Studies on the Consequences of the Chemical Interactions Occurring in the Cores of Nuclear Reactors

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Abstract— Water radiolysis is still up till now a controversial problem particularly in case of water chemistry of primary coolant systems in light water reactors (LWR), especially in BWRs.Oxygen arising from radiolysis of the reactor water in core affects to a large extent, as an oxidizing agent, the stress corrosion cracking (SCC) so also are the other chemical species produced by radiolysis of water.Power reactor systems are very numerous and very much complicated. In the essential parts of these reactors such as the reactor core , steam generators, as well as in the secondary circuits where water plays an important role as coolant or moderator or both, the integrity of the construction materials are vulnerable to adverse effects related to corrosion.In the present work the interaction of water in water cooled/moderated nuclear reactors with the reactor components under the strong irradiation field are studied in order to shed some light on the prevailing chemical interactions occurring in the reactor cores.In the present work: The changes occurring in the stray gamma/neutron irradiation field, the systems or components in LWR that are susceptible to the effect of the water used as a coolant or moderator has been studied in details. This comprised metals used in reactors particularly different types of steels used as well as zircaloy materials.

Keywords—Water Radiolysis, Coolant, Zircalloy Materials, Corrosion, Crud, Light Water Reactors, Water Chemistry.

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1 INTRODUCTION

Water chemistry is not only one of the most important parameters to maintain the plant reliability but also one of the most important indexes to measure plant operational conditions. Water chemistry improvements, e.g., hydrogen water chemistry in BWRs and suitable PH controls in PWRs, have been applied as suitable options for preventive maintenance.

Massive amounts of water chemistry data are collected in nuclear power plants to measure the plant operational conditions at every moment.

2 COOLANT CHARACTERISTICS IN DIFFERENT REACTOR TYPES

The coolant which passes through the nuclear reactors is used to transport the reactor heat either to a boiler where steam is formed to run a conventional turbine or it is used as a thermodynamic heat engine fluid and passes directly into the turbine and back to the reactor. Pressurized water, organic liquids, sodium, and most gas cooled nuclear power plants employ an intermediate steam boiler. Boiling water and some gas cooled reactors use the coolant directly in the turbine. [1]

Regardless of the method used, coolants should ideally have the following properties:

1. Low melting point
2. High boiling point
3. Non-corrosive properties
4. Low neutron absorption cross section
5. High moderating ratio (for thermal reactors)
6. Radiation stability
7. Thermal stability
8. Low induced radioactivity
9. No reaction with turbine working fluid
10. High heat transport and transfer coefficient
11. Low pumping power

No single coolant has all of these properties, and as a result a number of different coolants have been used in nuclear reactors. Each coolant with its own particular advantages would be suitable for a certain type of reactors. Among these coolants are light and heavy water (both pressurized and boiling), organic liquids, sodium, sodium potassium mixtures, fused salts, and a number of gases - air, carbon dioxide, helium, nitrogen, hydrogen and steam.

3 COOLANT IN LWRS

Currently the majority of nuclear power plants in the world are water-moderated, thermal reactors. They are categorized as either light water or heavy water reactors. Light water reactors use purified natural water (H_2O) as the coolant/moderator, while heavy water reactors employ heavy water, deuterium oxide (D_2O). In light water reactors, the water is either pressured to keep it in superheated form (in a pressurized water reactor, PWR) or allowed to vaporize, forming a mixture of water and steam (in a boiling water reactor, BWR). In a PWR, superheated water flowing through tubes in the reactor core transfers the heat generated by fission to a heat exchanger, which produces steam in a secondary loop to generate electricity. None of the water flowing through the reactor core leaves the containment structure. In a BWR, the water flowing through the core is converted directly to steam which leaves the containment structure to drive the turbines. Light water reactors use low enriched uranium as fuel. Enriched fuel is required because natural water absorbs some of the neutrons, reducing the number of nuclear fissions. All of the 103 nuclear power plants in the United States are light water reactors; 69 are PWRs and 34 are BWRs.

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With light water as coolant in nuclear power plants, the resulting high temperature water causes corrosion of structural materials, which leads to adverse effects in the plants, e.g., increasing shutdown radiation, generating defects in materials of major components and fuel claddings, and increasing the volume of radwaste sources. [2]

3.1 Water Chemistry and Cladding

Safety is one of the main issues in the power reactor development. Reactor safety largely depends on fuel element reliability which in its turn depends on compatibility of fuel cladding material with nuclear fuel from one side and water coolant from the other. This reliability is achieved by using a proper composition for pellet materials and construction of fuel elements by using proper cladding materials and by chemical conditioning of water coolant to prevent dangerous consequences of corrosion, erosion and other processes.

The problem of water chemistry and coolant –cladding interaction (CCI) for a long time was not under consideration, however, in recent years a growing interest in this problem can be observed.

Water cooled nuclear power reactor experience showed that even in normal working conditions after a certain period of time some undesirable effects in fuel elements cladding integrity can take place due to corrosion, erosion, hydration and deposition on heat transfer surfaces of corrosion products as well as other coolant impurities.

3.2 Coolant Purification

In order to prevent fuel element cladding and other structural materials damage due to corrosion during the reactor campaign, prevent thermal destruction of fuel element cladding due to deposition of corrosion products and other impurities, and to decrease the deposition of various impurities including radionuclides on heat exchangers and other equipment of the coolant circuit as well as to remove various impurities and radionuclide from the coolant, the following measures may be undertaken:

1. Reliable high strength corrosion resistant materials are used for fuel cladding and other components of the primary circuit.
2. Appropriate effective coolant purification systems are used to remove undesirable impurities.
3. Water conditioning is used to reduce corrosion processes or any influence or behavior of impurities in the circuit.

4 CLADDING BEHAVIOR AS INFLUENCED BY WATER CHEMISTRY

The cladding tube has to fight on two fronts: internally and externally.

