

NUCLEAR REACTOR MATERIALS AND CHEMISTRY

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Contents

1. Introduction - Reactor Types
 2. Boiling Water Reactors (BWRs)
 - 2.1. General Description
 - 2.2. Materials and Chemistry Considerations
 3. Pressurized Water Reactors (PWRs)
 - 3.1. General Description
 - 3.2. Materials and Chemistry Considerations
 4. CANDU Reactors
 - 4.1. General Description
 - 4.2. Materials and Chemistry Considerations
 5. Conclusion
- Glossary
Bibliography
Biographical Sketch

Summary

The water-cooled reactors BWRs, PWRs and CANDUs are widespread commercial nuclear generators of electricity. In the direct-cycle BWRs, the coolant boils in the core to produce steam for the turbine. Except for the zirconium alloy of the fuel assemblies, austenitic stainless steel is the major material in the reactor circuits. To minimize its degradation, normal water chemistry control entails maintaining high purity with low conductivity. Increasingly, hydrogen gas is being added to BWR coolant to counteract radiolysis and reduce further the possibility of localized corrosion. Hydrogen addition can be optimized by treating the circuits with noble metals such as platinum. To improve resistance to general corrosion and reduce activity transport, the coolant can be dosed with zinc.

The indirect-cycle PWRs also have austenitic materials as well as zirconium alloys in the primary circuit - stainless steel in the reactor and piping and nickel alloy in the steam generators. Localized and general corrosion and activity transport are reduced by adding hydrogen to the coolant and maintaining minimum alkalinity levels with lithium as boron concentrations vary. Zinc additions may provide further improvements. Secondary coolant chemistry is controlled with an oxygen scavenger and volatile bases to minimize corrosion around the steam circuit and material transport into the steam generator.

The indirect-cycle CANDUs have in-core components of zirconium alloy and steam

generators of nickel alloy; the extensive primary circuit piping is of carbon steel. Hydrogen and lithium are added to the primary coolant heavy water to maintain constant reducing conditions and alkalinity. This minimizes localized corrosion and fuel deposits but must be optimized to control general corrosion of reactor outlet piping. The low-temperature moderator circuit is of zirconium alloy, austenitic stainless steel and nickel alloy. The moderator heavy water is continuously purified and has a maximum alkalinity to ensure that soluble poisons remain in solution when injected. The secondary coolant system is similar to that of the PWRs.

1. Introduction – Reactor Types

As described elsewhere in this theme (*Nuclear Reactor Theory*, for example), nuclear power reactors derive their energy from the fissioning of an actinide-based fuel, in which a fissile isotope of an actinide element - such as U-235 occurring naturally in uranium - captures neutrons and fissions into (generally) two elements of lower mass (fission products), releasing energy and more neutrons to propagate the chain reaction. The fissioning occurs in an assemblage of fuel in the reactor core, which is designed to remove the fission energy as heat and is configured to control the nuclear reactions by optimizing the number of neutrons generated with neutron-absorbing devices such as control rods.

Power reactor systems operate with steam/water as the working fluid, in other words, the nuclear heat converts water to steam to operate a turbine-generator in a conventional thermal cycle. If the steam is raised by boiling the working-fluid water directly in the core, the system is called *direct cycle*; if an intermediate fluid transfers heat from the core to raise steam in separate heat exchangers or steam generators, the system is called *indirect cycle*. Some commercial, indirect-cycle power reactors are gas-cooled systems, such as the Magnox and Advanced Gas-cooled Reactor (AGR), both based on carbon-dioxide coolant, that are operating in Britain. Also, several experimental and prototype reactors have been constructed to operate with other intermediate fluids, such as helium (High-Temperature Gas-cooled Reactor, HTGR), liquid sodium or sodium-potassium alloy (Liquid-Metal-cooled Fast-Breeder Reactor, LMFBR) or molten salts. By far the majority of commercial reactors, however, are water-cooled. They are the ones described in this Article.

