EXPERIMENTAL INVESTIGATION OF CORROSION OF NUCLEAR MATERIALS AND RADIOISOTOPES RELEASE UNDER AGGRESSIVE LEACHING CONDITIONS

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The materials used in nuclear power plants are subject to a particularly aggressive environment. Radiation can induce crystalline structural stresses in materials, leading to possible important modifications of their properties, if compared to standard conditions. Thus ceramic materials, steels and other metallic alloys used in the commissioning of nuclear power reactors must meet very stringent requirements in terms of mechanical properties, thermal and chemical stability, resistance to corrosion in highly aggressive environments (for example because of the contact with hot reactive liquids) [1, 2]. There are two main aspects to be aware of regarding the interactions between these materials and coolants, namely the possible corrosion and the exchange of activated radioisotopes, which could pose serious environmental problems.

In general, corrosion is defined as an attack on a material as a result of chemical or electrochemical reactions with the surrounding medium [3]. It can be a complex phenomenon from a physicochemical point of view and different microscopic mechanisms are involved [4]. The rate of corrosion depends on the nature of the metal (i.e. on its purity, its galvanic potential), on the composition, on its microstructure, on the type and nature of the corrosion products, i.e. for instance whether they form a passivating layer or whether they dissolve easily in the medium), and on some parameters such as temperature, pressure, pH, etc. There are some cases where corrosion occurs in a uniform manner on the whole surface. However, corrosion preferentially starts where the surface energy is greater, in correspondence with cracks, defects, grain boundaries and impurities [5]. Corrosion can be intragranular or intergranular [6] depending on which part of material is more more subject to the degradation process. Microscopic aspects and corrosion mechanisms must be well known to design resistance methods of res. Water is a good solvent for many substance, but most of the metals and alloys are able to resist to it very well. The resistance to corrosion can however be very different when for instance, pH is not 7, or reactive substance are dissolved in it.

A physical phenomenon that cannot be underestimated is the radiolysis of water, i.e. the dissociation of water molecules due to the effect of ionizing radiation [7]. Radiolysis goes through different stages, each with its own timescale, and leads to the formation of highly reactive species, such as radicals, free electrons, ions, atomic oxygen, and to the variation of the pH [7]. FIG 1 shows a schematic representation of the processes occurring at different moments and the species that form when water molecules are subjected to ionizing radiation.

FIG. 1. Reactions occurring during water radiolysis.

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.

Despite this, these phenomena are very slow and can take years, indeed it is difficult to monitor radiolysis at laboratory scale within a reasonable time, but it is possible to emulate such conditions using highly concentrated H_2O_2 at a high temperature and different pH.

In the present study, 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_2O_2 was always in very large excess compared to the mass of metallic sample. Table 1 shows the metallic systems considered and the conditions used for them.

TABLE 1. EXPERIMENTS OF ACCELERATED CORROSION

Metallic system	HCl added	Time [min]				
Molybdenum	0	5	10	15	30	
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

Molybdenum, tungsten and few other metals react quickly with hydrogen peroxide [8], 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. Figures 2A and 2B show the weight variation of these metals, ΔP %, expressed as $(P_0 - P_t)/P_0 \times 100$ (P_0 and P_t being the initial weight and the weight of the metals at the moment t) as a function of time, under these experimental conditions (high and low corrosion

rate systems, respectively). Figure 2C shows the corrosion rate which can be estimated from such experiments, expressed as mg/min.
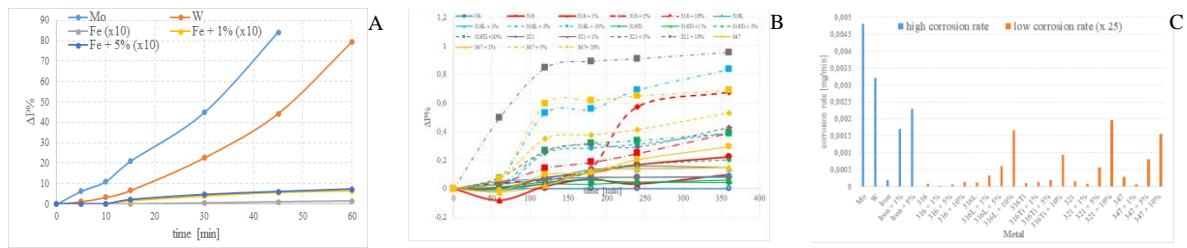
FIG. 2. Weight variation for different metals exposed to H_2O_2 at 70 °C, under different pH (A and B) and corrosion rate (C).

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: $H_2O_2 + 2H^+ 2e^- \rightarrow 2H_2O$, so that many metals under these conditions are oxidized to higher valence states. Often these ions are more soluble in aqueous media and this can explain why there is a release from the metals to the solution. 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 at high temperatures is a rather rapid concurrent phenomenon, that can be even be catalyzed by the metals themselves. For this reason, the corrosion rate is estimated on the basis of the mass variation measured after two hours for the materials with high resistance and after 30 minutes for the materials with low resistance.

