Hydrogen and NPP Life Management: Doel 3 and Tihange 2

Potential Effects of Process-generated Hydrogen on Reactor Pressure Vessel Walls affected by Hydrogen Flaking

ABSTRACT – Three years after its first detection, the problem of (hydrogen-related) cracks in RPV-steels is still imminent in the Belgian nuclear power reactors Doel 3 and Tihange 2. This report briefly elaborates on some reported findings and identifies possible mechanisms for the detected flaws in the reactor pressure vessel wall and the risks for further growth of these defects. The current study indisputably shows that – in agreement with general electrochemical corrosion theory, and despite some counter-arguments from other investigators – there are significant potential risks or (at least) uncertainties for process-generated hydrogen problems; enough to raise concerns about the fitness-for-service of the affected reactors, and also about similar reactors world-wide. Just one example are the recent findings in Swiss nuclear power plants. From a safety point of view, it should – as a basic minimum requirement – be recommended that meticulous inspection and continuous monitoring or surveillance programs be set up and implemented when keeping the reactors into operation.

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DRAFT REPORT
vs 0.2

This is an initial draft report, in order to document some of the scientific and technical concerns raised regarding the potential risks created by the operationally-generated hydrogen on the already hydrogen-affected RPV steel walls of Doel 3 and Tihange 2.

It also contains a more general warning for similar potentially affected NPPs in the world.

Parts of this draft still require further editing, as well as additional elaboration or investigation (e.g. ‘radiolysis’ part of section 3.3).

1. Introduction: Doel 3 and Tihange 2 – Hydrogen Flakes and Related Problems

1.1. Findings

The inner surface of a PWR reactor pressure vessel (RPV) is generally cladded with austenitic stainless steel in order to reduce corrosion rates and CRUD formation. A number of instances have been reported of this lining developing cracks, which will create direct contact of the base RPV metal (a ferritic low-alloy steel) with the high-temperature water of the primary circuit and possible progress of the cracks into the base material.

In June 2012 ultrasonic in-service inspections, using a new technique/instrumentation, were performed at the Belgian Doel 3 nuclear power plant (NPP), in order to check for such underclad cracking in the reactor pressure vessel, as had e.g. been found at Tricastin 1 in France.

Figure 1 shows a schematic illustration of the Doel 3 RPV. The total height of the vessel is approx. 13 meters (incl. the spherical top lid), with a diameter of 4.4 meters and a wall thickness of the cylindrical part of 205 mm. The primary water side of the RPV is cladded with a stainless steel Type 308/309 lining of approx. 7 mm thickness. The RPV base material is a SA 508 Cl. 3 low-alloy Mn-Mo-Ni steel (i.e. 1.2-1.5% Mn, 0.45-0.60% Mo, 0.40-1.00% Ni, max. 0.25% Cr, max. 0.25% C).

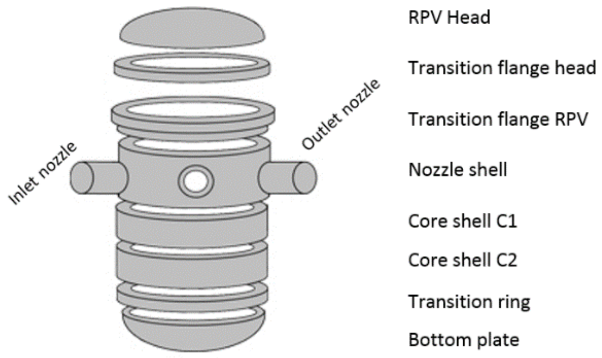


Figure 1: Illustration translated from FANC, showing the original forged steel ring sections of the RPV separated for clarity. These rings are welded together and cladded internally with a stainless steel lining to form the reactor pressure vessel.

No underclad cracking defects were detected. However, unexpected a-typical “indications” in the RPV shells were found in the first 30 mm of the material depth of the irradiated part of the Doel 3 RPV core shells. Hence, the operator ordered a full thickness RPV shell inspection in July 2012, which confirmed high numbers (thousands) of similar “indications”[1,2] down to a depth of 120 mm into the material, measuring from the reactor’s primary water side. It appeared that flaws were particularly dominant in the bottommost and upper core shells. The bulk of them are located in the base metal, outside the weld regions. Flaw densities as high as 40 indications per dm^3 had been found, with an initially reported total of 7776 indications in the core lower shell (core upper shell showed 931 indications).

The flaws appeared “almost circular in shape” with a reported average diameter of 10-14 mm, “although some had diameters as large as more than 20-25 mm” (some available data, however, showed significantly higher values, cf. infra – See Figures 2 and 3)[3,4]. It was also observed that the detected defects are oriented laminar or quasi-laminar[1,5,6] and that their position and orientation showed a pattern similar to the pattern of a zone of macro-segregations[7]. Bridging was found to occur only between flakes that are very close to each other.

At that time, FANC apparently also declared that similar UT inspections of the RPV head and upper rings in the 1990s found only a few indications[8]. Old UT-inspection records, dating from the time of fabrication of the forgings, also did not mention the significant presence of “indications”.

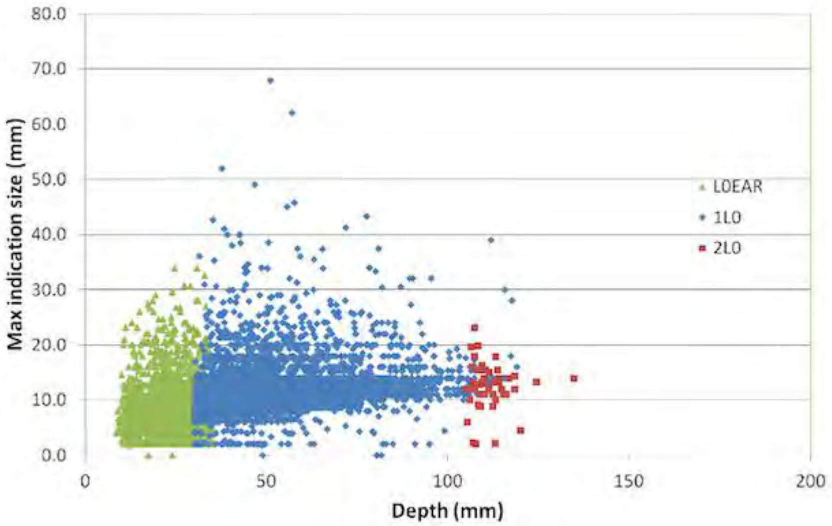


Figure 2: Doel 3 – Size of indications [max (x,y)] versus depth into the RPV steel wall (data 2012)[3].

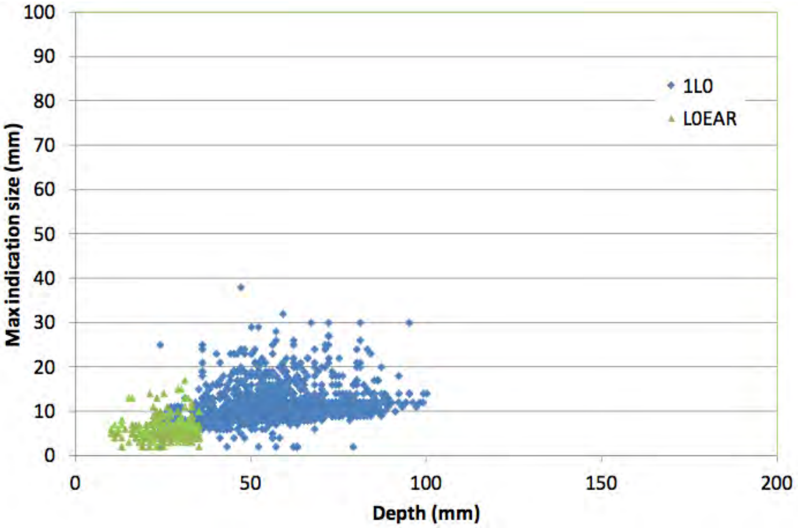


Figure 3: Tihange 2 – Size of indications [max (x,y)] versus depth into the RPV steel wall (data 2012) [3].

In September 2012 the same type of “indications”, but to a lesser extent, was also found in the Tihange 2 RPV shells during a similar inspection (Figure 3). Both RPV forgings were produced by the same fabricator with steel from the same supplier.

