Available online at www.sciencedirect.com

SCIENCE DIRECT®

ELSEVIER

Nuclear Instruments and Methods in Physics Research B 215 (2004) 181–186

NIM B
Beam Interactions with Materials & Atoms

www.elsevier.com/locate/nimb

Radiation effects in cold moderator materials: Experimental study of accumulation and release of chemical energy

E. Kulagin, S. Kulikov *, V. Melikhov, E. Shabalin

Frank Laboratory of Neutron Physics, Joint Institute for Nuclear Research, Moscow region, Joliot Curie 6, build. 119, S. Kulikov, 141980 2Dubna, Russia

Received 28 May 2003; received in revised form 19 August 2003

Abstract

Study of radiation resistance of hydrogenous materials at low temperatures is a first priority task in the design of advanced cold neutron moderators. At temperatures 20–100 K the most essential radiation effects in solid hydrogenous substances are:

- Formation of radiolytic hydrogen.
- Accumulation of "frozen" radicals, which results in a rise of a self-sustaining reaction of their recombination followed with unexpected fast heating of the moderator.
- Formation of high-molecular, high-boiling products of radiolysis.
- Decrease of thermal conductivity.

In the paper, the recently obtained results of the study of the accumulation of chemical energy and the conditions of its release performed with the URAM-2 cryogenic irradiation facility at the IBR-2 research reactor, are presented. Spontaneous releases of stored energy were detected in solid methane, water ice, hydrates of methane and tetrahydrofuran [Particles and Nuclei, Lett. 5 (2002) 82; Radiat. Phys. Chem. 67 (2003) 315] and in frozen mixtures of water ice with atomic hydrogen scavengers. A negligible amount of energy is accumulated in aromatic hydrocarbons which demonstrate no spontaneous self-heating under irradiation. All irradiation runs were performed at up to 20 MGy in the temperature range of 15–50 K.

PACS: 28.20.−v; 28.20.Gd; 61.80.Hg; 87.50.Gi
Keywords: Advanced cold neutron moderator; Reaction of radical recombination; Fast neutron irradiation

1. Introduction

Nowadays, in many neutron centres in the world scientists are trying to increase neutron

* Corresponding author. Tel.: +7-096-2165915; fax: +7-096-2165119.
E-mail address: ksa@nf.jinr.ru (S. Kulikov).

0168-583X/$ - see front matter © 2003 Elsevier B.V. All rights reserved.
doi:10.1016/j.nimb.2003.08.026

performance of their instruments by optimising the source. This is much cheaper than increasing of current in accelerators for spallation sources or of reactors' power and may give a gain factor of three in the neutron flux. But it is not easy to do. The use of solid moderators entail problems. One is that under irradiation the moderator materials accumulate energy as "frozen" radicals with a subsequent spontaneous or induced reaction of recombination (burp), which could damage the moderator container [3–6]. To investigate the behaviour of such materials, a cryogenic irradiation facility was decided to be built at the IBR-2 reactor.

Some preliminary measurements of the fast neutron flux, absorbed dose rate as well as the elaboration of sample preparation techniques preceded the construction.

The measurements gave: the fast neutrons flux is 3×10^{12} n/cm^2/s, absorbed dose rate in water is 110 Gy/s (about 20 Gy/s is induced by γ and about 90 Gy/s is induced by neutrons) [7]. These have allowed the construction of the URAM-2 cryogenic facility and start of investigations of suitable materials.

2. The conditions of irradiation

A conceptual design of the URAM-2 facility is in Fig. 1.