2. Boiling Water Reactor (BWRs)

2.1. General Description

The core of the direct-cycle Boiling Water Reactor (BWR) is contained within a pressure vessel as pictured diagrammatically in Figure 1. For a typical BWR of 1250 MW(e) capacity the vessel is about 22 m high and 6.4 m diameter and the core assemblage occupies about 3.8 m of the height in the centre. The space immediately above the core contains the standpipes and cyclone-type separators that separate steam from the steam-water mixture leaving the top of the core. Above these is an arrangement of plates and baffles that dry the steam to a moisture content of about 0.4 percent before it leaves the reactor vessel through the outlet nozzles. The separating and drying equipment must be lifted out to give access to the core when the reactor is shut down and the vessel head unbolted and removed for periodic refueling.

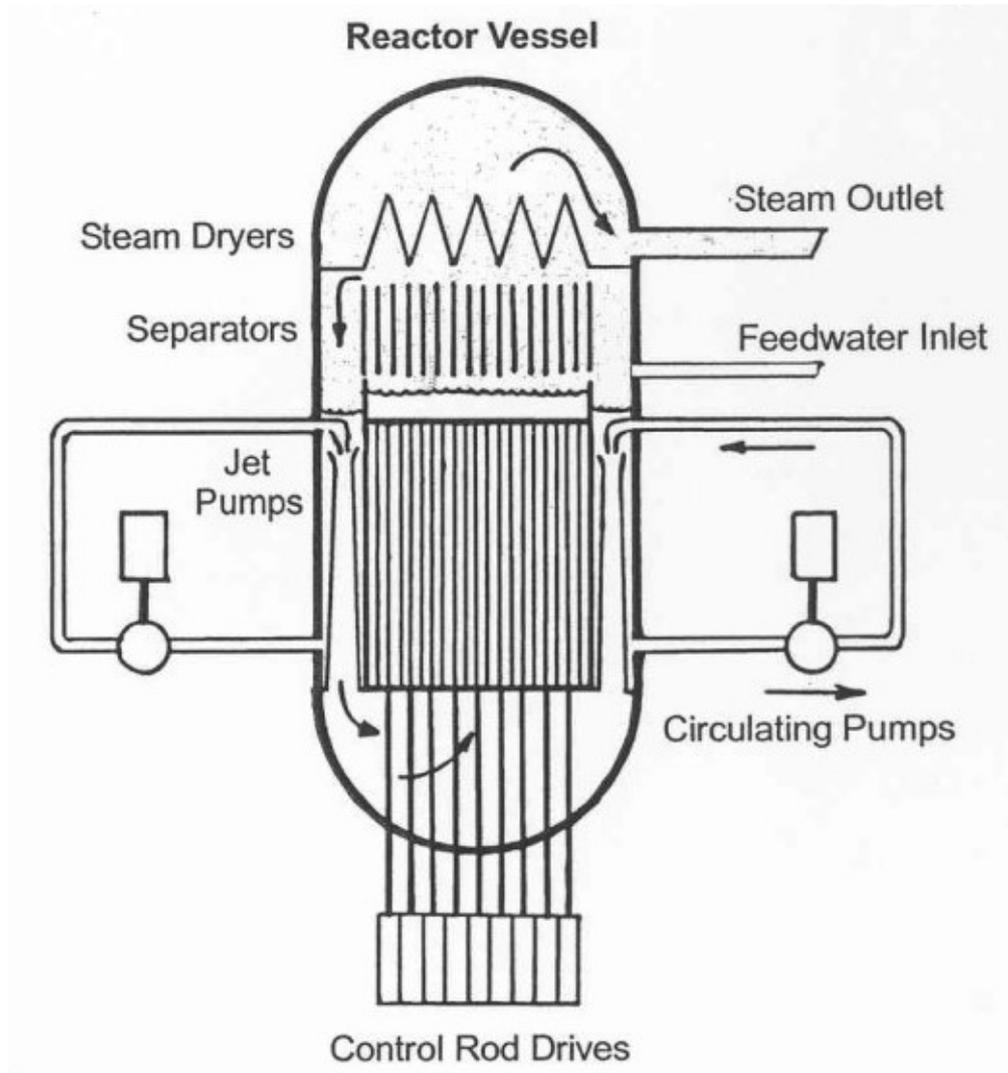


Figure 1: BWR core and pressure vessel

The water separated from the steam is channeled outwards from the separators and dryers towards the wall of the vessel and flows down the outside of a shroud that leads to the annulus around the core. It is augmented by feedwater that enters the vessel through the inlet nozzles. The downwards flow within the core shroud is boosted by a ring of twenty jet pumps driven by two external recirculating circuits with variable speed centrifugal pumps. About one third of the total reactor recirculating water is pumped through the external circuits. The jet pumps discharge towards the bottom of the vessel from where the water passes upwards through the vertical fuel rod assemblies and boils within the core.