1.2. Causes of the Cracks

Different investigations have been carried out since the flaws were first discovered[1-9]. They have highlighted so-called *'hydrogen flakes'* as being the root cause of the problem. These hydrogen flakes might arise during the fabrication of large steel ingots, which may affect mechanical properties of forged RPV steels.[10,11] Solidification of a large mass of steel is characterized by significant development of micro- and macro-defects in the ingot structure and a changing solubility of different elements during cooling (Figure 4). For example the solubility of hydrogen (e.g. originating from thermal dissociation of water molecules from damp scrap or atmospheric humidity, etc.) decreases during solidification and cooling down of the steel ingot. The solubility of hydrogen in steel at room temperature is approx. 0.1 ppm, compared to 30 ppm in the steel melt.

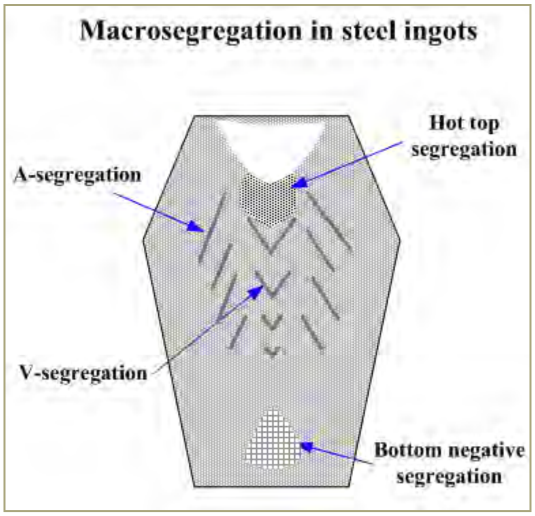


Figure 4: Schematic illustration of macro-segregation in steel ingots (source: www.substec.com).

Hydrogen atoms possess a high mobility in the steel matrix, but are collected at internal voids, such as non-metallic inclusions (sulfides, oxides), shrinkage pores, cracks caused by internal stresses, etc. Hydrogen atoms collected at such internal micro-voids combine and form gaseous hydrogen molecules H_2, which may cause formation of cracks ("flakes", in the traditional steel jargon) when the gas pressure exceeds the steel strength. These flakes are in fact (small) brittle hydrogen cracks (Figure 5). Hydrogen flakes (sometimes also called '*shatter cracks*': internal fissures seen in large forgings due to segregated hydrogen) were well known from the past. Metallurgists encountered flakes as early as in the first world-war in mechanical treatment of large preforms for gun barrels[12]. Thousands of research papers and several monographs have been published since that time but the problem has not ceased to be important. The possible formation of flakes is particular dangerous for parts fabricated from large ingots. A potential remedy is to use vacuum ladle degassing methods to decrease the content of hydrogen to 2 ppm, which should avoid or mitigate flake formation.

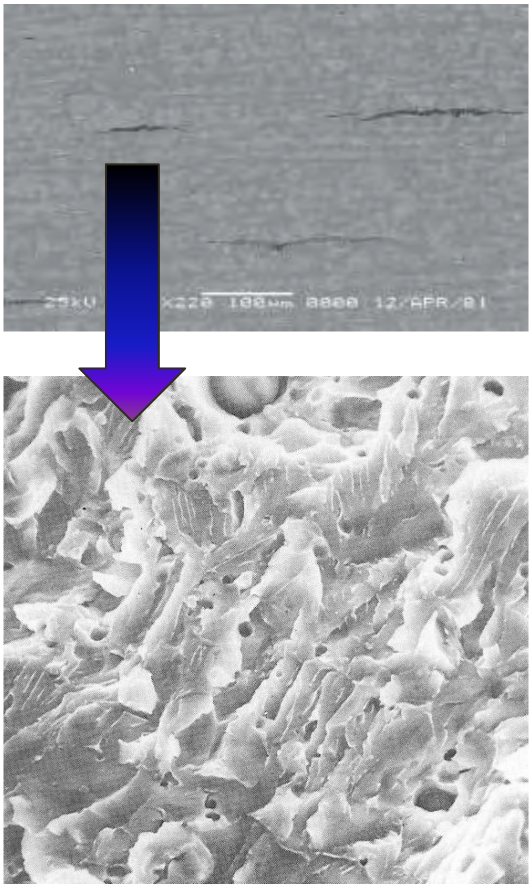


Figure 5: Typical “hydrogen flake” cracking in carbon or low-alloy steel. Specific features of hydrogen-induced brittle fracture are: micro-quasi-cleavage fracture, pores and fine hair-lines (indicating ductile fracture on a micro-scale).

Not all forged components of the Doel 3 and Tihange 2 RPVs contain the same amount of flaws. Based on an analysis of the ingot size and the combined sulfur and hydrogen content, there appears to be a good correlation with the intrinsic susceptibility to hydrogen flaking and the amount of flakes found in each forged component.

The key question remaining is about the *possible evolution over time of these so-called “hydrogen flakes”*. The position of the regulatory authorities and the operator, so far, has been that the defects found in the Doel and Tihange RPV “are usually associated with manufacturing and are not due to aging” and that it is “improbable” that the flaws have evolved since their formation. The only theoretical propagation mechanism still considered by the operator is *'low cycle fatigue'*[3], although this has been disputed by various corrosion experts. Also the limited experience about the influence of irradiation on flaw propagation in zones with hydrogen flakes is recognized, both by the operator and the regulatory agency. This latter phenomenon is currently still under investigation.

One of the main reasons for concluding that it is unlikely there has been a significant evolution of the voids over time is the claim that "there is currently no source of hydrogen anymore"[13] which could cause propagation of the cracks. This, however, is an erroneous conclusion and *there could be major questions regarding the stability of the flakes*.

1.3. Amount and Sizes of the Cracks

Not only larger numbers, but also increased average dimensions (Doel 3 & Tihange 2) and a strong increase of maximum dimensions of the "flakes" (i.e. for Tihange 2 upper core shell) have later been reported by the operator, e.g. during various presentations[14], when inspection results from 2012 and 2014 were compared.

Additional tests conducted in 2014 – with adapted equipment detection parameters – revealed 13,047 cracks in Doel 3 and 3,149 in Tihange 2. Reported maximum sizes are now up to 179 mm (vertical) by 72 mm (horizontal) for the Doel 3, and 155 mm (vertical) by 71 mm (horizontal) for the Tihange 2 RPV[15].

It may appear that not all of these changes can be easily explained by higher sensitivity settings or new data interpretation routines. Variations are claimed to be "within the accuracy of the technique" (and the statistical distribution), but this is clearly an item that should be clarified by further investigation and data analyses.

The current size of the voids is also not exactly in line with what is traditionally considered "typical" for hydrogen flaking phenomena (cf. infra).

2. Hydrogen in Steel

2.1. General

Hydrogen can be introduced into steel either by the steel-making or fabrication processes (cf. supra), or from subsequent service conditions. Hydrogen can enter and leave steel without ever making its presence known or it can cause insidious damage: blisters, embrittlement, or even attack on carbide phases with the formation of methane and methane blistering. Because of hydrogen's potentially damaging nature, numerous and extensive studies have been directed towards understanding both its behavior and its influence on the properties of steel. Also in the nuclear sector potential hydrogen degradation phenomena have received considerable attention already since the 1960s and 70s[16].

2.2. Atomic and Molecular Hydrogen

Before hydrogen can enter a solid metal, it must first adsorb on the metal surface as atomic hydrogen. Therefore, nascent or newly created atomic hydrogen (such as created by corrosion reactions, radiolysis, etc. – cf. infra) is quite potent for hydrogen entry into steel.

Atomic hydrogen can very easily diffuse through a metal lattice because of its small size (radius of free H-atoms = 0.58Å, dissolved in a metal lattice: 0.1 – 0.3 – 0.48 Å); molecules of hydrogen, however, cannot diffuse through a metal lattice because of their larger size (≈ 1.37 Å). Atomic hydrogen diffusing through a metal lattice can combine to form molecular hydrogen within structural defects such as voids, laminations, microcracks, or discontinuities around inclusions. It is almost generally accepted that, once molecular hydrogen has formed within an internal structural defect, its remains trapped there for all practical purposes.[17]

Here the molecular hydrogen can create blisters if pressure build-up is sufficiently high. Molecular hydrogen, however, does not cause embrittlement of the steel. The embrittling effects of hydrogen in steel are associated with the interstitial solution of atomic hydrogen in ferrite (alpha iron) or martensite. These embrittling effects are maximized when a saturated solution of hydrogen in alpha iron exists. Atomic hydrogen in the lattice does sometimes not affect the elastic properties of steel, but it greatly affects the plastic properties, particularly the capacity for localized plastic flow in the presence of a notch or other conditions leading to a triaxial stress-state (cf. flakes).