On the internal front, fuel pellets try to stick to the clad and expanding irregularly they stress the cladding tube; this leads to local strain, in spite of the fact that long irradiation impairs ductility of the cladding tube natural.[3]

Furthermore, a heat flux of about 1000kw per square meter of tube surface area flows through the tube; fission gases, released from the fuel, causes a pressure increase inside the tube and a tendency to escape through the micro-cracks formed in the clad and, worst of all, iodine induces stress-corrosion cracking.

Externally, high-temperature boiling water corrodes the tube surface at a non negligible rate, because of the large concentration of radiolytic oxygen plus irradiation.

If water does not boil, several ingredients are generally added, as hydrogen, lithium, hydroxide, boric acid … etc.

All these additions act to avoid cracking or corrosion in other components of the reactor, thus hydrogen is added to reduce the concentration of radiolytic oxygen in order to avoid stress-corrosion cracking of sensitized austenitic stainless steels present in the coolant pressure boundary; lithium hydroxide is added to raise the pH over neutral to protect low alloy steels and boric acid is added to control excess of reactivity.

The cladding tube will pick up hydrogen by corrosion, but it is necessary to keep the hydride tangentially oriented in the tube walls so that their ductility would not be affected.

All the dirt (usually called crud) released from other components has a tendency to deposit on the tube wall because of its high temperature, and ofcourse even a cladding tube does not feel happy in being coated with a strange material.

Migration and transport of irradiated in reactor core corrosion products and other impurities lead to formation of highly radioactive depossities in some parts of the primary circuit and to radioactive contamination of primary pipes and equipment (especially for BWR). This causes difficulties in maintenance and repair because of the high radioactive dose and necessitates the decontamination of some equipments and even the primary circuit as a whole, more serious problems connected with CCI might occur in abnormal conditions, for instance, zirconium alloy-water coolant reaction during a reactor accident which led to cladding failure and hydrogen formation. [4]

5 WATER CHEMISTRY ASPECTS OF POWER REACTOR DEVELOPMENT

5.1 Chemical Systems at Nuclear Power Plants

The normal functioning of a nuclear power plant is assured by various chemical systems and facilities which should guarantee fuel element cladding integrity and reliable performance of nuclear fuel, table 1 describes some chemical facilities which are normally constructed at nuclear power plants.[5]

TABLE 1
MAIN CHEMICAL FACILITIES AT NUCLEAR POWER PLANTS

Facilities	Facility purpose	Technology used
Reactor water by pass purification	Constant removal of corrosion products ,salts and radionuclides accumulated in the reactor circuit to maintain specified concentrations	Evaporation or filtration and ion exchanger
Condensate purification	Removal of salt impurities and corrosion products from the turbine condensate to prevent their entering to the reactor circuit	Separate or mixed – bed ion exchange
Fuel element cooling pond water purification	Provision of high transparency of water , removal of suspensions and radionuclides	Filtration on sorbents and ions
Waste water purification	Preventation of radionuclide contamination of the environment Waste water recirculation	Multistage purification with coagulation, evaporation, ion exchange
decontamination	Circuits and equipment washing from radioactive contamination	Washing with decontamination solution

Light water cooled reactors are the main type of reactors used for power production. Water as heat transfer medium is an aggressive substance being in contact with structural materials under work parameters. Reactor exploitation and development largely depends upon reliability of fuel elements under various reactors condition. Among many factors influencing fuel reliability are chemical conditions of coolant environment in reactor. Compatibility of fuel cladding with the coolant and with other structural material is an important aspect of fuel safety. Not only internal conditions inside reactor vessel are significant but the whole coolant circulation system should be considered , because those processes are of phisico – chemical nature. Special measures should be taken to prevent dangerous corrosion of cladding and other structural materials and corrosion products build up on internal surface.

These problems can be solved by proper selection of structural materials and water chemistry control in the primary circuits.

In PWRs, water chemistry is different in the primary and secondary cooling systems.

Major concerns of water chemistry in the primary cooling system are to control boron concentration to maintain the reactor reactivity and then to control radioactive corrosion products to keep a lower shutdown dose rate.[6]

The main concern in the secondary cooling system is to keep a suitable PH, which maintains sufficient integrity of the steam generator tubing.

In order to determine water qualities, e.g., concentrations of boron, lithium, hydrogen, oxygen and other anions and cations, PH, and conductivity, cooling water to be measured is cooled down and depressurized for application of proven on-line sensors the same as for BWRs.

5.2 Corrosion Products in Nuclear Reactors

At nuclear reactor high heat flux or longer residence time of fuel elements can lead to solid impurities deposition on heat transfer surfaces and to the possibility of fuel cladding failure.

In reactor conditions, the main scale-formation comes from suspended corrosion products of structural materials, and one of the major problems in the developments of high power plants is to prevent such deposition.

Of special importance are those problems concerning the single-circuit nuclear power station with carbon steels as structural materials.

Experience shows that corrosion products are not fully removed from the circuit by purification systems and this result in deposit removal from the reactor core and the circuit decontamination to improve radiation conditions needed for performing repair work.

To understand the problems of corrosion products deposit reduction, one must be familiar with regularities of the process of deposit formation. This requires a general understanding of water radiolysis process.[7]

6 WATER RADIOLYSIS

Water radiolysis in nuclear water cooled reactors is the main initiator of the chemical changes occurring in the reactor, internals including corrosion and crud formation.