The control-rod mechanisms occupy much of the vessel space below the core. Rod insertion from the bottom avoids the complex array of steam-separating and space-drying equipment at the top of the vessel and ensures better reactor control since the voidage due to steam bubbles is lower in the bottom half of the core and the neutron flux tends to peak there.

On leaving the reactor, the slightly moist steam at about 290°C enters the conventional

turbine-generator cycle as shown by the simplified circuit diagram in Figure 2. It expands through the high pressure (HP) turbine, then passes to the bank of low pressure (LP) turbines after having moisture removed and being reheated in the moisture separator reheater (MSR). This is a large vessel with an arrangement of baffles or cyclones and a tubed heat exchanger. Entrained moisture is removed from the HP turbine exhaust steam by the cyclones or baffles and the dried steam is then superheated by the tube bundle. The MSR is heated on the tube side with steam bled from the entrance to and sometimes part-way along the expansion stage of the HP turbine. After exhausting from the LP turbines the steam is condensed in the surface condenser.

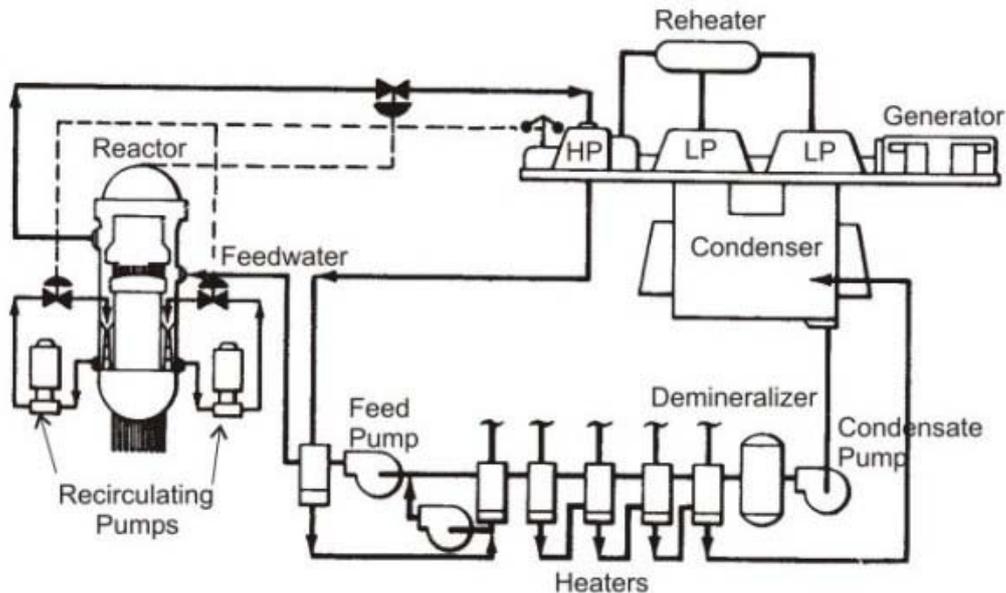


Figure 2: Simplified BWR circuit diagram

The condensate extraction pumps take condensate from the condenser hot well, pump it through the ion-exchange demineralizer and then along the feedtrain where it is heated first in the LP feedwater heaters and finally in the HP heater after being boosted in pressure by the feed pump. The feedwater enters the reactor at about 200°C. The feedwater heaters are tube-in-shell heat exchangers fed on the shell side with steam and moisture bled from the HP and LP turbines and with the drains from the MSR. In the scheme shown in Figure 2, the heater drains from the first two LP heaters cascade back to the condenser hot well while those from further downstream cascade back to the third heater from where they are pumped into the feedwater flow.