2.3. Water Chemistry, Corrosion Effects and Hydrogen

The “flaking” phenomenon described above (Section 1) is very reminiscent of well-known *‘hydrogen blistering’* or *hydrogen induced fracture* phenomena from corrosion in the chemical and petrochemical industries. Hydrogen blistering can occur when hydrogen enters steels as a result of the reduction reaction (hydrogen evolution via water and/or proton reduction) on a corroding metal surface. In this process, single-atoms of “nascent” hydrogen diffuse through the metal until they react with another atom, usually at inclusions or defects in the metal. The resultant diatomic hydrogen molecules are then too large to migrate through the metal lattice and become trapped. Eventually, a gas blister or internal crack could build up and may split the metal as schematically illustrated in Figure 6. Practical examples are shown in Figure 7.

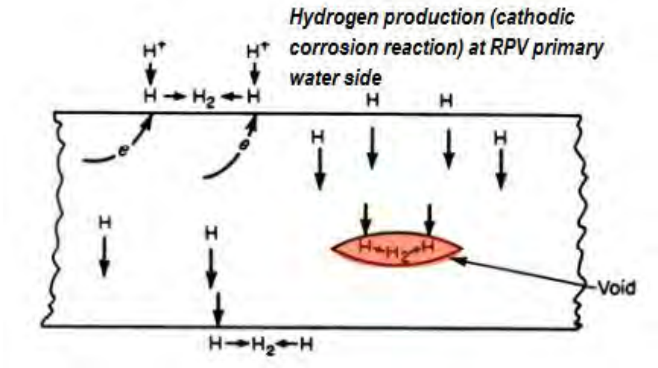
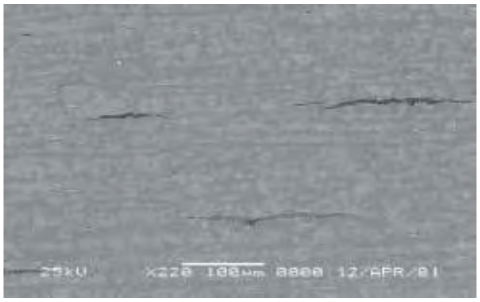


Figure 6: Schematic diagram of hydrogen diffusion and blister formation. Nascent atomic hydrogen adsorbs on the steel surface, then enters and diffuses through the steel until it encounters a defect or void where it can recombine into molecular hydrogen. As the molecular hydrogen forms in the defect area, the pressure increases causing growth and further separation of the flaw. The internal flaw growth can eventually result in an externally evident “blister”.



(a)

(b)

Figure 7: Typical hydrogen induced cracks
(source: MTI Atlas of Corrosion and Related Materials Failures – electronic ed.)

Hydrogen blistering or cracking is controlled by minimizing corrosion and is normally not a problem in neutral or alkaline environments and with high-quality steels that have low impurity and inclusion levels. Nevertheless also under the primary water chemistry conditions of the reactor coolant system (RCS) of PWRs, with a typical pH_T of approx. 6.9 to 7.4 (corresponding to a room temperature pH around 10; cf. Figure 8) the primary cathodic corrosion reaction will be:

$$H_2O + e^- \rightarrow H + OH^-$$

Even for very low corrosion rates of the stainless steel cladding (e.g. 0.1 to 1 micron/yr) this will result in significant quantities of corrosion-generated hydrogen atoms that may enter into the base metal (Cf. Section 3.4).

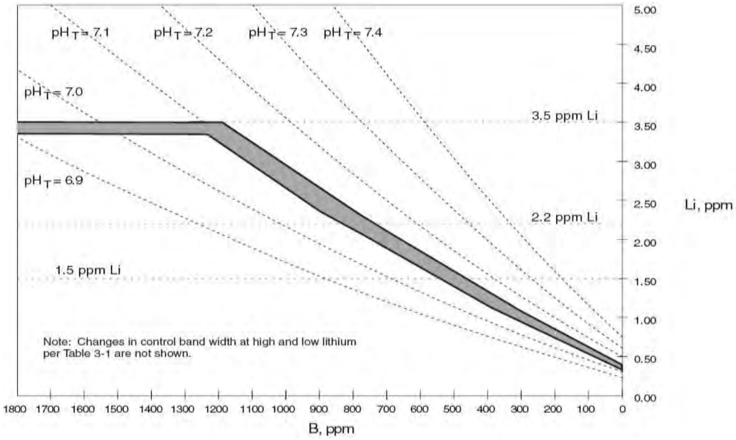


Figure 8: pH control in PWR primary coolant by adjusting the lithium concentration as the boron is consumed during fuel burn-up. The trajectory commonly employed over a typical fuel cycle is marked by the dark path (EPRI PWR Primary Water Chemistry Guidelines TR-105714-V1R4).

The internal austenitic stainless steel cladding of an RPV is sometimes considered to prevent hydrogen diffusion and potential hydrogen-induced cracking problems in the pressure vessels.

This, to our knowledge, has never been proven experimentally in an adequate way[18] and, at most, the cladding probably has only a "delaying" effect in transferring the nascent hydrogen to the cladding/base metal boundary, and further into the RPV steel matrix. The presence of flaws in this matrix (cf. "hydrogen flakes") represents ideal sinks (traps) for the hydrogen injected into the metal from the cathodic corrosion reaction (cf. Section 4).

In addition to the corrosion-generated hydrogen, there is also the issue of hydrogen radicals being formed as a result of the radiolysis of water and the reactions of H_2 with the radiolysis products[19] (e.g. OH· + H2 → H· + H2O); hydrogen is used in the RCS to suppress radiolytic oxygen and hydrogen peroxide formation. More details of all these effects are described elsewhere[20].

Another argument relates to the size of the observed defects (cf. Section 1.3). Typical void sizes of the "hydrogen flakes" were initially reported to be about 10 to 15 mm (with excursions to 25 or 30mm), while later inspections and data interpretations have reported actual sizes measured in 2012 already to be apparently significantly higher, with values up to ca. 68 mm for Doel 3 and ca. 38 mm for Tihange 2 (see Figures 2 and 3; cf. Section 1.3); later corrected to even greater values in 2014. These dimensions appear totally *a-typical* for traditional "hydrogen flaking" phenomena.

Finally, it should be noted that there are earlier other observations of hydrogen-induced blister cracking which have been reported in nuclear structural materials[21], and in the past there has been a lot of debate about the issue. A very old, specific, example of failures attributed to hydrogen occurred in retaining rings used to connect inlet assemblies to the reactor process tubes in a Hanford water cooled production reactor. Failures occurred in carbon steels and Type 420 stainless steel. The reported hydrogen sources were the fabrication process, hydrogen generated during corrosion of the ring by the process water, and from galvanic coupling[22].

In view of all of the above, the "trapping" of cathodically generated hydrogen (due to primary water corrosion reactions) – or hydrogen from other sources – inside existing "hydrogen flakes" is not improbable. Moreover, the (original) flakes may act as a *stress raiser*, which will enhance the diffusion of the hydrogen entering the steel to the stressed areas in the metal. Also the additional effect of irradiation is still largely unknown.

3. Hydrogen Source Term: Not Insignificant

3.1. General

Hydrogen can be introduced into RPV structural materials – i.e. steels and stainless steels – during irradiation exposure in the primary reactor water, by *a variety of mechanisms*. Examples are not only corrosion, but also fast neutron-induced transmutation mechanisms, recoil injection of protons after neutron-water collisions, radiolytic decomposition of water, and the equilibrium dissociation arising from hydrogen overpressures used in PWRs.

Amongst all those, traditionally the following three sources of nascent hydrogen have been considered to be most important in pressurized water reactor systems[23,24]:

1. Corrosion reaction at the steel-water interface, with the production of hydrogen in the cathodic half-cell reaction of the corrosion system;
2. Radiolytic decomposition of the water;
3. Dissociation of the hydrogen present in the water at the steel-water interface;

with the first source often cited to be the most relevant. As such, though, it appears that also radiolysis effects under neutron irradiation could increase the absorption of hydrogen from an aqueous environment in a significant way.

Often overlooked, but maybe not unimportant, are also the transmutant sources of hydrogen (often together with the generation of helium). In low-alloyed or stainless steels, hydrogen arising from transmutation is formed primarily from the various nickel isotopes, especially ^{58}Ni and other nickel daughter and granddaughter isotopes, interacting with fast neutrons. The production rate via this reaction is essentially linear with accumulating exposure. Other constituents of typical steels also generate hydrogen by (n, p) reactions, but cross sections are much smaller than those for nickel.