The irradiation cavity inside the capsule consists of two parts: the bottom hemispherical

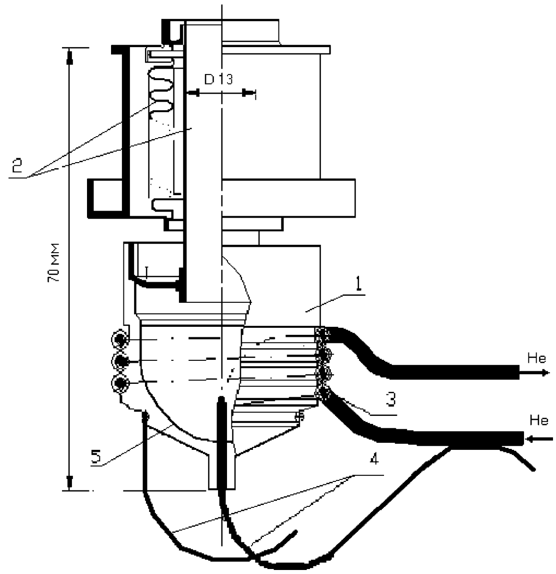

Fig. 2. The head part of the facility: (1) capsule, (2) a suspender (thermal bridge), (3) cooling helium tubes, (4) thermocouples, (5) irradiation cavity.

($d = 3$ cm) part and the upper cylindrical part (Fig. 2). The walls of the cavity are made of pure, oxygen-free copper (M1 purity in Russian standard, thermal conductivity 1000 W/m/K at 20 K). The surface area of the irradiation cavity is about 22 cm^2 and the inner volume is about 12 cm^3.

The temperature is monitored with five thermocouples at a frequency of either 1.25 or 5 Hz: one is at a distance of 8 mm from the bottom of

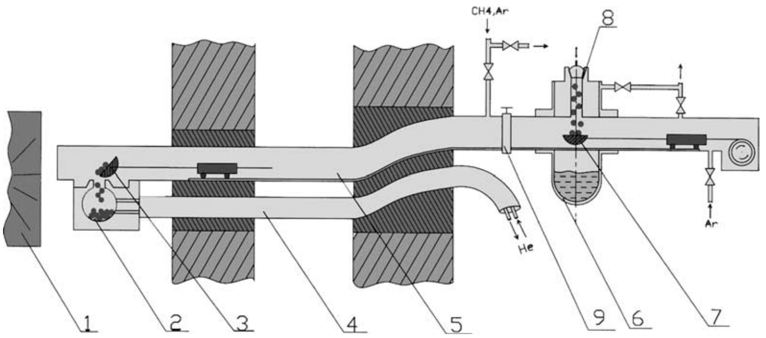

Fig. 1. The conceptual design of the URAM-2 irradiation facility: (1) IBR-2 reactor, (2) irradiation capsule, (3) carrying bowl with a cart in the "near-reactor" position, (4) helium pipelines, (5) evacuated transport passage, (6) nitrogen cryostat, (7) carrying bowl with a cart in "out-of-reactor" position, (8) charging tube with a plug, (9) vacuum lock.

the capsule, two are on the outer surface of the capsule and two measure the temperatures of incoming and emergent cooling helium.

The gas pressure monitoring is carried out with two gauges: 0–400 mbar, <0.1% accuracy at full scale, and 0–2 mbar, about 20% accuracy.

Also, the flow rate of helium is monitored (not all the time). By combining all these measurements the energy release in a burp can estimated within a 15% accuracy.

The stability of the temperature of the sample during irradiation is within ±0.3 K and the stability of dose rate is within ±1%.

The main parameters of the URAM-2 facility:

- maximal time of irradiation: about 50 h at 20 K,
- temperature range: 10–60 K,
- possible materials for sample preparation: pieces of ice, any gases or liquids,
- possibility to measure the pressure of hydrogen released during the experiment.

More detailed information about the URAM-2 facility is in [8,9]. However, some alterations have been made since their publication. For example, the carrying bowl is replaced with a new one suitable for carrying liquid substances; the helium Dewar of 100 l capacity is replaced with another vessel of 250 l capacity, and some parts of the liquid helium transport system are modified.

