A review of the cold neutron moderator materials: neutronic performance and radiation effects

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Abstract

Liquid hydrogen, ice and solid methane are common neutron moderating materials. More recently methane hydrate and mesitylene have been proposed to improve performance of these materials.

Liquid hydrogen is used in high-power spallation neutron sources since it is the only material that withstands such high power. Despite this, it is affected by radiation leading to spontaneous release of energy. It can be controlled by programmed annealings. Solid methane generally shows the highest neutron flux but, it is affected by radiation leading to formation of organic contaminants. In addition, spontaneous release of stored energy, that could damage the moderator container, was detected. Mesitylene is less affected by radiation and therefore, no spontaneous release of energy is observed or accumulation of any major contaminant. However, mesitylene shows a lower neutron energy spectrum than solid methane.

Methane hydrate was considered as an alternative. Nevertheless, reduced intensity of neutrons has been observed compared to solid methane.

This contribution provides a review of the main characteristics of these cold neutron moderator materials including the study of their respective neutron fluxes, the accumulation of energy in “frozen radicals” with the subsequent spontaneous release of energy and their thermal conductivities.

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1. An introduction to cold neutron moderator materials

A neutron moderator is a medium that reduces the speed of fast neutrons to levels that are interesting for different instruments. Neutrons primarily lose their energy by elastic collisions with atomic nuclei in their path. Protons are the most efficient particles for slowing down fast neutrons since both have the same mass. As Evans previously introduced [Evans (1995)], the maximum energy that a neutron can transfer, $E_t$, is given by

$$E_t = \frac{4 M}{(M + 1)^2} \quad (1)$$

Considering that $M = 1$ for a hydrogen atom, it is assumed that all the neutron energy may be transferred to the atom in a single collision. For a carbon atom $M = 12$ and therefore, the fraction of energy transferred is 0.28. It has been stated that hydrogenous materials are preferred for moderating neutrons [Evans (1995)].

Common cryogenic materials of interest as cold neutron moderators, due to their high proton density, are liquid hydrogen, ice or solid methane. More recently methane hydrate and mesitylene have been proposed to improve performance of these materials. All these materials are discussed in this contribution highlighting their neutronic performance and effects due to radiation.

2. Neutronic performance - The JESSICA Experiment

The test facility JESSICA (Julich Experimental Spallation Target Set-up In COSY Area) is installed in the synchrotron COSY at the Forschungszentrum Julich in Germany. JESSICA has been designed to reproduce experiments on a target-moderator-reflector system for the European Spallation Source (ESS).

The experiments performed in this facility, and presented in Figure 1, showed that at 20 K solid methane shows a maximum of its neutron flux at $\sim 4$ meV while ice shows the highest intensity at $\sim 8$ meV. The idea proposed at JESSICA was to combine both materials into one capable of exhibit the neutron flux of solid methane and ice over a broader energy range. Methane hydrate seemed the ideal candidate. This material contains a single methane molecule trapped in a cage-like structure of six frozen water molecules. Nevertheless, it was proven [Nunighoff et al. (2008)] that methane hydrate does not show the superposition of the ice and methane spectra but a similar shape as solid methane with an intensity reduced by a factor of three, as shown in Figure 1.

Solid methane shows higher neutron flux for energies lower than $\sim 8$ meV. However the flux of the ice moderator is superior in the interval between 8 meV $\sim 1$ eV. The spectrum of methane hydrate clearly shows that there is not a superposition of the energy spectra of each single material.

Mesitylene with its high hydrogen density and weakly hampered rotation of the methyl groups is an ideal candidate as cold neutron moderator material. Mesitylene is a derivative of the benzene with three methyl groups symmetrically placed on the ring. Solid mesitylene may exist in three different phases. Phase II, which shows the typical behavior of a disordered one, is the most interesting as an efficient cryogenic moderator material [Cantargi and Granada (2010)]. The spectrum of solid mesitylene at 20 K and phase III measured at JESSICA is shown in Figure 2 accompanied by solid methane, ice and liquid hydrogen.
Fig. 1. Measured energy spectra for ice, methane and methane hydrate. The shown data are normalized to the number of incident protons and are corrected for background and detector efficiency [Nunighoff et al. (2008)]. Reprinted with permission.