3.2. Corrosion-generated Hydrogen, Equilibrium Pressures and Rates of Formation

The issue has been raised whether corrosion-generated hydrogen (H/H_2) could cause sufficient pressure build-up in the (pre-existing) voids to cause growth of these “flakes”. In general, electrochemical potentials are a much more efficient driving force for hydrogen entry into the steel than high partial pressures of H_2 gas near the metal surface; i.e. “chemical charging” is much more effective than “gaseous charging” as it is called in some terminologies. It is the so-called ‘overpotential’, i.e. the displacement of the potential of an electrode from its reversible value, that will determine the actual corrosion and hydrogen evolution.

The driving force of a fraction of a volt in an electrolytic cell is equivalent to many thousand atmospheres of hydrogen pressure (Table 1).

$E = 0 - 0.0591\ pH - 0.0295 \log pH_2$	
At $pH_T \approx 7.1$	At $pH_T \approx 6.9$
$E = -0.5\ V \rightarrow pH_2 = 10^{2.75}$ atm $E = -0.6\ V \rightarrow pH_2 = 10^{6.12}$ atm $E = -0.7\ V \rightarrow pH_2 = 10^{9.51}$ atm	$E = -0.5\ V \rightarrow pH_2 = 10^{3.13}$ atm $E = -0.6\ V \rightarrow pH_2 = 10^{6.52}$ atm $E = -0.7\ V \rightarrow pH_2 = 10^{9.91}$ atm

Table 1: Equilibrium hydrogen partial pressures at different cathodic potentials in high-temperature aqueous alkaline environments.

However, taking into account that the electrochemical corrosion potentials (ECP) of austenitic stainless steels in PWR water are typically close to the so-called hydrogen evolution line, experts have claimed that the electrochemical driving force of the cathodically generated hydrogen would be too small to create a significant hydrogen pressure[25]. If the overpotential is zero, the hydrogen fugacity in the flakes at equilibrium will indeed be equal to that in the coolant (and be low).

This would be the case if, for instance, it is assumed that the primary oxidation reaction of the stainless steel (i.e. internal cladding of the RPV) at these low potentials is – only – the oxidation of metallic Ni to NiO (Figure 9). This Ni/NiO driving reaction may seem logical in the case of nickel-based alloys like Alloy 600, as is assumed in a number of publications to explain PWSCC phenomena in PWRs (Primary Water Stress Corrosion Cracking), but is not obvious for ferrous-based alloys like the stainless steel cladding (nickel only constituting 10 to 12% of the composition).

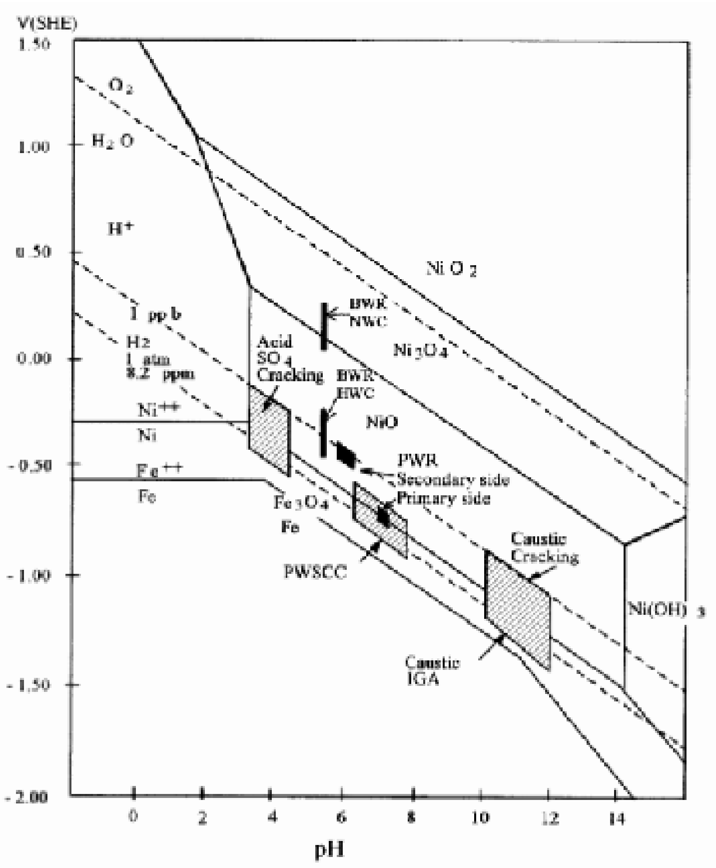


Figure 9: Simplified E-pH diagram for nickel and iron at 300°C showing the principal pH-potential combinations for PWR primary and secondary water, BWR Normal Water Chemistry (NWC) and BWR Hydrogen Water Chemistry (HWC) and the modes of stress corrosion cracking of Alloy 600[25]

There are a number of alternative reactions possible at these low potentials at 300°C, such as the oxidation of Fe to Fe_3O_4 (see Figure 9), or possibly even – depending on pH – conversion of Cr to e.g. Cr_2O_3 or some mixed Fe-Cr oxides (Figure 10). The corrosion potential (ECP), i.e. the "mixed potential", may in this case be almost the same, but it would create *much higher driving forces* for the hydrogen evolution reaction (300 to 400 mV for iron oxidation, or up to 600 or 700 mV for the latter cases), with orders of magnitude higher hydrogen evolution rates.

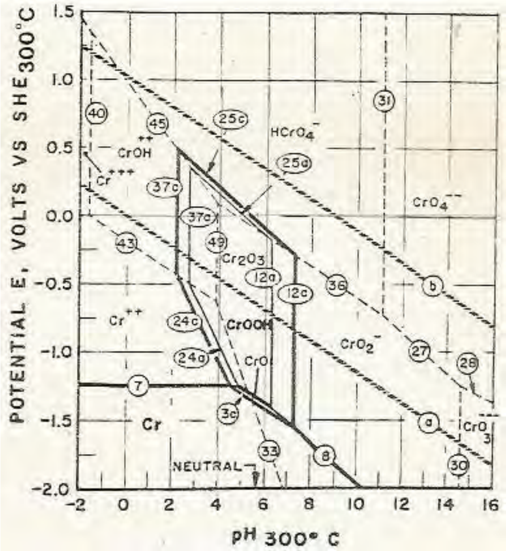


Figure 10: E-pH diagram for chromium at 300°C[26].

The likelihood of this is illustrated by a series of experimental electrochemical polarization curves from our own laboratory.[27,28] Slow scan potentiodynamic polarization tests on stainless steel type 304, as well as on the alloying elements Fe and Ni, in a range of high-temperature aqueous solutions at 300°C show that the polarization curve (E-i) for the hydrogen reaction is mostly very flat; i.e. the reaction is very little polarized, with low cathodic Tafel constants. This means that, the corrosion reactions are almost fully under so-called 'anodic control' and that, whatever the anodic reaction is, there will be little shift in the corrosion potential (ECP) and the ECP will in any case be close to the hydrogen evolution line. It is the type of anodic reaction and its polarization behavior that will almost totally determine the corrosion and the hydrogen evolution rate. This hydrogen evolution rate can vary by orders of magnitude, depending on the anodic reaction.

It should be mentioned that such additional or alternative oxidation reactions for the Ni/NiO couple might also explain the variation in actual potential measurement for stainless steel under PWR conditions (+/- 300 mV, not taking into account potential excursions during transient RCS conditions).

So, there is no concluding experimental proof or evidence that the hydrogen evolution driving force would indeed be small.

Although a native "hydrogen blistering" phenomenon in the 20 cm thick-walled reactor pressure vessel is not to be expected, a contribution of hydrogen and hydrogen pressures to phenomena like internal crack growth or some kind of “delayed cracking” of the existing voids (i.e. further growth of initiated flaws) definitely has to be considered and evaluated (cf. infra).

It should also be noted that transient conditions (i.e. temperature drops) may have a deleterious effect. They will not only affect the electrochemical potential and corrosion reactions – and the driving force for the hydrogen evolution – but, very importantly, also the hydrogen diffusion/capture in the metal structure.

