Reactor Boiler and Auxiliaries - Course 133

MODERATOR PROPERTIES AND COMPARISON

The only substances which could be considered as possible moderators are light water (H_2O), heavy water (D_2O), carbon (as graphite), beryllium, beryllium oxide, beryllium carbide, and hydrogen compounds such as the hydrocarbons or zirconium hydride. The properties of these materials will now be considered and their suitabilities as moderators discussed.

Carbon (Graphite)

The first reactor built used carbon in the form of graphite, as the moderator. It has been used extensively since as both moderator and reflector, particularly in the United Kingdom. Graphite occurs in considerable quantity in nature but the impurities contained in natural graphite affect neutron economy to such an extent that it is unsuitable as a moderator. Reactor-grade graphite is, therefore, produced artificially by mixing petroleum coke with a filler (coal-tar pitch), extruding the mixture into bars and baking the bars in gas or electric furnaces at temperatures up to 1500°C. This carbonizes the pitch and sets the binder and produces what is known as industrial carbon. The bulk density is then increased by impregnating with pitch under vacuum and re-baking. This is followed by a reheating treatment in an electric furnace at 2700°C to graphitize the product. Careful elimination of all neutron absorbers, in the raw material, is required if reactor-grade graphite is required. Even so the presence of such materials as boron is still likely and the extruded pieces have to be graded according to impurity content. The highest quality graphite is then used in the centre of the reactor and the lowest quality graphite on the outside.

The density of artificially produced graphite is much lower than that of natural graphite, its specific gravity being 1.6 compared with a theoretically attainable value of 2.25. This increases the volume of graphite moderator required. Table 1 below lists some important properties of artificial reactor-grade graphite at ordinary temperatures. These are typical values only and can vary considerably depending on the method of production and the raw materials used.

TABLE 1

Property	Parallel to extrusion axis	Perpendicular to extrusion axis
Coefficient of thermal expansion.	0.7×10^{-6} per^{o}F	1.5×10^{-6} per^{o}F
Thermal conductivity (Btu/hr-ft-^{o}F)	1.4×10^{4}	1.1×10^{4}
Tensile strength	2000 psi	700 psi
Compressive strength	6000 psi	6000 psi
Sublimation temperature	6600 ^{o}F	

The advantages of using graphite as a moderator are:-

(1) Its moderating ratio is second only to heavy water and it can, therefore, be used as a moderator in a heterogeneous system using natural uranium metal as fuel. However the moderating ratio is not large enough to enable it to be used with oxide or carbide fuel.

(2) Graphite, of reactor grade,is readily available at reasonable cost.

(3) It has good mechanical properties and can be used as a reactor structural material without having to be contained. The fuel channels themselves can be holes in the graphite structure or can be supported by the graphite. Its use as a structural material is enhanced by the fact that it is easily machined to close tolerances.

(4) It has a high thermal conductivity so that heat produced in the graphite, by radiation absorption, is easily dissipated and removed.

(5) Graphite has excellent resistance to thermal shock.

(6) It has excellent high-temperature properties, its tensile strength, for instance, increasing up to 4500°F. This factor combined with its thermal shock resistance, makes it potentially valuable in a high temperature reactor.

(7) Little oxidation occurs below 750°F or so and no chemical reaction occurs at such temperatures between graphite and carbon dioxide, used as a heat transport fluid.

The use of graphite as a moderator has the following disadvantages:

(1) It has a relatively long slowing down length so that fuel channels must be fairly widely separated for effective moderation. This factor combined with its relatively small moderating ratio results in a large size core compared with cores using light or heavy water as moderator. The United Kingdom reactors have cores 40 to 50 ft in diameter and up to 25 ft in height. Such massive graphite structures pose problems of support and containment and the large steel pressure vessel required sets limits on the possible vessel thickness and, consequently, on heat transport fluid pressure. The replacement of steel by prestressed concrete has, to some extent, eliminated these problems.

(2) The small moderating ratio precludes the use of uranium dioxide fuel unless the fuel is enriched. Severe limitations are also placed on the materials that can be used in the core for such things as fuel sheaths. These factors result in moderate heat transport temperatures and low fuel burnups.