2.2. Materials and Chemistry Considerations

The fuel assemblies are 7 x 7 or 8 x 8 arrays of fuel rods and there are typically 548 of them running the full height of the core - 3.8 m. Each rod is a 15 mm diameter sheath of Zircaloy-2 containing a stack of cylindrical pellets of UO₂ enriched in the fissile isotope U-235. The standard enrichment is in the range of 2-3½ percent (whereas natural uranium contains 0.7 percent) but fuel rods in the corners or along the edges of the arrays may have other enrichments to shape the neutron flux. In addition, some rods may be fueled with

UO₂ mixed with gadolinium oxide, for gadolinium is an effective burnable poison in that it absorbs neutrons but in time becomes depleted in the absorbing isotopes. Such gadolinia rods can therefore be used to compensate for excess reactivity when new fuel has been loaded. About one-third of the core inventory is replaced with fresh fuel at each refueling outage.

Each fuel array is contained within a square-section channel of Zircaloy-4 sheet to prevent cross-flow of the two-phase coolant rising through the core. Such assemblies are mounted in sets of four in a square pitch between the support grids at the top and bottom of the core. The four blades of a cruciform-section control rod occupy the interstices between the four fuel assemblies and are attached to the positioning mechanisms below the core. The control rod blades contain boron carbide, an efficient neutron absorber, sheathed in tubes of stainless steel. Originally, control rod blades and core ancillary equipment such as support grids were constructed of austenitic alloys such as stainless steel or nickel alloy. However, to avoid localized corrosion in the high radiation fields in the core and the production and release of radioactive corrosion products such as Co-60, other alloys such as those based on zirconium are preferred for components in contact with the coolant.

Although zirconium is quite a reactive metal (for example, it is pyrophoric and must be machined and worked in air with care) it passivates readily by forming a thin, adherent film of oxide. Thus, when zirconium and its alloys are exposed to pure, high-temperature water or steam, the following corrosion reaction occurs:



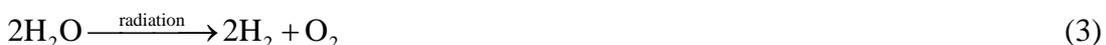
Depending upon the conditions and the alloy, a proportion of the hydrogen generated according to Eq. (1) is absorbed by the metal and, as mentioned in *Power Plant Materials*, may precipitate as hydride (Zr₂H₃) and weaken the alloy structure under some circumstances.

The kinetics of corrosion of zirconium and the Zircalloys in high-temperature water or steam generally involve an initial period of several months to a year - depending on the temperature - during which the rate falls according to an approximately cubic expression:

$$\Delta W = K t^{0.3} \quad (2)$$

where ΔW is the weight gain of the metal at time t and K is a constant. Following a transition, when the corrosion rate increases sharply, a constant rate is achieved. The zirconium-niobium alloys display no such transition (at least, over the decades of exposure experienced to date).

In a BWR, although the coolant chemistry is normally designated to be pure water with a very low conductivity, the intense radiation field in the core causes some decomposition of the water molecules by radiolysis to produce dissolved gases:



The reaction is not instantaneous, and several unstable radicals and molecules such as $\text{OH}\cdot$, $\text{H}\cdot$, HO_2 and H_2O_2 are formed as transient species. These can be quite corrosive - more so than the ultimate mixture of products hydrogen and oxygen in Eq. (3) - and may live long enough to react with surfaces in the core or even to be carried out of the core by the coolant flow. Hydrogen peroxide, H_2O_2 , for example, can exist for a few seconds in a BWR environment and so finds its way partly around the coolant circuits.