3.3. Other Hydrogen Sources and Hydrogen Traps

There is much uncertainty about the significance of the other sources of hydrogen. Models for the estimation of *“radiolytic hydrogen”*, for instance, have been developed by one of the current authors for BWR media[29,30,31], as well as for PWR systems[32]. However, this modelling approach should be compared with experimental data. In this respect, for example, the influence of temperature on the electrochemical response to irradiation has been investigated in PWR-simulating media[33]. Quantitative data on hydrogen development for the current case are lacking, but irradiation appears to cause a negative shift of the ECP, as has been validated experimentally. Between 300 and 200°C these potential drops due to irradiation are in the range of only -5 to -20 mV but for temperatures below 200°C the amplitude of those potential drops strongly increases to more than -300 mV [33], which will affect the hydrogen evolution rates.

Hydrogen gas is also added to the primary circuit coolant at concentrations usually ranging between 25 and 50 cm^3 H_2/kg H_2O at standard temperature and pressure (STP). This probably only has little effect in the current case, although studies have shown that there definitely is an effect of hydrogen overpressure on the electrochemical behavior of materials like Alloy 600 or 690 in PWR primary water environments[34]. For example Totuska and Szklarka-Smialowska[35] conducted slow strain rate tests (SSRT) in 0.01 M boron and 0.001 M lithium high-temperature water with 0.005 and 0.1 MPa hydrogen overpressure under electrochemical controlled potentials, and found significantly higher anodic current densities and about 60 mV more negative open-circuit potentials (ECP) at the higher hydrogen partial pressures. More data are reviewed by Uchida[36].

“Transmutation hydrogen” in the steel is another issue, of much broader relevance than the current hydrogen flaking problem. Whereas (atomic) hydrogen is thought to be very mobile in steels at LWR-relevant temperatures (and therefore in the past was generally assumed to diffuse out of the material as a result of its high diffusivity while very little would be retained), however now it has been shown that in certain cases the retained hydrogen levels significantly exceed the levels calculated on the basis of relevant (n, p) transmutation reactions. There is ample evidence that hydrogen can be stored in significant quantities in highly irradiated steels under certain conditions[37]. The level of excess hydrogen depends on both the irradiated microstructure and on

exposure to a hydrogen-containing environment. In particular, hydrogen retention appears to be accelerated when significant amounts of helium are co-generated.[38,39] Similar synergistic effects will result from other radiation-induced defects. More importantly, however, hydrogen arising from non-transmutation sources might also be stored. This is a particularly important consideration in LWRs with their water coolant medium.[40]

As an example, several hundred appm of (excess) hydrogen were detected in a number of studies and these atoms were presumed to be trapped at radiation defects such as black spot damage, dislocation loops and network dislocations[37]. However, in materials containing either gas bubbles or voids, hydrogen levels as high as ~4000 appm have been measured and found to be retained as long as 13 years after irradiation. It was proposed that these large amounts of hydrogen were stored in the cavities.

In an irradiated baffle bolt from the Tihange 1 PWR, such levels of hydrogen were measured in two positions along the shank where ~0.2% [37] swelling was associated with cavities ~8 nm in diameter [18, 43a, b]. In contrast, hydrogen levels three to seven times lower were present near the bolt head where <0.01% swelling was present as a significantly lower number density of <1 nm diameter cavities.

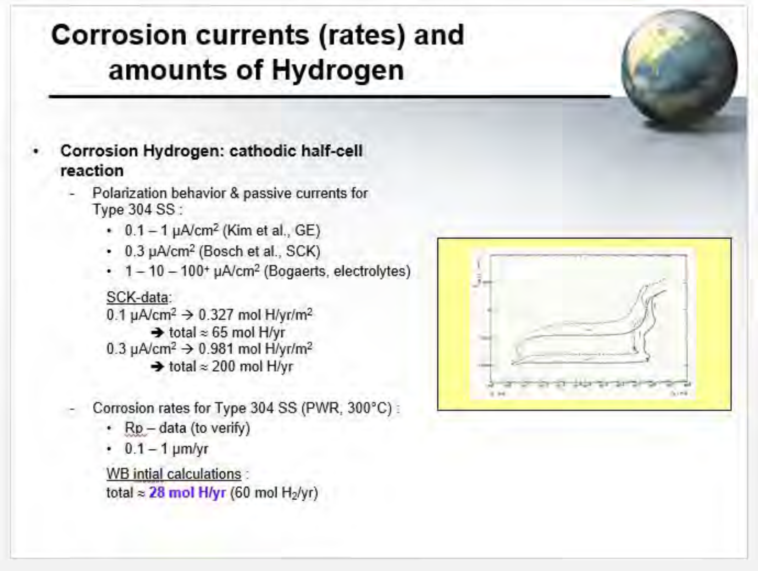
In this context, it should also be remembered that tests carried out in the Belgian research reactor BR2 on behalf of operator Electrabel to assess the mechanical properties of a flaked material (originating from an AREVA steam generator shell, VB395) under irradiation, produced some unexpected results. The tests showed a number of discrepancies and embrittlement appeared to be greater than one would expect based on the trend curves reported in existing literature, whereas the material hardening appeared to be in line with the licensee's predictions.[41] Also a second irradiation campaign confirmed the unexpected behavior but did not provide a clear explanation for this, what was called, *"non-hardening embrittlement"* phenomenon.

3.4. Significant Quantities at a Microscopic Level

Whatever the source term, the driving force and the eventual pressure build-up in the "flakes" or voids will be, it is sure that significant hydrogen quantities are generated at the metal/water interface, part of which will enter the metal wall. Part of this will be corrosion-related, but there are various other sources as discussed above.

We have calculated that, for an assumed corrosion rate of the stainless steel exposed to the primary water of 0.1 to 1 micrometer/year (a realistic value), a total of ~28 mol/yr of H (or correspondingly ~ 60 mol H_2) will be generated. This corresponds to some 10^{24} to 10^{25} hydrogen atoms that are produced at the RPV wall (≤ 200 m^2) during a reactor cycle of one year, just from the corrosion reaction at the metal/water interface alone. In terms of hydrogen gas volumes this would be 1.3 m^3 STP.

SCK data[42] even show higher corrosion-hydrogen productions, up to 65 or 200 mol H/yr (Figure 11).



Corrosion currents (rates) and amounts of Hydrogen

- **Corrosion Hydrogen: cathodic half-cell reaction**
  - Polarization behavior & passive currents for Type 304 SS :
    - 0.1 – 1 μA/cm^2 (Kim et al., GE)
    - 0.3 μA/cm^2 (Bosch et al., SCK)
    - 1 – 10 – 100^+ μA/cm^2 (Bogaerts, electrolytes)

    SCK-data:
    0.1 μA/cm^2 → 0.327 mol H/yr/m^2
    ➔ total ≈ 65 mol H/yr
    0.3 μA/cm^2 → 0.981 mol H/yr/m^2
    ➔ total ≈ 200 mol H/yr
  - Corrosion rates for Type 304 SS (PWR, 300°C) :
    - Rp – data (to verify)
    - 0.1 – 1 μm/yr

    WB intial calculations :
    total ≈ **28 mol H/yr** (60 mol H_2/yr)

Figure 11: Slide summarizing corrosion rate estimates and related hydrogen production volumes.

How much of this produced hydrogen will effectively enter into the steel wall is open to debate. Figures op to 90% have been mentioned[43], but 50 to 20% or less could be a more realistic estimate. It should be remembered, however, that hydrogen evolution – i.e. the amount of molecular hydrogen that is released from the metal surface and not being absorbed into the base metal matrix – occurs as a result of the following reactions:

$$H^+ + e^- \rightarrow H_{ads}$$

$$2\,H_{ads} \rightarrow H_2$$

In these, the latter reaction step is known to be relatively slow, and its rate determines the overall production of hydrogen gas, the rest being absorbed into the base metal. The increased concentration of surface hydrogen favors entrance and absorption of hydrogen atoms into the metal lattice and this entrance will further be enhanced by the high H-diffusion rates at the elevated temperatures.

Although diffusion rates are high, once entered, hydrogen could be retained in the metal lattice by a number of factors.

4. Hydrogen Sinks and Accumulation

4.1. General: Hydrogen Concentrations and Trapping

In contrast to e.g. helium, produced by interaction of boron and nickel with fast and especially thermal neutrons, it is still commonly assumed that most of the hydrogen entering or produced within a steel or stainless steel – whatever the hydrogen source is – cannot be retained in the metal at high concentrations and will (try to) diffuse out of the steel.

Interaction between diffusing hydrogen and metal lattice defects or impurities can, however, significantly retard hydrogen movement, resulting in an effective diffusivity that is lower than expected.