(3) The coefficient of thermal expansion of graphite parallel to the extrusion axis differs from that perpendicular to it. Care must therefore be exercised in allowing for this differential expansion when the graphite blocks are assembled.

(4) There is not decrease in strength of graphite under irradiation. However, dimensional changes occur. These dimensional changes also differ parallel to and perpendicular to the extrusion axis. The graphite expands perpendicular to this axis but it may expand or contract, in a direction parallel to the axis, depending on the irradiation exposure. These effects must be allowed for in the design of the reactor to prevent distortion of the fuel channels during operation.

The thermal conductivity decreases under irradiation and can become a factor of 40 or more lower than it was before reactor startup. This could have a marked effect on heat dissipation and removal.

Irradiation of graphite causes an accumulation of stored energy in the graphite lattice, which is sometimes called Wigner energy. If this was allowed to go unchecked, it would continue to accumulate until a very unstable condition is reached. At this point all the energy is suddenly released causing the graphite temperature to rise to perhaps 1800°F or more.

These radiation effects are less marked at temperatures above 660°F or so. However, it is the practice in graphite moderated reactors to operate at fairly low temperatures. This permits the temperature to be raised, at predetermined intervals, to anneal the radiation damage and release the stored energy. The temperature rise resulting from this energy release is controlled by adjusting the heat transport flow. The Windscale reactor was seriously damaged by local overheating which occurred during such a periodic energy release.

(5) Even carbon dioxide reacts with graphite at higher temperatures which again tends to limit the heat transport temperature. The addition of methane to the carbon dioxide helps to inhibit the reaction and raise the temperature limitation.

Graphite is also attacked by liquid metals so that unclad graphite cannot be used with liquid metal heat transport fluids.

Beryllium

Beryllium is the only light metal with a high melting point. The specific gravity varies from 1.81 to 1.86, the higher valves being due to the presence of beryllium oxide, which has a specific gravity of 3.0. The mineral beryl is not found in large deposits and its occurrence is erratic and difficult to predict. Beryllium billets or slabs can be made by melting the metal in a beryllium oxide crucible and pouring into a graphite mold. However, cracks develop very easily and the cast material is not easily fabricated.

It is difficult to machine without causing surface damage. Hence the principle form of beryllium suitable for commercial fabrication is that made by vacuum pressing the hot powder at around 2000°F. The resulting material can be machined quite easily and this is, frequently, all the treatment it receives. However it can be fabricated by extruding, rolling or forging at about 2000°F.

Some of the properties of beryllium, produced by hot-pressing, are listed in Table 2 below.

TABLE 2

Tensile strength	45,000 psi
Melting point	2,340 °F
Coeff. of expansion	9.5×10^{-6} per °F
Thermal conductivity	2.85×10^{4} Btu/hr-ft-°F)

Beryllium has a slightly smaller moderating ratio than carbon and, like graphite, it could only be used with natural uranium metal fuel. However, it has a much better slowing down power and a shorter slowing down length. It would therefore lend itself to the design of smaller reactors with slightly enriched fuel. It is particularly attractive as a moderator because it is a metal and it would appear particularly suitable as a moderator in a space vehicle power unit.

It does not suffer serious attack in air below 1100°F but could not be recommended, in air, above this temperature. The corrosion rate of pure beryllium in deaerated, deionized water at 600°F is relatively small and decreases with time due to the formation of a protective oxide film. It has good resistance to molten sodium in the absence of oxygen. In addition it has a high thermal conductivity.

The use of beryllium in reactor construction has been limited for the following reasons:-

(1) It is an expensive material.

(2) It is brittle and its ductility may be zero under certain conditions.

(3) It is extremely toxic and this complicates its fabrication procedures.

(4) Helium gas is formed in the material by the following reactions:-

$$_4Be^9 + {}_0n^1 = {}_2He^6 + {}_2He^4 \quad (\alpha)$$

$$_4Be^9 + {}_0n^1 = {}_4Be^8 + 2\,{}_0n^1$$

$$_4Be^8 \rightarrow 2\,{}_2He^4 \quad (2\alpha)$$

This gas may collect as bubbles and cause local swelling.