The interaction between ionizing radiation (electrons, ɣ rays) and water leads to the formation of electronically excited and ionized molecules as follows: [8]

$$H_2O \rightarrow H_2O^* \rightarrow H + OH \qquad (1)$$
$$\quad \Lsh\ H_2O^+ +\ e_{\text{excited}}$$

$$e^- \xrightarrow{\text{Deexcitation}} e_{th} \quad (2)$$

$$e_{th} +\ H_2O \rightarrow e^-_{aq} \qquad (3)$$

The gross products of water radiolysis and their G values at PH7 are given as follows:

$$H_2O \ \rightarrow \underset{(2.7)}{e^-_{aq}}\ ,\ \underset{(0.6)}{H^{\cdot}}\ ,\underset{(2.8)}{OH^{\cdot}}\ ,\underset{(0.45)}{H_2O}\ ,\underset{(0.7)}{H_2O_2}\ ,\underset{(3.2)}{H^+{}_{aq}}\ ,\underset{(0.5)}{OH^-{}_{aq}} \qquad (4)$$

The G values are used to compare the radiation effects on different materials.

The G value is defined as the number of changed molecules due to absorption of 100ev (1.60 x10^{-7} j) energy. In order to convert G values into SI units multiply G values by 0.10364 to obtain G value in μ mol/j.

The G values of initial radiolysis products of water with different types of radiation are given in the following table under different condition:

TABLE2
G VALUES OF INITIAL RADIOLYSIS AT DIFFERENT TEMPERATURE PRODUCTS [9]

	e^-_{aq}	H^+	$H^{\cdot}$	OH^-	H_2O	H_2O_2
γ- rays Room Temp.	2.7	2.7	0.6	2.9	0.4	0.6
Neutrons Room Temp.	0.93	0.93	0.5	1.09	0.88	0.99
γ- rays or neutrons (300° - 400° C)	0.4	0.4	0.3	4.7	2.0	0

It could be observed that at elevated temperature more oxidizing species are formed which could probably enhance corrosion in reactor components.

The excited and ionized molecules can produce several very reactive primary species i.e. OH^{-}, e_{aq}^{-} , $H^{\cdot}$ as well as some other simple and molecular products according to the following equations of the major primary products reactions and their rates given in table 3.[10]

TABLE 3
REACTION RATE CONSTANTS OF WATER RADIOLYSIS AT ELEVATED AND NORMAL TEMPERATURES

Reaction	Rate constant at 280°C (L.MOL.S)	Rate constant at normal Temp. ($dm^3\ mol^{-1}\ s^{-1}$)
$e_{aq}^{-} + e_{aq}^{-} = H_2 + 2OH_{aq}^{-}$	---	3.20 E10
$e_{aq}^{-} + H_2O = H + OH^{-}$	1.65 E02	---
$e_{aq}^{-} + H^{+} = H$	2.84 E11	3.20 E10
$e_{aq}^{-} + OH = OH^{-}$	3.10 E11	2.50 E10
$e_{aq}^{-} + H_2O_2 = OH + OH^{-}$	1.34 E11	---
$e_{aq}^{-} + HO_2 = H0_2^{-}$	2.06 E11	---
$e_{aq}^{-} + O_2 = 0_2^{-}$	1.96 E11	1.96 E10
$OH + OH = H_2O_2$	4.65 E10	6.00 E09
$OH + H_2 = H + H_2O$	4.82 E08	3.50 E07
$OH + H_2O_2 = HO_2 + H2O$	4.82 E08	---
$OH + HO_2 = O_2 + H_2O$	1.24 E11	---
$OH^{-} + H_2O_2 = H0_2^{-} + H_2O$	5.97 E09	---
$OH^{-} + H = e_{aq}^{-} + H_2O$	6.63 E08	---
$H_2O + e_{aq}^{-} + H = H_2 + OH^{-}$	6.22 E09	---
$2H_2O + 2e_{aq}^{-} = H_2 + 2OH^{-}$	3.00 E07	---
$H_2O + e_{aq}^{-} + 0_2^{-} = H0_2^{-} + OH^{-}$	1.04 E10	---
$H_2O + e_{aq}^{-} + H0_2^{-} = 2OH^{-}$	8.70 E08	---
$H + H = H_2$	1.03 E11	1.00 E-10
$H_{aq}^{+} + OH_{aq}^{-} = H_2O$	---	1.40 E-07
$H + e_{aq}^{-} = H_2 + OH_{aq}^{-}$	---	2.00 E-10
$H + OH_{aq}^{-} = e_{aq}^{-}$	---	2.50 E-07
$H + OH = H_2O$	2.06 E11	2.50 E10
$H + H_2O = H_2 + OH$	8.14 E02	---
$H + O_2 = HO_2$	1.96 E11	2.10 E10
$H + HO_2 = H_2O_2$	2.06 E11	---
$H + 0_2^{-} = H0_2^{-}$	2.06 E11	---
$H + H_2O_2 = OH + H_2O$	1.13 E09	---
$H0_2^{-} + H_2O = OH^{-} + H_2O_2$	1.89 E07	---

In the presence of O_2 in water the reducing species H-atoms and the solvated electrons e_{aq}^{-} are transformed into oxidizing species perhyoxyl radical $H0_2^{\cdot}$ and perydroxide radical $0_2^{\cdot-}$.

$$H + O_2 \rightarrow H0_2^{\cdot-} \quad (5)$$
$$e_{aq}^{-} + O_2 \rightarrow 0_2^{\cdot} \quad (6)$$
$$H0_2^{\cdot} \rightleftharpoons H + 0_2^{\cdot-} \quad (PK=4.8) \quad (7)$$

These radical anions together with OH radicals can initiate oxidation process i.e. can initiate corrosion of metallic surface. [11]

$$OH + H_2 \rightarrow H_2O + H \ (K=1.5x\ 10^{7}\ dm^{3}\ mol^{-1}\ s^{-1}) \ (8)$$

The $H^{\cdot}$ and $OH^{\cdot}$radicals formed from excited molecules recombine at sites of their high concentration to yield most molecular products H_2 and H_2O_2, moreover, a certain amount of H_2 and H_2O_2 also formed by direct water decomposition.

$$H_2O + H_2O^{*} \rightarrow H_2 + H_2O_2 \quad (9)$$

The hydro peroxide radical $H0_2^{\cdot}$ may appear in spurs by the following reactions:

$$H_2O_2 + 0^{\cdot}H \rightarrow H0_2^{\cdot} + H_2O \quad (10)$$
$$2OH \rightarrow H0_2^{\cdot} + H \quad (11)$$

However the yield of $H0_2^{\cdot}$ is very small and it is possible to neglect its formation as a primary product.