It has been established that hydrogen can be present in steel in various states, namely, atomic-protonic hydrogen dissolved in the crystal lattice ("free", diffusion mobile), atomic hydrogen bound to defects of the crystal structure (dislocations, vacancies, intergrain and interphase boundaries – Figure 12), molecular hydrogen bound with micro- and macrovoids, hydrogen bound chemically to nonmetals (C, O, S, N), for example in an oxidized state in the form of water vapor adsorbed in pores and hydroxyl groups incorporated in nonmetallic inclusions[12], or even in the form of compounds of the solid-solution type in the form of hydrocarbides, etc.

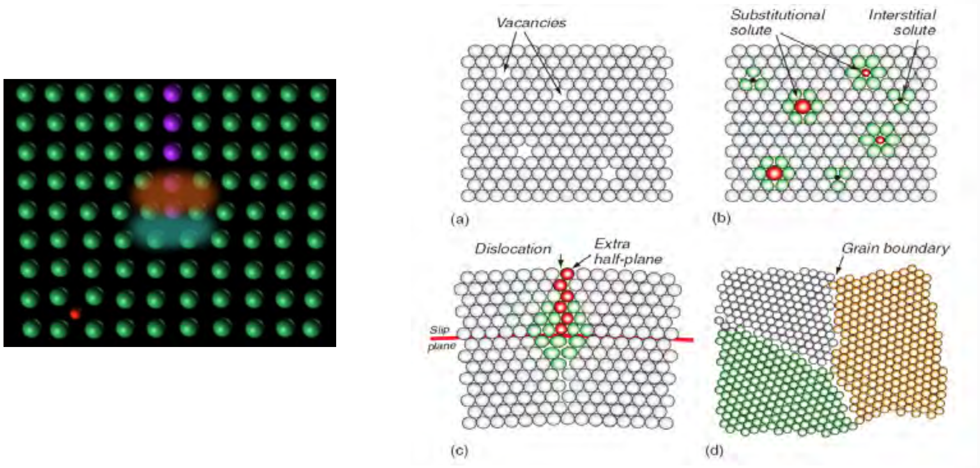


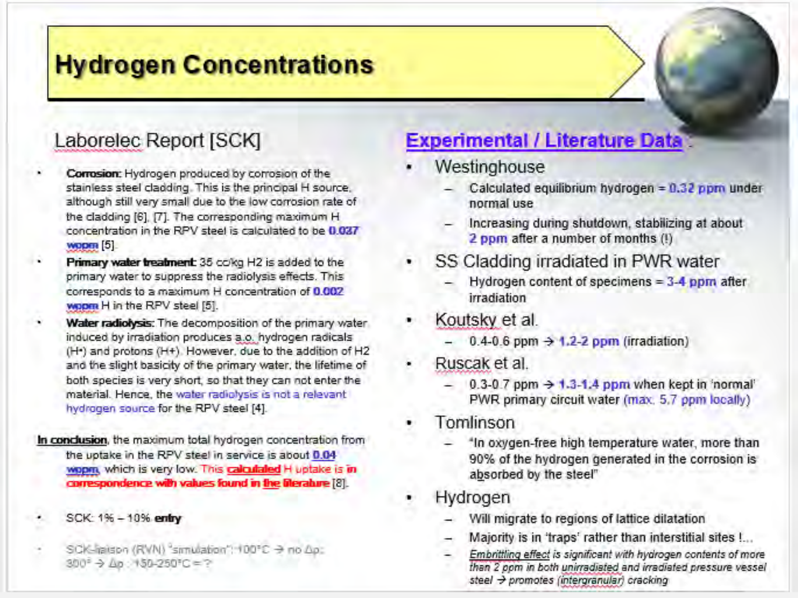
Figure 12: Illustration of some microstructural crystal defects and potential trapping sites.

It is now accepted that the larger proportion of hydrogen in steel is located at traps rather than at interstitial sites, and it has been established that this trapping of H results in lower values of the diffusion coefficient than if H remained entirely within the lattice. Although an increase in temperature increases the diffusion coefficient, the situation is complicated by the H located at traps and this should be reflected in the effect of temperature of charging on the saturated H content of steels. Old results[44] already indicated that at a given temperature the lattice hydrogen will be practically independent of the composition of the steel, which indicates that variations in hydrogen content of steels of different compositions and structures is due to hydrogen located at traps.

Some models have been proposed to relate the overall diffusion to the number of trap sites and the probability of capture and release from the trap. Detailed interpretations of the available experimental data, however, often remain impossible due to limitations in the exact understanding of the trapping process(es) [45, 46].

The various data, however, show that retained hydrogen concentrations can be considerable. A Laborelec report to the operator[47], based on calculations from SCK-CEN, mentions a maximum total hydrogen uptake concentration in the RPV of about 0.04 wppm H, and states that this is "in correspondence with values found in literature". This again is erroneous. Actual values from the old source referred to (i.e. Harries and Broomfield, 1963[23]] effectively correspond to 0.244 wppm H at 250°C, a factor of 6 higher (when corrosion rates are assumed to be very low).

Other international sources show similar effective H-concentration values. Old data from Whitman[24] mention hydrogen concentrations in low-alloy steel RPV steel of 0.3 ppm under operational RCS conditions. Other data are shown in Figure 13. They are generally in line with each other.



Hydrogen Concentrations

Laborelec Report [SCK]

- **Corrosion:** Hydrogen produced by corrosion of the stainless steel cladding. This is the principal H source, although still very small due to the low corrosion rate of the cladding [6], [7]. The corresponding maximum H concentration in the RPV steel is calculated to be **0.037 wppm** [5].
- **Primary water treatment:** 35 cc/kg H2 is added to the primary water to suppress the radiolysis effects. This corresponds to a maximum H concentration of **0.002 wppm** H in the RPV steel [5].
- **Water radiolysis:** The decomposition of the primary water induced by irradiation produces a.o. hydrogen radicals (H•) and protons (H+). However, due to the addition of H2 and the slight basicity of the primary water, the lifetime of both species is very short, so that they can not enter the material. Hence, the water radiolysis is not a relevant hydrogen source for the RPV steel [4].

In conclusion, the maximum total hydrogen concentration from the uptake in the RPV steel in service is about **0.04 wppm**, which is very low. This **calculated** H uptake is **in correspondence with values found in the literature** [8].

- SCK: 1% – 10% **entry**
- SCK-liaison (RVN) "simulation": 100°C → no Δp; 300° → Δp ; 150-250°C = ?

Experimental / Literature Data

- Westinghouse
  - Calculated equilibrium hydrogen = **0.32 ppm** under normal use
  - Increasing during shutdown, stabilizing at about **2 ppm** after a number of months (!)
- SS Cladding irradiated in PWR water
  - Hydrogen content of specimens = **3-4 ppm** after irradiation
- Koutsky et al.
  - 0.4-0.6 ppm → **1.2-2 ppm** (irradiation)
- Ruscak et al.
  - 0.3-0.7 ppm → **1.3-1.4 ppm** when kept in 'normal' PWR primary circuit water (max. 5.7 ppm locally)
- Tomlinson
  - "In oxygen-free high temperature water, more than 90% of the hydrogen generated in the corrosion is absorbed by the steel"
- Hydrogen
  - Will migrate to regions of lattice dilatation
  - Majority is in 'traps' rather than interstitial sites !...
  - *Embrittling effect is significant with hydrogen contents of more than 2 ppm in both unirradiated and irradiated pressure vessel steel → promotes (intergranular) cracking*

Figure 13: Slide summarizing literature data on RPV hydrogen concentrations.

From these data, it is not sure that traditional low-alloy RPV steels will undergo direct hydrogen damage such as *blistering* or *fissuring* from service conditions encountered during operation of water-cooled reactor systems, but effects on mechanical properties cannot be excluded; especially not under irradiation conditions and with transient temperatures.

It has been shown repeatedly that irradiation may highly enhance the hydrogen uptake and trapping, and a number of (synergistic) effects may arise[48]:

- Neutron irradiation of RPV steel at relatively low temperatures can increase by several factors the hydrogen solubility. Experiments clearly reveal that the greater the neutron fluence, the greater the hydrogen content in the metal, with a one-order of magnitude increase of the hydrogen solubility in an irradiated metal, compared to an unirraditated sample;
- Irradiation of the steel within the temperature range 50-180°C leads to a sharp decrease of hydrogen diffusion coefficients. Radiation-induced defects act as hydrogen traps. Post-irradiation “annealing” at 300°C partially causes the recovery of the hydrogen diffusion coefficient, but a residual effect persists;
- Low-intensity hydrogen charging (e.g. as a result of corrosion) results in a very high hydrogen content in irradiated steel, especially after irradiation ($1x10^{20}$ n/cm^2) at lower temperatures, e.g. 50 C (transient values up to 30 ppm !);
- Mechanical tests, both on smooth and notched specimens, also show that such low-intensity hydrogen charging only slightly modified strength parameters but could lead to a drastic decrease of plasticity; the effect being particularly pronounced for notched specimens;
- Exposures to high temperatures (e.g. 300-340°C) seem to be less damaging, but test on steel at 140-180°C showed large effects, suggesting that hydrogen embrittlement of RPV steel in transient regimes of operation is probable.