3. The experimental details

About 700 h of irradiation runs with the aim of accumulating of the chemical energy to have a posterior spontaneous or induced burping in the next materials at low temperatures: methane, water, water mixed in different proportions with H_2O_2, $KMnO_4$, C_2H_5OH, methane hydrate, tetrohydrofuran hydrate, mesitylene, mesitylene + toluene, were carried out. In almost all of the experimental runs the burping was observed as a sharp jump in the readings of the thermocouples making it possible to calculate the stored energy and estimate the energy accumulation rate.

4. Results

4.1. Water ice

All water ice samples, including those doped with peroxide and potassium permanganate and an ice mixture of water with alcohol, demonstrated spontaneous burping. The times to the burp varied and were not strictly determined by the absorbed dose. For pure ice samples of equal size, the times varied from 5 to 11 h for the irradiation temperature ~20–25 K. The samples doped with peroxide (5% by weight) (Fig. 3), potassium permanganate (6%) (Fig. 4), and the mixture with alcohol demonstrated a similar behaviour.

An increase of peroxide content to 15% by weight reduced the time to burping (from 6 to 4 h). One continuous irradiation run proceeded until four spontaneous burps happened. They followed one another with no regular periodicity (Fig. 5). So, one may conclude that spontaneous burps are determined not only by the concentration of radicals but also by some other factors, e.g. the amount of the accumulated defects.

Most informative of the obtained results is the dependence of the time to burping on the size of

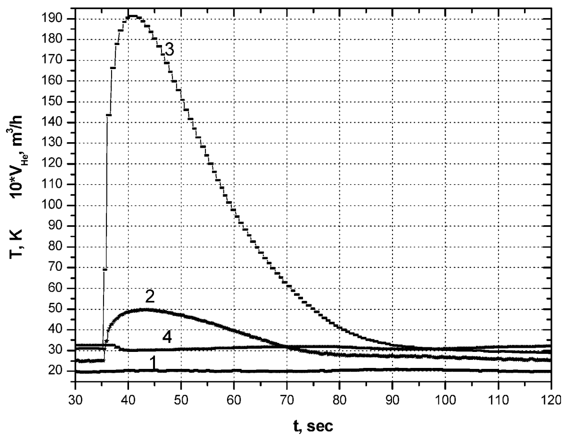

Fig. 3. The readings of the thermocouples and helium flow meter during spontaneous release of the stored energy in a mixture of water and peroxide 5% weight (1 – temperature of the cooling helium, 2 – temperature of the copper walls of the irradiation capsule, 3 – temperature of the ice, 8 mm away from the walls, 4 – helium flow rate).

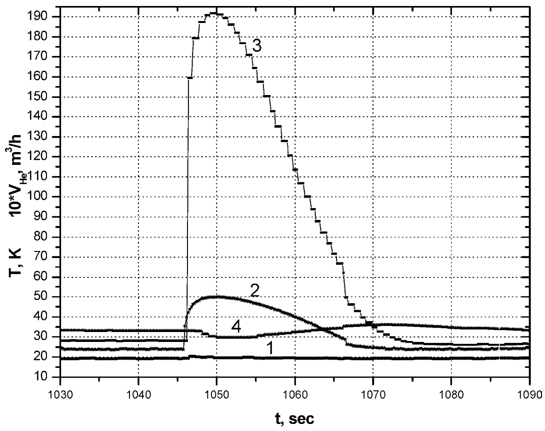

Fig. 4. The readings of the thermocouples and helium flow meter during spontaneous release of the stored energy in a mixture of water and 6% $KMnO_4$ (1 – temperature of the cooling helium, 2 – temperature of the copper walls of the irradiation capsule, 3 – temperature of the ice, 8 mm away from the walls, 4 – helium flow rate).