The probability of recombination of $H^{\cdot}$ and $OH^{\cdot}$ to form water molecule in the liquid phase is 0.1, while in gaseous phase under 10 MPa it is 10^{-3} only.

Therefore recombination in steam and steam/water mixture is sluggish than in water i.e. radiolysis of water in a boiling system involving steam formation is greater than in the condensed state.[12]

The formed short lived free radical products of water radiolysis, except H_2, are very reactive.

Atomic hydrogen is a reducing agent and its reducing capacity enhances with PH of the medium.

In acid media $H^{\cdot}$may show oxidizing properties OH radicals possess oxidizing properties. At PH >9 it dissociates by the reaction:

$$0^{\cdot}H \rightarrow H^{+} + O^{-} \quad (12)$$

Molecular hydrogen H_2 does not react directly with dissolved substances, it may however, interact with $OH^{\cdot}$ by the reaction:

$$H_2 + OH^{\cdot} \rightarrow H^{\cdot} + H_2O \quad (13)$$

The radical $H0_2^{\cdot}$ can dissociate as follows:

$$H0_2^{\cdot} \rightarrow H^{+} + 0_2^{-} \quad (14)$$

This radical is strong oxidizer. It should be noted that the direct effect of radiation on the dissolved substance is negligibly small. Any radical which has avoided recombination and diffused into the depth of solution finally can react with the dissolved substances even if their concentration is lower than 10^{-4} M.[13]

In the absence of dissolved substances the molecular products react with radicals:

$$H_2O_2 + H^{\cdot} \rightarrow OH^{\cdot} + H_2O \quad (15)$$

Consequently, the concentrations of molecular products gradually increases to a certain constant value. The presence of dissolved substances reacting with radicals prevents the molecular products from the reverse reaction.

The concentration of dissolved substance sufficient to completely suppress the reverse reaction depends on the nature of the substances and is 10^{-5} to 10^{-3} M.

Radiolysis of pure water yield in addition to H_2 and H_2O_2 and oxygen in minute amounts. Its occurrence is associated with the formation of $HO._2$ by the reaction:

$H_2O_2 + OH \rightarrow HO_2 + H_2O$ (16)

And its subsequent interaction with the radical and molecular products of radiolysis as follows:

$0^{\cdot}H + H0_2^{\cdot} \rightarrow H_2O + O_2$ (17)
$H_2O_2 + H0_2^{\cdot} \rightarrow H_2O + O_2 + 0^{\cdot}H$ (18)
$H0_2^{\cdot} + HO_2 \rightarrow H_2O_2 + O_2$ (19)

7 RADIOLYSIS OF WATER IN NUCLEAR REACTORS

In PWRs, high temperature (and consequently a considerable rate of recombination) and also accumulation of hydrogen prevent water radiolysis. No oxygen is detected in the primary circuit in water having electrical conductivity of 10^{-1} μS cm^{-1} at the concentration of 25-50 cm^3 /Kg.

If oxygen finds its way to the primary circuit with feed water it is consumed in the reaction with H2 and in corrosion, Within 12 minute oxygen concentration drops to half its initial value.[14]

To reduce the rate of steel corrosion ammonia is added (in doses) to water in the primary circuit of water cooled and moderated power reactors. It also acts as a source of hydrogen.

Boric acid is added to the primary circuit in water cooled and moderated power reactor for mild control. α- Particles (E= 0.49 MeV) and ɣ rays (E=2.3MeV) resulting from10B(n,α)^7 Li enhance radiolysis.

If the primary circuit contains excess oxygen, it combines with H_2 and N_2 dissolved in water to produce HNO_3 and consequently the PH may drop to 3.5. This is the so called acid well, neither air nor nitrogen are inert under irradiation. Oxygen is normally removed from the circuit water by thermal deaeration. Remaining oxygen combines with hydrogen and as this happens nitrogen remains in the water.

Ammonia is synthesized in the absence of oxygen in the coolant from nitrogen and hydrogen during reactor operation, its rate of formation is proportional to the reactor capacity and concentration of nitrogen in water but is independent of hydrogen concentration. Ammonia decomposes in the core zone and after long time operation of the reactor equilibrium is established between the synthesis and decomposition of ammonia at PH 8 and 9.

In BWR, radiolysis proceeds more strongly than in PWR, recombination is more difficult in steam phase than in the condensed phase, moreover, hydrogen goes mainly to steam and then discharged from the system through the condenser ejector. Consequently, hydrogen does not accumulate in the system.[15]

In a vessel type BWR water serves as a coolant and moderator. The radiation energy received in water is obviously greater than a channel type BWR where graphite is the moderator. Thus the relative release of radiation energy in the coolant in different BWR types of reactors varies within a wide range.

In vessel type BWR up to 1.6 – 2 % of the reactor total power may be liberated in the coolant.

In channel type graphite moderated reactor equipped with rod type fuel elements the energy given to the coolant in about 0.6 % of the capacity.

The rate of oxygen formation in vessel type BWR is higher than in the channel type reactor thus the oxygen concentration in steam generated by NPP in a vessel type reactor may reach 25 – 35 mg/kg. While in channel type reactor the concentration is 5 to 15 mg/kg.

Therefore the oxygen content of a channel type cooled graphite moderated reactor is lower than in a vessel type reactor and is in order to reduce oxygen content in steam, hydrogen or ammonia are injected to the coolant.