FIG 3 shows the 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.

| Mo | W | Fe + 5% HCl | Steel 321 + 10% HCl | Steel 347 + 10% HCl |
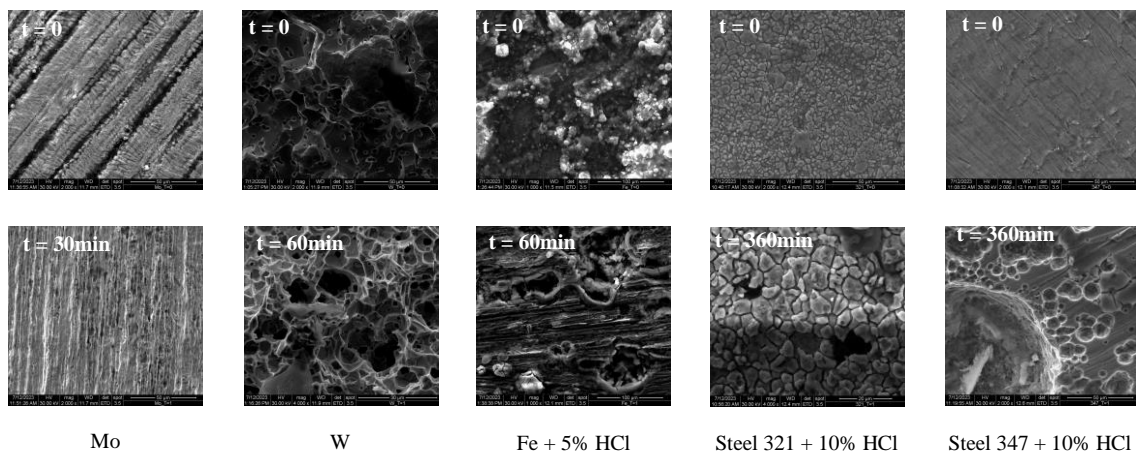
FIG. 3. SEM images of different sample before (top line) and after reaction (bottom line) with H_2O_2

The corrosion process strongly depends on the nature of the metal (niobium for example does not react), on the composition, on the presence of mechanical stresses and on the initial morphology and structure of the surfaces and it is therefore difficult to draw general conclusions; nevertheless 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. For instance, in the

case of molybdenum after only thirty minutes, small craters appear. 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. Corroded areas and craters have different widths and depths and often the wider ones are proportionately much deeper. These corrosion marks, especially the larger ones, are often separated by thin walls that meet at angles of about 120°. The process begins in the parts of the surface with the highest energy and in the case of intergranular case 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 begun than on parts which have not yet been touched. Intergranular corrosion can evolve over time, depending on the material, in different ways: it can be uniform, with the all the boundaries among the grains becoming more and more marked and eventually some grains may even become detached, or it can become very localized and lead to a real pitting, or it can have intermediate characteristics. A schematic depiction of the process is shown in FIG 4.
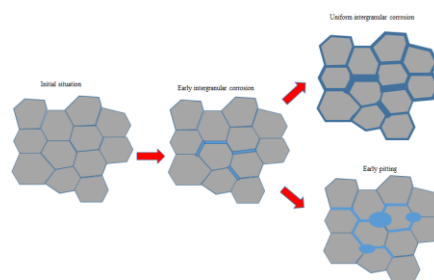
FIG. 4. Scheme of intergranular corrosion mechanisms

Despite the fact that these considerations are rigorously valid for metals and alloys, 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 (their density is lower than the theoretical one of that material) residues of air, of liquids from the processing can remain in these pores and eventually they can release the contents. In the nuclear field this is a serious problem, because radioisotopes can be formed by the action of neutron fluxes.

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

The water can therefore absorb long-lived radioisotopes [9], therefore special attention must be paid those with great environmental mobility, like tritium, of the radiocarbon ^{14}C, or the ^{36}Cl. Each of these may easily enter the environmental cycle, in case of incident or because of small water leaks.

It is interesting to study how these radioisotopes can be released along the whole lifecycle of the original materials (metals, graphite, ceramics, …) both in operating conditions or in an accelerated way, under more aggressive situations. One of the aims of this work is to present the preliminary results of the design and implementation of a system for collection and analysis of the release of carbon and chlorine, from steel and graphite and other materials used in nuclear plants, under aggressive leaching conditions. The release will then be investigated by mass spectrometry measurements, electronic microscopy and spectroscopic methods to collect information about the resistance over time of these materials and the corrosion mechanisms that may occur in these conditions. FIG 5 shows the design of a corrosion experimental chamber for the tested materials, in which both liquids and gaseous substances can be sampled.
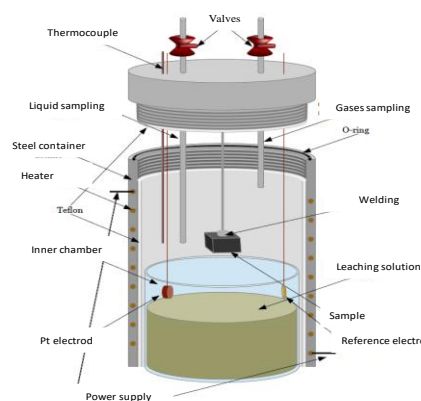
FIG. 5. Scheme of the chamber for corrosion experiments under aggressive conditions

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.

This suggests that the substances contained in the internal porosity can also easily escape into the water. Further investigation will be done using this system and simulating more complex and not-stationary conditions of the liquids surrounding the metallic materials and the graphite, focusing on the understanding and monitoring of the corrosion mechanism.

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