It should be noted that in a closed system Reaction (3) will proceed until a certain concentration of hydrogen and oxygen is attained, when the recombination back reaction balances the decomposition and results in a steady state. In fact, by the addition of an excess of hydrogen to the system (as is practised in the indirect cycle PWRs and CANDU reactors, for example) the back reaction is made predominant and the radiolysis is effectively stifled. The BWR, however, is an open system with considerable in-core boiling that tends to strip dissolved gases to the vapor phase where radiolysis and recombination reactions are much less efficient. Normal water chemistry (NWC) in BWRs, then, results in an oxygen concentration of about $200 \mu\text{g kg}^{-1}$ and a stoichiometric hydrogen concentration of about $25 \mu\text{g kg}^{-1}$ in the coolant in the core circuits.

Such oxygen levels adversely affect circuit materials. For example, the corrosion rate of Zircaloy in high-temperature water is affected little by dissolved oxygen in the absence of radiation but is greatly increased by oxygen and radiation together. The fuel rod sheaths in BWRs therefore develop quite thick ZrO_2 films and may display nodular corrosion in which oxide grows in thick patches. Also, austenitic alloys such as stainless steels or Inconels can crack by stress corrosion cracking (SCC) when the electrochemical corrosion potential (ECP) is high, as in oxygenated environments, particularly if they are in a sensitized condition. High radiation fields around core components can exacerbate cracking in the phenomenon of irradiation-assisted stress corrosion cracking (IASCC). Since the BWR pressure vessel is made of 150 mm thick high-strength steel overlaid with austenitic stainless steel and is connected to the recirculation piping and other circuits made of stainless steel, SCC can be a problem. In fact, several reactors have replaced their recirculation piping because of oxygen-induced SCC.

One method of counteracting the radiolytic production of oxygen in BWRs is to add hydrogen gas to the coolant. At the level of a few tenths to one or two mg kg^{-1} in the feedwater (depending upon the detailed design of the reactor), enough hydrogen survives the in-core gas-stripping process and stays in the water phase long enough to lower the ECP and suppress oxygen to non-aggressive levels. Such hydrogen water chemistry (HWC) is becoming common practice in many BWRs and in some instances has been supplemented with the addition of soluble salts of noble metals such as platinum and rhodium. The addition to the coolant of the noble metal during low-temperature shut-down conditions deposits a microscopically thin layer on the surfaces of reactor circuit components and promotes the recombination reactions during operation so that oxygen levels are reduced with smaller amounts of added hydrogen.

The oxygen and hydrogen levels in the coolant and the resulting oxidizing/reducing properties have an impact on the radiation levels around a BWR during operation. One way that this occurs involves the in-core transmutation of oxygen atoms in the coolant water molecules by neutrons. Thus, the nucleus of an oxygen atom can capture a high-

energy neutron to produce nitrogen:



The isotope of nitrogen so produced, N-16, is radioactive. It emits energetic β particles and γ rays and has a half-life of 7.2 s. Under NWC in BWRs, the oxidizing conditions leave the N-16 as a molecule or ion like the nitrate ion that prefers the water phase to the steam phase. Under HWC conditions, however, the N-16 forms a reduced species such as ammonia that is volatile and travels with the steam to the turbine, giving rise to radiation fields that can hamper access to the steam-cycle components for maintenance, adjustments etc. during operation (the short half-life means that the radiation has effectively disappeared a few minutes after being formed, so that N-16 is non-existent during reactor shut-downs). The use of lower hydrogen levels with noble metal additions can optimize the oxidizing/reducing properties of the coolant to control oxygen and at the same time minimize N-16 carry-over.