The content of H_2O_2 is 30 mg/kg in operation and 1.5 mg/kg during shut down.

Radiolysis in a single circuit BWR may be suppressed by continuous addition of H_2 or NH_3 in doses to the coolant.

Thus, injection of 160 ml/l into the feed water reduces the oxygen content in steam to 15 – 10 % of its former value. Further increase of H_2 content up to 3000 ml/l has practically no effect on oxygen concentration in steam.

It should be noted that continuous massive injection of H_2 is economically objectionable.

Increasing PH of the reactor water to 8 as a result of ammonia injection decreases the oxygen content in steam by a factor of 3 to 5.

With a channel type reactor, the oxygen content in steam is 5 to 6 mg/kg, the oxygen yield is 6.2lMW^{-1} h^{-1}, the degree of ammonia decomposition per/1MW of reactor water lies within 8.5~9 %.

0.05 g/h of Nitrates and nitrites form per 1MW of reactor power.Their content in the reaction water reaches 0.1 mg/l.

To fully suppress the radiolysis in a BWR, the ammonia content in water should be not less than 10mg/kg.

The ammonia supply to compensate for its loss should be 4% of the amount required to suppress the radiolysis. This injection of ammonia in such an amount into the water of a boiling reactor requires that the pipe assemblies of condensers and heaters be made of stainless steel, and not of copper since copper intensifies the scale formation. Zinc being a product of brass corrosion increases the activity of coolant and equipment.

In research reactors having power up to 18MW the content of radyolitic hydrogen in water does not exceed 4.5 ml /kg and for hydrogen peroxide 10 mg /kg.

The concentration of hydrogen in air volumes of the reaction is below 1%, the explosive concentration being 4%.

The hydrogen content in water is independent of power at its high values. This is due to the fact that an increase in the water absorbed dose increases the specific density of radicals and consequently the intensity of recombination.

The concentration of H_2O_2 varies only slightly at temperature up to 323° K and abruptly drops because of its decomposition at above 323° K.

The concentration of dissolved hydrogen is practically independent of the water flow velocity in the core zone, the experience gained in operation of pool – type reactors with power up to 18Mw has confirmed the possibility of the long term operation without degassing systems.

When coolant enters the core in an emergency, the radiolytic hydrogen forms and due consideration should be given to that hydrogen that may be produced in the reactor building in explosive concentration.

8 FORMATION OF CORROSION PRODUCTS

8.1 Crud Cycle and Growth

The corrosion products that are normally assumed to be existing as films, deposits and in suspension or solution are somewhat mobile in all models, with the degree of mobility increasing from film to deposit to suspended and dissolved corrosion products. It has been shown that corrosion products undergo continual movement throughout the primary heat transport system, being deposited in one location for some time and then being transported to another site and redeposited. [16]

In physical adsorption the adsorbate is weakly held by the adsorbent, in this reversible process the weak wander Waal's forces limit the adsorbed layer to a few molecules in thickness. Only if this is followed by some chemical bond formation process, causing molecules to be more firmly attached to the system surfaces, this can be of importance crud growth could occur, This could be an important part of the mechanism of attachment of radionuclides to circulating and deposited crud.

Radionuclides may become attached to a surface by chemisorptions mechanism where strong chemical bonds are formed between ions in solution and certain atoms in the surfaces. Ion exchange between radionuclides in solution and ions in both circulating and deposited crud is probably the major mechanism for the introduction of radioactivity into the crud. A radionuclide deposited on a surface by an ion exchange reaction may move to a lattice vacancy within the surface and become permanently attached.

Precipitation of material from solution may also be expected as coolant temperature changes outside the reactor core leading to supersaturated condition, coolant being at or near saturation limits for various corrosion products. The corrosion film formed in-situ and later on the deposited crud may provide nuclei for deposition of excess crud from solution, the precipitated molecules may be chemically bonded to the existing solids leading to crud growth.

8.2 Oxide Films Formed as Corrosion Products

At low temperature, ferrous hydroxide is the first product of iron – water reaction as shown:

$Fe \rightarrow Fe^{2+} + 2e^{-}$ Anodic (20)

$Fe^{2+} + 2OH^{-} \rightarrow Fe(OH)_2$ Anodic (21)

$2e^{-} + 2H_2O \rightarrow 2OH^{-} + H_2$ (Cathodic,O_2 absent)(22)

$2e^{-} + 1/2\, O_2 + H_2O \rightarrow 2OH^{-}$ (Cathodic,O_2 absent)(23)

Ferrous hydroxide $Fe(OH)_2$ initially formed rapidly changes to high insoluble magnetite Fe_3O_4 ,particularly in high temperature water under alkaline reducing conditions according to Schikorr reaction:[17]

$3Fe(OH)_2 \rightarrow Fe_3O_4 + H_2\uparrow + 2H_2O$ (24)

The above solution mechanism is responsible for the formation of visibly crystalline and adherent magnetite films on carbon steel constructional surfaces of primary heat transport systems in PHWRs, under alkaline (Ph ≈10~10.5) and reducing (dissolved<15ppb) conditions of water chemistry at high temperature (above200° C).

The oxide corrosion product formed on stainless steels and other Ni,Cr and Fe alloys consist of magnetite and other oxides of Fe,Cr and N. The film formation here is extremely sensitive to temperature and water chemistry conditions such as PH, dissolved O_2 and coolant composition.

The peculiarity of the oxide films formed on stainless steels is that they tend to change with time and those formed after long exposure are difficult to remove.

The magnetite film Fe_3O_4 is generally of spinel type M`(MM`O_4) where M is divalent metal ion and M` is a trivalent metal ion , any one of the transition elements Cr,Ni,Co and Mn can take the place of Fe atoms as substitutional impurities in magnetite spinel, this type of imperfection is actually favored because of favorable size and charge of the ions and leads to the variable composition of the corrosion product film under different conditions at different items.