An alternative material to beryllium metal is beryllium oxide (BeO). Apart from its good moderating properties, beryllium oxide has the advantages of having a high melting point (4620°F), low vapour pressure in a dry atmosphere and excellent thermal shock resistance for a ceramic material. It also has a very high thermal conductivity for a ceramic (2.1×10^4 Btu/hr-ft-°F) and is stable and inert to most materials. Its tensile strength (15,000 psi) and its compressive strength (114,000 psi) at ordinary temperatures are far superior to graphite.

However, one reason why it has not been more widely employed is that, when hot, it vapourizes in moist air due to the formation of the hydroxide. Like beryllium metal it is toxic. Its strength and thermal conductivity decrease with increase in temperature. The change in thermal conductivity is so drastic that, at 1800°F, it is only one-tenth of the value quoted above. It has questionable resistance to thermal stresses. Unlike the metal, it is dimensionally unstable under irradiation, the dimensional changes noted being of the order of 1%.

Beryllium carbide (Be_2C) is another potential moderating material, having a specific gravity of 2.44. It is quite stable under irradiation. However, it is also toxic and is very reactive with water and water vapour even at ordinary temperatures. It also reacts with oxygen and nitrogen at elevated temperatures and it would, therefore, have to be clad to overcome this problem. It has poor resistance to thermal shock.

Light Water (H_2O)

Many reactors, currently in operation, use light water as the moderator. In most cases the water also serves as the heat transport fluid and even as shielding material. However, only its properties pertinent to its use as a moderator will be discussed here. The additional requirements of water as a heat transport fluid or as a shielding material are discussed elsewhere.

Light water is attractive as a moderator because of its low cost, its excellent slowing down power and its small slowing down length. However its moderating ratio is too low to permit it to be used with natural uranium fuel even in metal form. Some slight enrichment of the fuel is required. However, if enrichment facilities are available, the small slowing down length makes it possible to design a reactor of relatively small size. The fact that water can be used as both moderator and heat transport fluid may be considered an added advantage. A single fluid system only is then required and the fuel channels in the reactor need only be thin tubes required to guide the water over the fuel. This helps to decrease neutron capture in the core material. However, it also means that a pressure vessel concept has to be used with all its inherent disadvantages.

Water melts at 32°F and will not, therefore, solidify during reactor shutdown. It boils at 212°F and requires pressurizing at elevated temperatures if boiling is to be prevented. This is not a disadvantage if the moderator is separated from the heat transport fluid and, consequently kept at a low temperature. Water has a relatively poor thermal conductivity (0.32 Btu/hr-ft-°F) but resonable heat transfer rates can be obtained with water.

The water must be free from impurities since these not only capture neutrons but they also become radioactive as a result of neutron capture. This may result in high radiation fields near the moderator system and may also cause permanent contamination of the system. It is relatively easy to circulate water through filters and demineralizers to remove such impurities. However radioactive nuclei (O-19 and N-16) are still produced as a result of neutron capture in oxygen nuclei. This prevents access to the moderator system during reactor operation but, because of the short half-lives of these radioactive nuclei, access to the moderator system is possible shortly after reactor shutdown. Water treatment is also important to minimize corrosion and scale formation. Careful control of pH is required if aluminum or carbon steel is used in the moderator system, otherwise the choice of material would be limited to stainless steel or zirconium. Chemical or heat treatment of the system may also be required in order to form a protective oxide layer on the pipe surfaces and this is normally done during commissioning.

Water does not decompose at elevated temperature but it does however, decompose when irradiated according to the equation:-

$$H_2O = H + OH$$

The H and OH may recombine thus:-

$$H + OH = H_2O$$

in which case there is no net decomposition, or they may combine as follows:-

$$H + H = H_2$$

$$OH + OH = H_2O_2$$

The hydrogen peroxide can then decompose according to:-

$$H_2O_2 = H_2O + 1/2\ O_2$$

The overall result is the formation of hydrogen, oxygen and hydrogen peroxide. Dissolved impurities in the water increases the severity of the radiolytic damage.

There are several consequences of this radiolytic decomposition. The oxygen formed may dissolve in the water and cause increased corrosion. If the hydrogen concentration is allowed to increase, it could become an explosion hazard in the presence of oxygen. If the gases produced are allowed to accumulate, a steady state is eventually reached when the rate of recombination is equal to the rate of dissociation. Should the gas concentrations, at this point, be tolerable no further action is required. However, if the concentrations are excessive, recombination units must be provided to recombine the hydrogen and oxygen to form water.