Fig. 2. Measured energy spectra for ice, solid methane, mesitylene and liquid hydrogen at 20 K. The shown data are normalized to the number of incident protons and are corrected for background and detector efficiency [Nunighoff et al. (2008)]. Reprinted with permission.

Mesitylene shows a similar spectrum like liquid hydrogen, only in the interval between 20 meV and 1 eV mesitylene is superior to liquid hydrogen [Nunighoff et al. (2008)]. Even though, it is believed that the performance of mesitylene may be improved in solid phase II.
3. Radiation effects

The radiation effects importantly depend on the moderator material. Liquid hydrogen is widely used in reactors and high-power spallation sources. Solid methane, due to its poor thermal conductivity is used in neutron sources of lower power. Mesitylene is being considered as an alternative as it is less affected by radiation.

The control of the energy accumulated in the moderator material as a consequence of radiolysis products is of vital importance since it is susceptible of spontaneous release of energy damaging the moderator can.

The improvement of the thermal conductivity of the moderator material is necessary in order to avoid melting in solid state.

3.1. Materials

Many research reactors use H$_2$ or D$_2$ as cold neutron moderator materials. The main advantages of deuterium are its good scattering quality and the low absorption. However the mean free path of neutrons in deuterium is high (>100 mm) compared to the same value in hydrogen (<20 mm) which means that bigger moderator volumes are needed when deuterium is used. Deuterium moderators are not used in short pulse sources, because they require a large moderator volume which leads to pulse broadening [Barnert-Wiemer (2012)]. Hydrogen shows good scattering performance but high absorption of neutrons, by a factor of 300 compared to D$_2$. An additional problem comes from the ortho-para conversion. At room temperature, liquid hydrogen presents the “normal” ratio of 75% ortho and 25% para-hydrogen. However, this changes at low temperatures. At ~20 K the ortho type slowly converts to the para type to complete a proportion of 99% para-hydrogen. Each conversion from ortho to para at this temperature releases 1.47 meV. Below a neutron energy of 100 meV the mean neutron scattering cross section depends on the ratio of ortho and para hydrogen [Barnert-Wiemer (2012)].

In addition, the low proton density of the H$_2$ (0.042 protons / A at 20 K), compared to that of the solid methane (0.079 protons / A at 20 K), leads to broad pulses of short wavelengths neutrons [Barnert-Wiemer (2012)].

Solid methane represents a dense source of hydrogen and has shown the most efficient cold neutron spectrum at energies lower than 10 meV and higher than 2 eV [Cantargi and Granada (2010)] but it forms carbon-based deposits after irradiation, mainly (-CH$_2$)$_n$. These deposits restrict the flow of methane and reduce the efficiency of the moderator [Evans (1995)]. The mechanism for the production of H$_2$ and the carbon deposits is considered to be [Barnert-Wiemer (2012)]

$$\text{CH}_4 + \text{energy} \rightarrow \cdot\text{CH}_3 + \cdot\text{H} \quad (2)$$

followed by recombination

$$\cdot\text{CH}_3 + \cdot\text{H} \rightarrow \text{H}_2 + \cdot\text{CH}_2 \quad (3)$$

This is the mechanism considered to be responsible for the formation of hydrogen gas in addition to

$$\cdot\text{H} + \cdot\text{H} \rightarrow \text{H}_2 + 104 \text{ kcal} \quad (4)$$

which produces an accumulation of energy and can lead to an abrupt release of energy (burp) as explained in the following section. The ·CH$_2$ recombine to form the wax-like alkane (-CH$_2$)$_n$.

Besides, radioactive isotopes are formed as a consequence of the exposition of moderators to high radiation fields. This entails that spent methane can not be release to the atmosphere.
Mesitylene has freely rotating methyl groups and is definitely less affected by radiation. Nevertheless, it has fewer low frequency modes per proton and lower proton densities than solid methane [Barnert-Wiemer (2012)].

3.2. Spontaneous release of energy

The following experiments were undertaken at the URAM-2 criogenic irradiation facility installed at the IBR-2 research reactor in Russia with a neutron flux of $3 \times 10^{12}$ n/cm$^2$/s and absorbed dose rate in water of 110 Gy/s (~20 Gy/s is induced by $\gamma$ and about 90 Gy/s is induced by neutrons) [Kulagin et al. (2004)].