9 AQUEOUS CORROSION OF ZIRCALOYS

9.1 Effect of PH Control Agents

Ammonia and lithium hydroxide are the common additives to the reactor coolant for control of corrosion products transport. There is either very little or negligible effect of alkali on zircaloy corrosion rates or hydrogen pick-up. That is the time to reach transition is not affected.

However, excessive lithium hydroxide concentration raising the PH above 11.5 accelerates the pre-transition corrosion rates because of the possible formation of lithium zirconate. This acceleration of the corrosion rate has been associated with the aggressive cation and anion namely Li^{+} and OH^{-}.

It has been suggested that a possible lithium substitution on the oxygen deficient ZrO_2 lattice and the increase in anion vacancies could result in the acceleration of corrosion rates hence the concentration of lithium hydroxide in the core should be avoided by an optimum core design .In addition, the crud deposition on the core surface should be minimized so that lithium hideout and subsequent boiling within the crud do not a raise.

9.2 Effect of boric acid addition

Use of boric acid for chemical shim and auxiliary reactivity control purpose, at concentration ranging from 10-1500 ppm boron has been found to be having no effect on zircaloy corrosion. [18]

9.3 Hydrogen pick-up

The aqueous corrosion of zircaloys generates gaseous hydrogen which under the existing temperature and thermal gradients forms zirconium hydride ZrH1.5 beyond a certain threshold concentration of ZrH1.5 platelets of the hydride is formed leading to poor ductility and consequently a brittle failure under stress.

Hydrogen pick up being a function of corrosion is low in the pre transition region and high in the post transition region, it is also affected by alloy composition.

For example for zircaloy-2, it is about 0.004mg/dm^2/day at 310°C while for zircaloy-4 it is about 0.0015mg/dm^2/day at the same temperature.

9.4 Effect of dissolved gases

The hydrogen pick up for zircaloys increases rapidly with decreasing dissolved O_2. Hydrogen over pressure to the tune of 2500Psi (as partial pressure H_2) increases the hydrogen pickup for zircaloys by a factor of 2-3 in the pre-transition region. N general dissolved O_2 and H_2 concentrations which exist in the operating BWRs (dissolved O_2~ 300 ppb along with stoichiometric amount of H_2) and PHWRs (3-30Ml/Kg of added H_2/D_2<15 ppb dissolved O_2) cause little effect on either the hydrogen pickup or aqueous corrosion of zircaloys. The reason which has been attributed to the reduced hydrogen pick up in nuclear power stations is the low hydrogen partial pressure in solutions.

In PHWRs helium nitrogen mixture are being used as cover gas for heavy water in PHT storage tank due to economic reasons. Based on its saturation solubility at low temperature the maximum nitrogen that can be expected to get dissolved in coolant is about 13ppm.

It's known that the presence of nitrogen in zircaloy-2, greater than 40ppm decreases the corrosion resistance of the alloy through possible formation of zirconium nitride. As there is always a protective oxide layer over the zircaloy surface, a nitrogen pick up to the extent of 40ppm from the coolant is expected to take a very long time.[19]

10 MECHANISM OF AQUEOUS CORROSION

Zircaloy corrodes in water to form black adherent corrosion film of ZrO_2 at a rate which is time and temperature dependent. The corrosion rate curve shows a break called the (transition point). The pre and post transition corrosion rates are described by the equation:

$$\Delta c = kt^n \qquad (25)$$

Where: Δc: is the weight gain in mg/dm^2, k: proportionally constant to match for the dimensions, t: is the time, n: is the exponent.

The value of n at 360°C and 2700 Psi is around 0.35 for pre-transition and around 1 for post transition region. This variation in the exponent causing the cubic and linear dependence essentially arises from the differing mechanisms. Diffusion of oxygen anion O^{2-} through the oxide layer in the pre-transition region and cracking of the inner protective layer followed by rapid transport of oxidizing species to the metal surface in the post transition region are being thought of as probable mechanisms.

The electrical conductivity of the oxide layer in the pre transition region can be associated with the observed inflection in the corrosion rate curve. The transition point occurs early as the temperature is increased. Although post transition corrosion rates vary as a function of temperature, the pretransition corrosion rates do not.

11 OUT OF FLUX CORROSION

Out of flux corrosion tests were performed in water in static autoclaves at three temperatures: 240°, 280°, 315°C and in steam at 400° and 450°C. [20]

Zircaloy-2 and zircaloy-4 when exposed to water with a temperature range of 240°~315° C formed a stable protective oxide film. At least during exposure lasting as long as 600 days no transition was observed. The weight gained after 600 days ranged from about 8~10mg/dm^2. At 240°C to about 30~33 mg/dm^2 at 315°C.

The zirconium-2.5 Nb alloy showed 3 to 4 times higher corrosion rate.A transition point was observed after about 80 days at 315°C and 150 days at 280°C post transition values of the exponent "n" were close to 1.

No transition was observed in Ozhennite 0.5, zirconium 1Nb alloys during an exposure time in water exceeding 1 year. Corrosion rate for these alloys were somewhat higher (30~40 percent) than the corrosion rates obtained for zircalloys at the same temperature. The Zr-1Cr-0.1Fe alloy behaved like the 2.5Nb alloy. The highest corrosion rates were obtained by the Zr-1Cu-0.4Fe alloy specially in as received condition. Heat treatments such as β quenching or β quenching followed by α annealing improved the corrosion behavior of the alloy in water, but the corrosion rates were always very high. White loose oxide appeared after exposure of less than 1 year at 315°C.

Zircaloy-2 showed a transition of the corrosion rate after about 40~50 days at 400°C and 15~25 days at 450°C, the post transition corrosion rates were 0.9 mg/dm^2 day at 400°C and 4.5 mg/dm^2 day at 450°C. The alloy containing 1Sn-1Nb-0.5Fe showed lower corrosion rates than zircaloy-2 at 400°C.