Heavy Water (D_2O)

Heavy water has an exceptionally high moderating ratio and a long diffusion length. Its slowing down length is shorter than that of graphite and about twice that of light water. Therefore, the fuel channel separation with heavy water should be larger than with light water and smaller than with graphite. However, in D_2O moderated reactors, advantage is frequently taken of the low neutron capture in heavy water. The fuel channel separation is made larger than the minimum required for the neutron of average energy. This ensures that most of the neutrons become thermalized before entering the fuel and this increases the resonance escape probability (p). The reactor is then said to be overmoderated and the reactor pitch may then be equal to or greater than the pitch in a graphite moderated reactor. However, the size of the D_2O reactor is still considerably less than the graphite reactor. The main advantage of using heavy water as the moderator is that it enables natural uranium oxide fuel to be used in a reactor the size of which is still considerably smaller than the graphite moderated natural uranium reactor. The oxide fuel improves the fuel integrity and enables high fuel burnups to be achieved without enrichment.

Heavy water, as a moderator, has similar physical characteristics to light water. The same problems occur with radiolytic decomposition and it is even more important to ensure that the D_2O is free from impurities. The same corrosion problems can also occur. However, there are some factors involved which are peculiar to heavy water. These are:-

(1) The high cost of heavy water which increases the initial capital cost of the reactor.

(2) The limitation that is placed on core material in order to maintain neutron economy and to ensure that natural UO_2 fuel can be used and high burnups achieved. Core structural material must be aluminum, zirconium or their alloys.

(3) The necessity of keeping heavy water losses to a minimum. Since radiolytic decomposition involves a loss of heavy water, recombination units are required to recover it. The heavy water system should, wherever possible, be of welded construction. D_2O leak detection systems are required. Since leakage can not be entirely avoided, (e.g. valve stems, pump seals etc), heavy water collection systems are required to recover the water with a minimum of downgrading. Heavy water recovery systems are necessary in heavy water areas where leakages are possible and the ventilation systems for these areas are closed circulation systems with dryers to remove D_2O vapour from the air. All these requirements tend to increase the initial capital cost of the station.

(4) Tritium is produced in heavy water by neutron capture in deuterium:-

$$_1H^2 + {}_0n^1 = {}_1H^3 + \gamma$$

The tritium, (H^3 or $_1T^3$), has a 12 year half-life and, therefore, accumulates in the water. It is a beta particle emitter and is absorbed into body tissue like hydrogen, in the form of water (TDO). It is, therefore, a total body emitter, with a 12 day biological half-life and presents a serious health hazard.

Heavy water leakage must be kept to a minimum because of the tritium hazard as well as for economic reasons. Care must be taken to avoid leakage of tritiated vapour into accessible areas of the station. Handling of tritiated heavy water requires special techniques and precautions to avoid tritium intake into the body. Before entry can be allowed into areas containing heavy water vapour, the area must be purged, and the heavy water loss accepted, or special protective equipment must be worn to prevent tritium intake. Over a long period of time the tritium concentration may become prohibitive necessitating replacing the tritiated water.

(5) Heavy water freezes at 38.9°F and there is a possibility that the heavy water would freeze, during a reactor shutdown, in, say, a heat exchanger where it is cooled by river water or lake water in the winter.

Organic Materials

Organic compounds, such as the polephenyls have moderating properties very similar to light water. The moderating ratio of the terphenyls is 80 compared with 72 for H_2O, whereas the slowing down power is 0.73 compared with 1.53 for H_2O. Like water, they can be used in reactors of relatively small size, although fuel enrichment is required. The following table lists some of the physical properties of organic compounds.