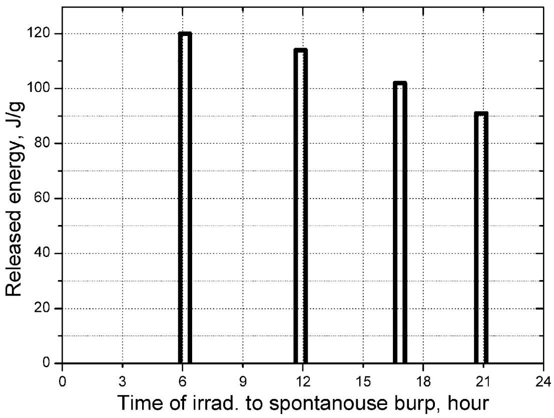

Fig. 5. The energy released in spontaneous burps versus the time of one irradiation run (mixture of 85% H_2O and 15% H_2O_2).

the sample. The smallest pure water samples of 0.4 g (it was a segment 3 mm thick) showed a burp after ~20 h of irradiation against 8.4 h averaged over all spontaneous burps for bigger samples ($\geqslant$ 2.5 g). It confirms that for small samples of ice ($\leqslant$ 5–7 mm) the critical concentration depends on either the size or volume of the sample.

The rate of accumulation of the stored energy in all doped samples of ice at the beginning of irradiation is close to that for pure water ice which is equal to 21–24 J/g/h. It was found to be a little lower (by ~30%) for the alcohol mixture. Naturally, the rate decreases with the time of irradiation. At an irradiation temperature of 25 K the rate falls to ~13 J/g/h, between 10 and 20 h of irradiation. Accordingly, a maximal stored energy of 240 J/g was released in a sample of 0.4 g. The energy released at spontaneous burps is higher for the 5% peroxide mixture (about 30–40%) and is lower for the alcohol mixture compared to pure water ice.

The maximal rate of energy accumulation in water ice was estimated to be as high as 5.4% ± 0.4% of the absorbed dose rate.

The accumulation of the stored energy tends to saturation which cannot be reached as a spontaneous burp occurs earlier at irradiation temperature less than 35–40 K. The saturation curve is close to exponential (Fig. 6). The higher the temperature, the shorter the saturation time: τ (h) $\sim 0.53(50 - T_{\mathrm{irr}})$. Virtual saturation values of the accumulated energy can be calculated by the relation Q_∞ (J/g) $\sim 11(50 - T_{\mathrm{irr}})$. These are 25–30% (for $T \leqslant 35$ K), which is higher than that predicted in [11] where the experimental data on gamma irradiated ice were used.

4.2. Methane

Apart from the results [1,2] only one spontaneous burp occurred in a 5 mm thick methane

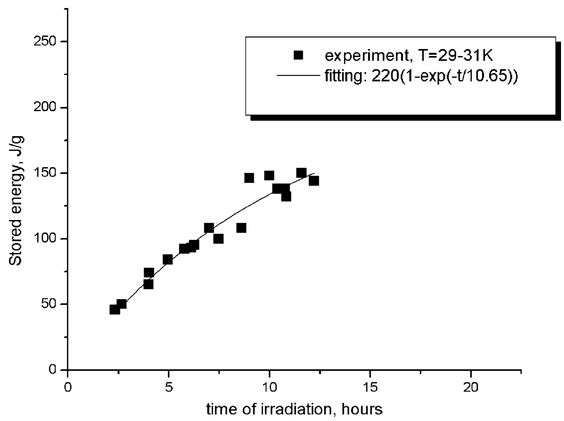

Fig. 6. The stored energy versus the time of irradiation in experiments with water ice.

spherical shell at 20–22 K after 11 h of irradiation this time (Fig. 7). Another methane spherical shell of half thickness showed no spontaneous burp even after 26 h. The principal contradiction between the URAM-2 results and those of the use of cold moderators at IBR-2, IPNS and KENS, namely lack of spontaneous burps is possibly eliminated by these experiments. The reason for a very low probability of spontaneous burps in the *URAM-2 irradiation capsule may be its small volume*. It seems that occurrence of spontaneous burps more depends on the volume (mass) of the sample than on its characteristic size (for example: the characteristic size of a plate/cylinder is its thickness/radius for any volume). In the URAM-1 experiments [3] where the mass of methane was also small (about 16 g) no spontaneous burps were registered, though the characteristic cooling size of the sample (1 cm) was close to that of the solid methane moderator at the IBR-2 reactor.