At 450°C a substantial improvement was observed for Ozhennite 0.5 and 2.5Nb alloy, which showed a weight gain approximately half that of zircaloy-2 after 1 year`s exposure. Low corrosion rates were obtained at these temperatures for the 1Cr-0.15Fe alloy, transition was observed after 65 and 35 days at 400° and 450°C respectively independently of heat treatments.

The lowest corrosion rates were obtained with the 1Cu-0.4Fe alloy, after exposure of more than 1 year at 450°C.No transition has occurred, and no white oxide has been observed, in fact after one year`s exposure at 450°C the weight gain was about 200 mg/dm^2.

At 450° C the zirconium 1Cu-0.4Fe alloy presented the lowest pick up of hydrogen: 250ppm of H_2 after a one year exposure. The highest pickups were observed inzircalloy-2 and zircalloy-4 with hydrogen concentrations ranging from 550ppm.

12 IN FLUX CORROSION EXPERIMENTS

The corrosion behavior of some of these alloys was determined in the halden boiling water reactor (HBWR), two experiments were performed, in the first, the coupons were exposed directly to the boiling heavy water reactor at 240°±2 C. The chemistry of the cooling water was typical for a BWR with an oxygen content of 0.03 ppm.

Three sets of identical speciments were exposed for 75200 and 450 full power days respectively. The speciments irradiated for the longest period received a neutron flux of about $7x10^{23}$ n/m² (E>1meV).

In the second experiment the specimens were tested in a pressurized heavy water in pile loop at approximately 275° and 240°C (15Mpa). It was a closed circuit system with sub-cooled boiling water without any control of radiolysis gasses. The corrosion results were typical for reduced conditions, with low weight gain apparently led to an overpressure of deuterium.[21]

Two sets of specimens were irradiated for about 180 full power days ,and received a neutron flow of about 3x1023 n/m² (E>1meV). The alloys were separated in two groups when tested in primary water at 240 °C. The first group included zircalloy-2 ,Zr-2.5Nb and Zr-1Nb-Sn0.5Fe,which all had a corrosion rate of around 0.1mg/dm² /day after 450 full power days.

The second group of alloys, including ozhennite-0.5, Zr-1Cr0.15Fe, and Zr-1Cu-0.4 Fe alloys.

When compared with out of pile tests, the irradiation enhancement was about seven for the first group of alloys and much higher. For the second group, these observations are in good agreement with previous results for the different alloys tested in the same reactor.

The Zr-1Cr-0.5Fe alloy had the highest weight gain at 275°C ,being about twice that under gone by zircaloy-2 ,the Zr-1Sn-1Nb-0.5Fe and the Zr2.5Nb alloy Ozhennite-0.5 had the lowest weight gain of the tested alloys, the result were comparable to results obtained in out of flux environments.

This is most probably a result of the reducing conditions rather than slightly lower neutron flux compared to the conditions in the reactor tank.

13 NODULARCORROSION

Nodular corrosion is a type of localized oxidation appearing on the zircaloys under boiling water reactor conditions (i.e. high oxygen), the nodules are typically 0.5~1 mm wide. They can spread and coalesce to cover rather large areas. The attack can be up to 150~200 microns deep.

It has been demonstrated that zirconium alloys also can suffer a nodular type of attack in steam environments at high temperature between 500° and 550°C.

In such tests, niobium containing alloys have remained free of nodules while the tin containing alloys have suffered nodular corrosion. The tests were performed in small inconel autoclaves for 6~8 hours at 500°C and 15 Mpa. The Zr-1Np-1Sn-0.5Fe alloy was tested together with zircaloy-2. The Zr - 2.5Nb alloy was included in a few test runs to ensure that the previously observed immunity of this alloy also applied in the case of these tests.[22]

It is obvious, however, that zircaloy-2 is prone to this type of attack, as models occurred in 4 out of 5 runs for one batch of zircalloy and 3 out of 4 runs for another batch. The Zr-1Nb-1Sn-0.5Fe alloy had no signs of nodular corrosion and relatively low weight gains in all five runs. The balance between Niobium and tin seems thus to be high enough to protect the alloy from this type of attack. Furthermore, it is worth noting that the addition of 0.5 percent Fe appears to be harmless in this respect.

14 COMBATING AGAINST CRUD FORMATION IN NUCLEAR POWER REACTOR

Radiation chemistry in aqueous systems is closely related to the problems such as corrosion of zircalloy, formation of insoluble corrosion product or crud, stress corrosion cracking of stainless steel in BWR and the radioactive waste management.[23]

It has been reported by Ishigure in a series of papers that gamma radiation enhances the release of iron crud from stainless steel and carbon steel in boiling water reactors and the crud($\alpha - Fe_2O_3$) formation mechanism was assumed to be as follows:

$Fe + 1/2\ O_2 + 2H^+ \leftrightharpoons Fe^{2+} + H_2O$ (26)
$2Fe^{2+} + 2H^+ + 1/2\ O_2 \leftrightharpoons 2Fe^{3+} + H_2O$ (27)
$Fe^2 + OH \leftrightharpoons Fe^{3+} + OH^-$ (28)
$3Fe^{3+} + 3H_2O \leftrightharpoons 3Fe(OH)_3 + 3H^+$ (29)
$2Fe(OH)_3 \leftrightharpoons Fe_2O_3 + 3H_2O$ (30)

The oxidation reaction of ferrous ion was assumed to be rate determining at the low dissolved oxygen level in order to explain the experimental results obtained by the authors in the above reaction mechanism , only a typical oxidation reaction is shown, though the actual oxidation reactions are more complicated, involving other chemical species.[24], [25]

It has been shown in some studies that organic alcohols, aldehydes, organic acids and phenol or 4- ethyle pyridine are capable of stabilizing the valence of Fe (II) in aqueous acidic systems with long gamma irradiation doses.

