concentrated hydrogen peroxide. Very thin flakes are released from massive samples, from the surface.



# Conclusions

- Many metals are very resistant to the action of pure water and corrosion can take an extremely long time.
- However, radiolysis of water, a series of complex chemical and physical phenomena, can induce the appearance of radicals and other aggressive species.
- The effect of radiolysis can be simulated with hydrogen peroxide solutions at different pHs.
- In these conditions many metals and steels become more vulnerable and corrosion is much faster.
- In these cases, the mechanism is mainly pitting and intergranular corrosion.
- Aggressive solutions can also be useful for studying the behavior of other systems and their evolution over time.

Thanks for the attention

Alberto Ubaldini  
alberto.ubaldini@enea.it