Radicals are being formed due to the radiolysis of solid methane. The solid needs to be warmed periodically in order to avoid an abrupt release of energy due to spontaneous recombination reaction of those radicals (burp), seen in Figure 4.

![Fig. 4. The readings of thermocouples and helium flow meter during spontaneous release of the stored energy in solid methane (1 – temperature of the cooling helium, 2 – temperature of the copper walls of the irradiation capsule, 3 – temperature of methane, 8 mm away from the walls, 4 – helium flow rate.) [Kulagin et al. (2004) Reprinted with permission.]

The probability of getting a burp after certain irradiation dose depends on its volume, regardless its configuration (pellets or a solid block). It follows from the semi-empirical model of burp formation: a burp occurs whenever the concentration of radicals reaches a critical value (necessary condition) and at least one hot point of ignition exists at the moment (sufficient condition) [Shabalin (2012)].

This burp can damage the moderator container if an anneal is missed, as it happened twice in the ISIS neutron spallation source at the Rutherford Appleton Laboratory [Bewley (2012)]. In addition, at URAM they also registered a spontaneous burp [Kulikov (2012)] when methane hydrate was irradiated during 13 hours at 20 K, as shown in Figure 5.
Methane hydrate does not seem to be a quite good alternative to solid methane since it generally shows a lower neutron flux but the same spontaneous release of energy.

Mesitylene is less affected by radiation and shows no spontaneous energy release, as seen in Figure 6.

The most powerful spontaneous burp is observed due to the radiation of water ice at very low temperature as shown in Figure 7.
Fig. 7. The readings of the thermocouples and helium flow meter during spontaneous release of the stored energy in a mixture of water and peroxide 5% weight (1 – temperature of the cooling helium, 2 – temperature of the cooper walls of the irradiation capsule, 3 – temperature of the ice, 8 mm away from the walls, 4 – helium flow rate) [Kulagin et al. (2004)]. Reprinted with permission.

Possible additives (e.g. ethylene) have been considered in order to reduce the radical production. Nevertheless, it has been found that the effect of these scavengers has practically no influence since they are degraded by the radiation itself and therefore, their effect very soon vanishes [Shabalin (2012)].

Catalysts seem to be more useful, including aluminum foam mentioned in the next section. However, they are not as effective since the contacting surface can not be high enough otherwise, there would be a small amount of cold neutrons [Shabalin (2012)].

3.3 Thermal conductivity

The thermal conductivity of solid methane is low (< 0.4 W/m·K below 32 K). Therefore, solid methane should not be used as a compact block since the heat would not be conducted fast enough to the surface to be removed by the coolant. This would lead to melting and finally evaporation of the methane. Alternatively, solid methane can be added as small pellets or filling the holes of an aluminum foam which in turn helps to improve the thermal conductivity of solid methane.

Thermal conductivity values for other interesting cold neutron moderator materials are presented in Figure 9 for temperatures lower than 40 K.

The thermal conductivity of mesitylene clearly increases with decreasing temperature oppositely to what occurs to the rest of materials.

As seen in Figure 8, the referenced high thermal conductivity of ice at low temperature (40 W/m·K at 20 K) is unrealistic after irradiation by $1 \times 10^{15}$ n / cm² and more. Shabalin et al. had no option except adding solid argon to maintain low temperature of the ice beads pile [Shabalin (2012)].
Fig. 8. Temperature dependence of thermal conductivity of ice and molecular crystals at the state of saturation of radiation induced defects [Shabalin (2012)].

4. Summary and conclusions

Most aspects have been covered in this revision of cold neutron moderating materials. Liquid hydrogen is used in high power spallation neutron sources, it is anyway affected by radiation and periodic annealing is necessary. Solid methane has shown in general the highest neutron fluxes, although it is affected by radiation-generated molecular hydrogen and other organic contaminants which may produce strains and block the system respectively. Mesitylene is observed to be less affected by radiation. However, neutron fluxes are much lower than in solid methane. The intensity of cold neutrons is reduced by a factor of three when using a methane hydrate moderator instead of solid methane moderator.

Catalysts, such as aluminum foam, have proved to be quite effective in improving the thermal conductivity of some moderator materials. Nevertheless, radical scavengers are expected to degrade due to the neutron beam and therefore, be much less useful.

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