It could be therefore assumed that the crud formation process could be controlled by adding some organic or inorganic additives to the cooling water of the BWR power reactors.

As reveled from the data shown in figs 1, 2, 3, and 4 it is possible to suggest the use of phenol, acetaldehyde and organic alcohols for valance stabilization of Fe (II) ions in aqueous acidic system under gamma irradiation. By so doing crud formation in BWR systems could probably be suppressed.

This in turn will have a good impact on the reliability of the reactor systems containing light water as a cooling material in BWR.[26],[27],[28]

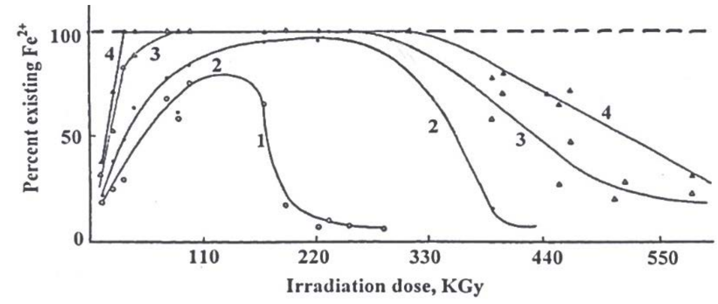

Fig.1.Percent existing Fe^{2+}in γ- irradiated 10^{-3}M Fe^{2+} solution (0.08 N

H_2SO_4) containing different concentrations of phenol: curve(1) 3.2x 10^{-4}M,curve(2) 9.6x 10^{-4}M, curve(3) 16.06x 10^{-4}M, curve(4) 32.06x 10^{-4}M,and (----) 100% protection line, (___) Actual protection line.

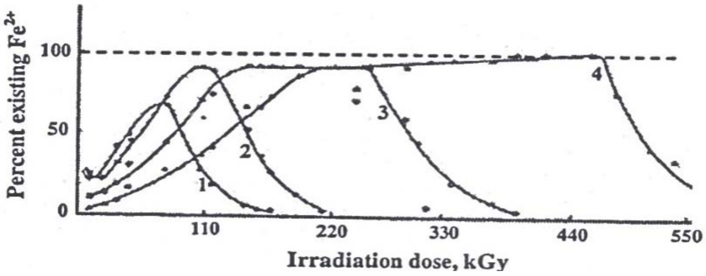

Fig.2.Percent existing Fe^{2+} in ɣ- irradiated 10^{-3}M Fe^{2+} solution (0.08 N H_2SO_4) containing Acetaldehyde at various concentrations: curve(1) 1.6 x 10^{-3}M, curve(2) 3.2 x 10^{-3}M, curve(3) 8.0 x 10^{-3}M, curve(4) 16.0 x 10^{-3}M, and (----) 100% protection line, (___) Actual protection line.

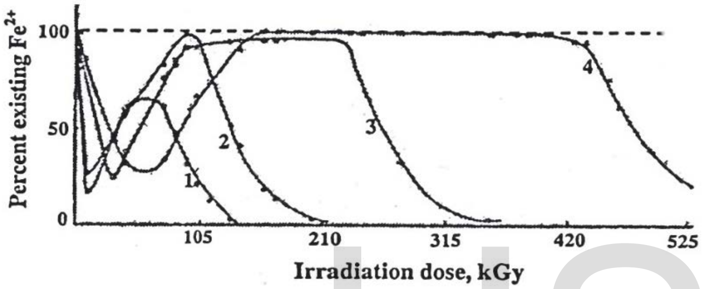

Fig.3.Percent existing Fe^{2+} in ɣ- irradiated 10^{-3}M Fe^{2+} solution (0.08 N H_2SO_4) containing propionic acid at various concentrations: curve(1) 1.6 x 10^{-3}M, curve(2) 3.2 x 10^{-3}M, curve(3) 8.0 x 10^{-3}M, curve(4) 16.0 x 10^{-3}M, and (----) 100% protection line, (___) Actual protection line.

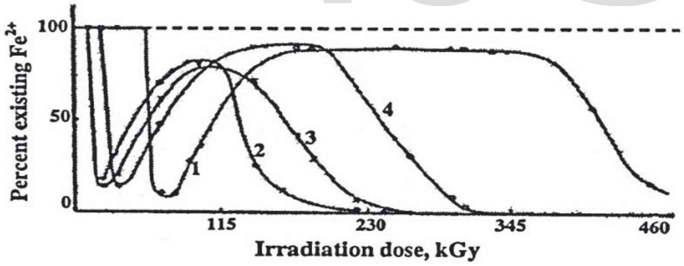

Fig.4.Percent existing Fe^{2+} in ɣ- irradiated 10^{-3}M Fe^{2+} solution (0.08 N H_2SO_4) containing ethanol at various concentrations: curve (1) 3.2 x 10^{-3}M, curve(2) 4.8 x 10^{-3}M, curve(3) 8.0 x 10^{-3}M, curve(4) 14.0 x 10^{-3}M, and (----) 100% protection line, (___) Actual protection line.

15 CONCLUSION

Nuclear power reactors are an important element in the future of electric energy production policy.

In the present study the different types and component materials of nuclear power reactors had been studied. Since water is the dominant cooling element in the fission energy removal systems, its interaction with different components of the metallic reactor systems e.g. pipes, pressure vessels, pumps, etc. has been studied in details with special emphasis on the behavior of stainless steel structures and zircaloy cladding which represents an important trend in this study.

One of the sensitive problems in nuclear power reactors in service is crud formation which interferes with the safe and regular work of the reactors.

It has been suggested that by adding, some organic chemicals like organic alcohols or acids to reactor cooling waters, Fe(II) which is formed in the reactor irradiation field could be stabilized which suppresses the formation of crud particularly in BWRs.

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