Although dissolved oxygen in the reactor coolant can be damaging to core circuit materials, in the feedwater it has the beneficial effect of promoting more protective corrosion product films on feedtrain components made of steel. Thus, copper alloys are nowadays avoided for the tube bundles of feedwater heaters because copper corrosion products carried into the reactor can provoke galvanic corrosion of components along the way and can seriously impair boiling heat transfer by depositing on fuel rods - perhaps to the extent of provoking fuel failure by overheating. Carbon steel and stainless steel are therefore used instead of copper alloys. The oxide films on these components and on the steel piping in high-temperature water tend to contain a significant proportion of ferric oxide (e.g., hematite or Fe_2O_3) along with ferrous-ferric oxide (i.e., magnetite or Fe_3O_4) when oxygen is present. The more protective nature of the higher oxides of iron allows fewer corrosion products to be released into the feedwater and the burden of corrosion products in the reactor coolant is consequently less. Deposits of particulate iron oxide, known as *crud*, on the fuel are thinner and the subsequent generation of long-lived radioactivity, such as that due to Co-60, by the transmutation of impurity atoms such as those of cobalt in the crud is lessened.

For this reason, some BWRs add oxygen at concentrations in the tens of $\mu\text{g kg}^{-1}$ range to the feedwater (at such low levels, feedwater oxygen has little effect on the oxidizing nature of the reactor recirculating coolant). If the corrosion product burden is not controlled and fuel deposits are allowed to become thick, the distribution around the coolant circuit of radioactive species such as Co-60 that are released from the core gives rise to radiation fields around components that can seriously impair shut-down maintenance activities. To some extent an ion-exchange clean-up system that is located on a by-pass line off the recirculation loops controls levels of impurities and radioactivity in the reactor coolant. Accordingly, some fission products that may be released from faulty fuel along with some of the radioactive corrosion products are removed. The clean-up capacity is limited, however, and cannot compete with radioactivity production from a core with heavy fuel deposits.

In several BWRs the production and distribution of radioactive corrosion products around

the coolant circuits are controlled by adding zinc to the reactor water. At coolant concentrations up to about $20 \mu\text{g kg}^{-1}$, zinc ions are incorporated into the oxide films on alloys such as steels to make them more protective. On stainless steels, for example, the promotion of zinc chromite, ZrCr_2O_4 , in the inner protective layer rather than the usual iron chromite, FeCr_2O_4 , leads to a much thinner oxide generally and blocks the incorporation of radioactive ions such as ${}_{27}^{60}\text{Co}^{2+}$.

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Biographical Sketch

Derek Lister, B.Sc. Tech., M.Sc. Tech., Ph.D., M.I.Chem.E., C.Eng., F.C.I.C., was born in Nelson Lancashire, England in 1939. He was educated at the local secondary technical school, the University of Manchester and the University of Leicester, obtaining his bachelor's and master's degrees in chemical engineering and his Ph.D. in physical chemistry. He spent three years with the Atomic Power Division of English Electric Co., developing Magnox and AGR nuclear fuel, and four years as a Research Fellow at Leicester University, studying crystal growth and electron spin resonance, before joining Atomic Energy of Canada Ltd. at the Chalk River Nuclear Laboratories in 1969.

After a short period in CANDU nuclear fuel development he became involved in research into reactor chemistry. This was concerned mainly with chemistry control and corrosion in CANDU reactors, though contract research was done for the U.S. nuclear industry as well. He became Senior Scientist and, in 1992, when Manager of the System Chemistry and Corrosion Branch, he was awarded the NB Power/AECL/NSERC Industrial Research Chair in Nuclear Engineering at the University of New Brunswick and moved to Fredericton.

At UNB, he contributes to the Option in Nuclear and Power Plant Engineering in the Chemical Engineering Department and to other undergraduate courses. He has designed and constructed a research laboratory containing high-pressure, high-temperature equipment for studying reactor and power plant chemistry and corrosion and carries out research for the Canadian and overseas nuclear industries. He has published extensively in the fields of reactor chemistry and corrosion and heat exchanger fouling. He is now Chair of the Chemical Engineering Department as well as holder of the research chair and holds technical advisory positions on several national and international bodies. He enjoys skiing, tennis, drawing and painting and French and English literature.

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