Also a review of German research programs from the 1970s-1980s, evaluating the effects of macro/micro segregations as well as hydrogen flakes on the mechanical properties of RPV materials – both with and without irradiation – concludes that the hydrogen content in combination with segregations has overall detrimental effects on the mechanical properties, especially under irradiation conditions. In addition, the segregations cause a large scattering of impact energies in Charpy impact tests[11].

4.2. Hydrogen Retention in the Flakes

Thermal desorption spectroscopy and hydrogen permeation measurements at the University of Cambridge have recently demonstrated very clearly that macroscopic, tiny cracks in a steel sample can provide extremely powerful hydrogen traps[49]. In steels with *internal defects* such as inclusions, laminations or pre-existing hydrogen defects such as “flakes”, the absorbed hydrogen atoms accumulate and recombine to form molecular hydrogen at these interfaces. Due to the impossibility of molecular hydrogen to diffuse out of steel, they accumulate and cause high pressure at such internal defects. This high pressure depends on the concentration of absorbed hydrogen in the metal, the trapped-to-dissolved hydrogen ratio and the temperature[50].

Especially sharp temperature decreases could have disastrous effects.

An SCK study[42] has estimated the hypothetical pressure build-up in the existing voids to be 2900 atmosphere (bar) when cooling down from 300°C to room temperature, assuming that no hydrogen could escape from the void and assuming that the void fraction is very small and a bulk hydrogen concentration in the RPV steel of 0.04 ppm exists. With increasing void fraction the internal flake pressure is said to decrease and the theoretical model results in a pressure of 316 bar with a void fraction of 0.0001%.[42] Assuming a more realistic hydrogen concentration of a few ppm, this would again still mean a pressure of a few thousand atmosphere.

In their model, however, the authors of the SCK study have disputed the impossibility of molecular hydrogen to move out of the steel. This is not in accordance with general scientific and engineering literature and is largely based on a number of assumptions regarding the overall validity of Sieverts' law[51,52] for diffusion/permeation of hydrogen through a steel wall and the reliability of its parameters[42].

However, the scatter on these parameters is enormous, with more than four orders or magnitude difference at the lower temperatures (Figure 14). A number of publications have therefore been trying to improve the (too) simplistic model of the law. In all metals and alloys that have been investigated there is evidence of significant influence of both surface phenomena and internal defects and impurities on absorption and permeation of hydrogen, resulting in large deviations from ideal behavior[53,54,55] (Figure 14) – See also Section 4.1 above.

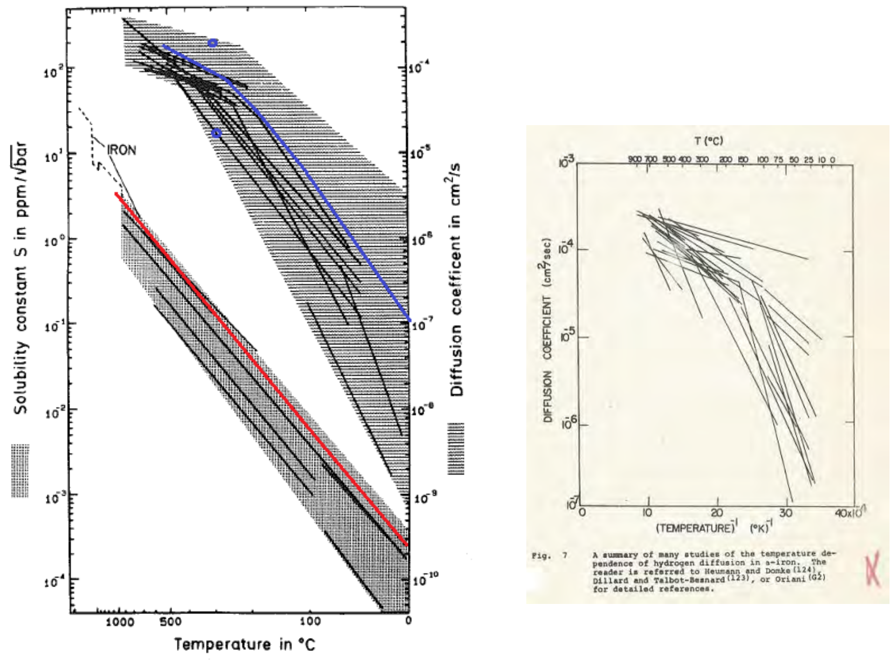


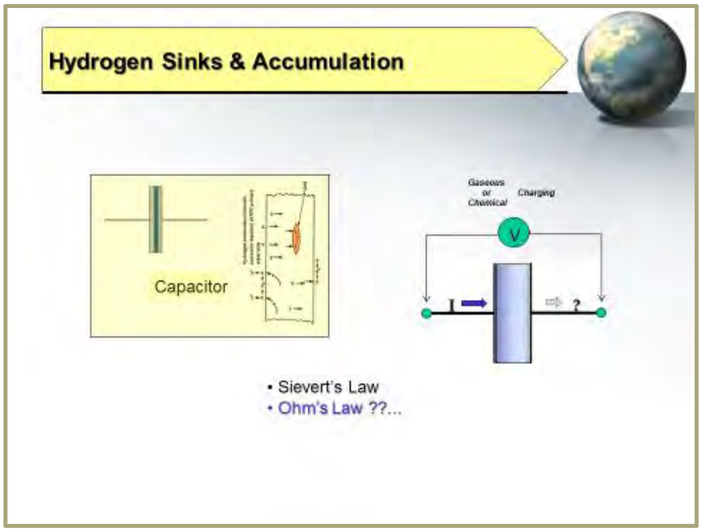
Fig. 7 A summary of many studies of the temperature dependence of hydrogen diffusion in a-iron. The reader is referred to Heumann and Domke(124), Dillard and Talbot-Besnard(123), or Oriani(G2) for detailed references.

Figure 14: Sieverts' constant and diffusion coefficient of hydrogen in steel as a function of temperature; remark the very large data variations at lower temperatures.

According to general corrosion engineering literature and the current authors' opinion, it should merely be seen that the existing "hydrogen flakes" will act as an almost irreversible trap for diffusing hydrogen. The effect of the flaws on hydrogen diffusivity can be compared to the effect of a capacitor on electrical current flow (Figure 15). Like Ohm's law is not applicable to the electrical current transfer across the capacitor, also Sieverts' law only determines the overall driving force, but not the behavior and H-transfer across the flake.

It also means that transient conditions, i.e. regarding temperature, could be very important (cf. Section 4.3). This is also recognized by Bosch and Vankeerberghen[42] when describing possible situations during reactor shutdown and outage.

Recent studies on the effect of hydrogen in flake-bearing steels[56] have also shown the possible effects on *hydrogen-induced delayed cracking* and the effect of flakes on *reduced impact toughness* and *increased fatigue crack growth rates*.



Hydrogen Sinks & Accumulation

- Sievert's Law
- Ohm's Law ??...

Figure 15: Electrical analogue for hydrogen transfer and trapping in (micro-)voids in a steel wall.

4.3. Potential Effects on Material Properties: Mechanical Aspects, HIC, Delayed Cracking or Other Phenomena

It is well known that the mechanical properties of high-strength ferritic steels can be severely degraded by hydrogen and therefore the *hydrogen embrittlement phenomenon* has great practical significance for this class of steels. On the other hand lower-strength steels (yield strength less than 690 MN/m^2) have generally been considered to be immune to hydrogen. However, the last two decades or so, a number of studies have demonstrated that such ferritic steels are also susceptible to hydrogen embrittlement[57,58,59].