TABLE 3

	Isopropyl Diphenyl	Diphenyl	Santowax R	Santowax O-M
Melting point (°F)	-40 to +28	157	140-293	100
Boiling point (°F)	552	491	700	650
Vapour pressure at 800°F (psia)	190	220	38	57
Specific gravity at 600°F	0.78	0.87	0.86	0.75
Specific heat at 600°F (Btu/lb-°F)	0.6	0.61	0.60	0.60
Thermal conductivity (Btu/hr-ft.-°F)	0.066	0.066	0.066	0.066

As may be seen, from this table, the santowaxes, which are mixtures of terphenyls, have high boiling points and low vapour pressures at temperatures above their boiling points. They would require very little pressurization up to 800°F. However this property really enhances their suitability as a heat transport fluid, unless they were used as a combined heat transport and moderator fluid in a pressure vessel type of reactor. In fact there seems little advantage in using organic liquids as moderators unless this type of arrangement is used, particularly as they have a fairly high melting point and could not, therefore, be cooled too much. Used in this way, they have the following additional advantages:-

(1) No chemical reactions between organics and fuel, fuel cladding or water.

(2) Negligible corrosion rates permitting the use of standard materials for fuel channels and cladding provided that they are suitable otherwise.

(3) Require only conventional "hot oil" pumps and circuit equipment.

(4) No radioactivity induced by neutron capture in the organic liquids themselves but only in impurities.

(5) Fair high temperature stability up to 800°F.

(6) They are fairly cheap (17 - 20¢ per lb).

Organic liquids do, on the other hand, have the following limitations:-

(1) Most are solid at room temperature and, so, trace-heating or preheating is required in the system.

(2) Organic compounds suffer radiation damage at all temperatures but the damage is greater at elevated temperatures. The effect of radiation is to produce gases, such as hydrogen, and cause polymerization of the molecules which results in the formation of tars or coke or varnish and cause increases in the viscosity. Continual purification, by distillation, is, therefore, required. The concentration of the higher polymers is kept at around 30%. This decreases the rate of radiolytic damage. A degassing system is also required.

From the point of view of radiation damage, the terphenyls are more stable than the diphenyls. Even so, it has been estimated that, for a 240 Mwt reactor with organic moderator and heat transport fluid, the rate of radiolytic damage would be more than 1 lb per Mw Hr at 675°F and that 260 lb/hr of organic make-up would be required to replace the damaged material.

(3) Organic liquids have much lower heat-transfer coefficients than such liquids as water and liquid sodium. The heat transfer properties can be improved by placing lateral fins on the fuel elements but this is really a heat transport problem.

Zirconium Hydride ($Zr\ H_2$)

This compound offers interesting and unusual moderator possibilities. It is prepared by heating zirconium metal in hydrogen gas at about 660°F. When fully hydrided, the hydrogen atom density in it approaches that in water. Consequently, the hydride has good moderating properties, particularly as the zirconium has a small neutron capture cross-section. Its moderating ratio is somewhat lower than light water but its slowing down power is second only to light water. The use of zirconium hydride as a moderator with enriched fuel would, therefore, result in a relatively small reactor.

The material is stable at temperatures below 1000°F. In powder form it has poor thermal conductivity and would require special cooling, in reactors operating at moderate or high power levels, to keep its temperature down. In the T R I G A (Training, Research, Isotope, General Atomics) reactor the hydride is incorporated with the uranium in the fuel elements. The thermal conductivity of the material then approaches that of zirconium metal.

ASSIGNMENT

1. (a) By considering any of the appropriate nuclear parameters compare the suitability of H_2O, D_2O, beryllium, graphite and terphenyls for use of moderators with natural uranium metal and natural uranium oxide.

   (b) Also compare the sizes and fuel channel separation that can be obtained with these moderating materials.

   (c) Why does the actual pitch in a D_2O moderated reactor frequently not correspond to what would be expected under 1b?

2. (a) Why, in the case of a liquid moderator, would corrosion be undesirable and how might it limit the choice of core structural material?

   (b) How is corrosion controlled in water moderated reactors?

3. (a) What advantages does a solid moderator have over a liquid moderator?

   (b) What additional physical properties must they have under these circumstances?

   (c) How do graphite, beryllium oxide and beryllium metal compare as far as these properties are concerned?

4. How does nuclear radiation affect the properties of

   (a) Graphite

   (b) Beryllium

   (c) Water

   (d) Organics

   and how are the effects of the property changes reduced or minimized?

5. Name three factors, that are peculiar to the use of heavy water as a moderator and indicate, briefly, their effects on station design, capital cost or operating costs.

A. Williams