At the lower end of the low-strength steels (< especially ca. 535 MPa yield strength), which will normally remain ductile after hydrogen absorption, and in the presence of thinner sections and very high hydrogen pressures, a real externally visible "blister" will form. Hydrogen blisters will typically nucleate at non-metallic inclusions; *this occurs particularly when the non-metallic inclusions are distributed in layers or fibers arranged perpendicularly to the flux of the diffusing hydrogen* (compare with the current failure case). In higher strength steels or embrittled steels (little plastic deformation) or in thick sections, a crack – rather than a blister – develops when the hydrogen gas precipitates at internal interfaces. This form of crack is normally called *hydrogen-induced cracking (HIC)*. Sometimes small hydrogen-induced cracks in adjacent parallel planes, as shown in Figure 7, link in the through-thickness direction and develop *stepwise cracks*.

Industrial experience shows that hydrogen blistering or HIC may result from corrosion rates as low as a few microns per year after long periods of time (10 – 12 yrs) or it may develop much more rapidly (0.5 – 2 yrs) where corrosion rates are high[17].

The ferritic low-alloy steels used for the construction of nuclear reactor components, such as RPVs, are also known to suffer from *neutron irradiation embrittlement*. This phenomenon which causes a large increase in tensile strength and a drastic loss of ductility and toughness, is an important problem concerning the RPV safety.

In addition to the neutron embrittlement, the pressure vessel and other components of a water cooled reactor can absorb hydrogen produced by corrosion as well as by hydrolysis of high-temperature water (cf. Section 3). It therefore appears that for the safety of reactor components made of steel, it is necessary to consider the *susceptibility to hydrogen embrittlement in addition to, and in combination with, irradiation embrittlement*.

In recent years an increasing attention is also concentrated on the problem of through-wall failure occurrence possibility in corrosion resisting welded cladding, and development of underclad and other types of cracks in the base material of PWR pressure vessels[60]. This was also the origin of the inspections in Doel 3 and Tihange. Usually the corrosion assisted crack growth is studied as a function of applied stress and of electrochemical parameters of the corrosive environment. In the presence of constant stress (i.e. SCC), similarly as with fatigue loading, the crack propagation process in appropriate conditions is however determined mostly by effects of hydrogen, i.e. by hydrogen embrittlement. *The hydrogen embrittlement of steel as a consequence of hydrogen release and trapping inside of cracks, or in their region, could become especially critical for the stability or growth rate of cracks during planned or accidental transients of PWRs* as described by Koutsky et al.[59].

In spite of the fact that environment sensitive cracking properties of pressure vessel steel have been studied to a large extent[61] (Appendix A of Section XI of the ASME Boiler and Pressure Vessel Code even presents a procedure for estimating the remaining useful life of a cracked reactor pressure vessel or nozzle), specific data on the hydrogen embrittlement of nuclear RPV materials is rather limited.

It has, for example, been postulated that the levels of hydrogen described in Section 4.1 above may lead to a catastrophic failure of irradiation-hardened steel operating at a temperature where outgassing of hydrogen is not significant[62,58].

Amongst many others, Takaku and Kayano[63] have shown that about 2 ppm of hydrogen can cause significant reduction in ductility and notch tensile strength in irradiated nuclear pressure vessel steels.

Also extensive studies by Koutsky et al.[64,65,66] on hydrogen embrittlement of RPV steels in static and dynamic tests for both irradiated and unirraditated states, have clearly shown that if the hydrogen content exceeds 2 ppm, this hydrogen content promotes intergranular cracking, leading to the conclusion that hydrogen may play an important role in understanding the anomalous cracking behavior of some surveillance specimens (associated with intergranular cracking).

Hänninen, reviewing various international studies on the 'conjoint actions of hydrogen and irradiation embrittlement on the pressure vessel steel of nuclear plants', summarizes in a (confidential) report that also a number of Japanese studies concluded that, although hydrogen at a level of ca. 2 - 2.3 ppm did not have a major effect on the hardness and tensile test results, tests did provide indications of a possible embrittlement in the impact tests and in delayed fracture tests (cf. also findings of "non-hardening embrittlement"[67] in SCK investigations related to the current case).

Many of the above failure modes are time dependent and, thus, are expected to become more prevalent when the power plants are aging. So, these modes of degradation are of major concern when safety margins and plant life extension problems are considered.

Also reactor operation modes may become increasingly important with age. The solubility of hydrogen in steel decreases sharply as the temperature drops. On reactor shutdown, the decreased solubility of the hydrogen can lead to problems if the hydrogen does not have time to diffuse out of the steel. Steel charged with atomic hydrogen at higher temperatures (>120 C) can show embrittlement if subsequently stressed at lower temperatures, e.g. on shutdown of equipment. Shutdown of high-pressure reactors after a prolonged period of operation at elevated temperatures tends to result in oversaturation of the materials with hydrogen, which has to be removed by way of effusion. The latter is governed by the laws of diffusion which make it necessary to take into account also decreasing diffusion coefficients with decreasing temperature. If excess hydrogen remains in the material after cooling down to ambient temperature, *delayed cracking* may occur, similar to flaking as a result of metallurgical hydrogen introduced during steelmaking[68,69].

5. Final Discussion and Conclusions

After almost 3 years of investigations, it remains unclear if the cracks found in the Belgian NPPs Doel 3 and Tihange 2 are "only" manufacturing artifacts, or if there is also an "operational component" contributing to the current problems and operational risks; i.e. whether the cracks are still progressing and whether there are other phenomena, e.g. similar to 'hydrogen blistering' processes, contributing to the problem (e.g. some kind of ‘delayed cracking’ or HIC). Additional hydrogen might indeed come from the cathodic corrosion reactions occurring on the primary water side of the reactor pressure vessel or from other sources such as the radiolysis of the reactor water, or even from nuclear transmutation reactions.

During operation, there is a permanent flux of (corrosion-originating or other) atomic hydrogen through the RPV wall – the flux might be large or small – and this hydrogen could easily get trapped into the voids or “flakes” that are present. An eventual pressure build-up in the flakes will result in growing cracks and other materials degradation phenomena.

Whatever interpretations, disputes, models, theories, etc. there might be, it is a sure fact that the RPV wall will indeed be *exposed* to significant additional quantities of hydrogen during operation. Significant amounts of hydrogen will also *enter* (or be generated) within the – already flawed – steel wall.

Such operationally-generated hydrogen will, basically, have two *effects*:

(1) Either it will cause or aggravate embrittlement of the steel (i.e. also aided by the irradiation);
(2) Or, more direct and abrupt effects may be caused by “loading” the pre-existing flaws, either through the generation of high hydrogen pressures within the voids, or (and) by the building-up of high triaxial stresses at the edges of the flakes, leading to further progressing of the cracks, even with very low external stress levels.

From an engineering point of view this is an unprecedented challenge, especially because of the very high density, the large dimensions, and the great penetration depth of the voids in the metal wall as they have been detected. It is unclear whether this will mean the end of the operation of the reactors, but it certainly is a dominating element in their *life management*. Other studies need to verify the possible acceptance of the current condition from a mechanical point of view but, if eventually restarted, close-interval surveys and monitoring programs definitely need to be set up for the Doel 3 and Tihange 2 NPPs.

It is also not just Doel 3 and Tihange 2 in Belgium that could be affected. The RPVs were fabricated by the, now bankrupt, RDM (Rotterdamsche Droogdok Maatschappij, Netherlands), which also manufactured RPVs for at least 20 other reactors that are operating in seven countries around the world, including some 10 in the United States. Of course, also other factors like steel supplier and steel composition, cladding process and final assembling will have played an important role in the development of the observed damage, so that not all RDM-manufactured RPVs are necessarily dubious.

In this respect, however, it should be considered more cumbersome that also other RPVs, not manufactured by RDM, are possibly affected. Arguments that the Belgian phenomenon would be solely caused by manufacturing issues are severely challenged by recent findings in Switzerland (Beznau), where the RPV – produced by a different manufacturer – is apparently showing similar defects (or UST "indications") as the Belgian reactors[70].

Although further investigations are needed in the Beznau case, it appears more and more doubtful that the detected artifacts would only be materials and processing related and that no operational factors are involved. Also, data supposed to prove that there has not been any evolution over time of the cracks or so-called 'hydrogen flakes' in Doel and Tihange (sizes of some cracks > 10 centimeters) at least appear to be disputable.

Given all this, and in view of the theoretical evidence and experimental findings discussed in the previous chapters, it seems highly unlikely that the (pre-existing) cracks have not been growing over time of operation and that they are stable at this moment.

Therefore, if continued operation would be decided, scrutinous surveillance programs would be necessary.

If some of the initial hypotheses discussed above were proven to be true, there might be a huge impact on currently operating PWRs.

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