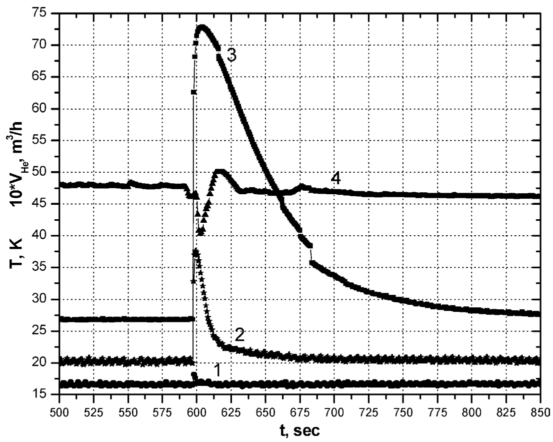

Fig. 7. The readings of the thermocouples and helium flow meter during spontaneous release of the stored energy in solid methane (1 – temperature of the cooling helium, 2 – temperature of the copper walls of the irradiation capsule, 3 – temperature of methane, 8 mm away from the walls, 4 – helium flow rate).

The maximal rate of energy accumulation in solid methane (at temperatures over 20 K) is estimated to be as high as $1.6\% \pm 0.2\%$ of the absorbed dose rate. The characteristics of burps in methane are in [1–4,10].

4.3. Aromatic hydrocarbons

Radiation effects in aromatic hydrocarbons appear to be significantly less than in the other substances studied. The samples studied were solid mesitylene at $T = 20$–36 K in three structural states: phase 1 ("proton glass"), phase 2 (high temperature phase), a sample with all three

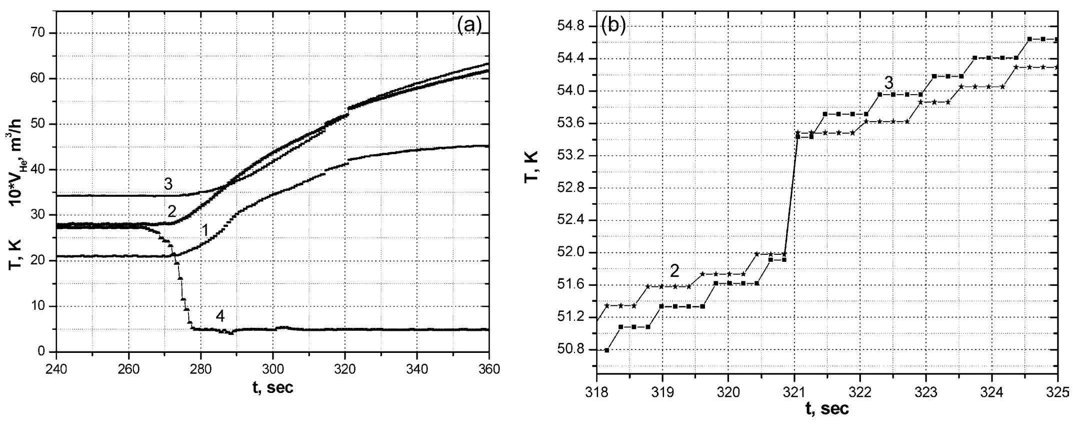

Fig. 8. (a) The readings from the thermocouples and helium flow meter during induced release of the stored energy in mesitylene (1 – temperature of the cooling helium 2 – temperature of the copper walls of the irradiation capsule, 3 – temperature of mesitylene at 8 mm from the walls, 4 – helium flow rate). (b) (rescaled (a)): The readings of the thermocouples during induced release of the stored energy in mesitylene (2 – temperature of the walls of the irradiation capsule, 3 – temperature of mesitylene 8 mm away of the walls).

phases mixed, and a mixture of mesitylene with toluene. There were not observed spontaneous burps but weak induced burps (Fig. 8(a) and (b)) in all samples of aromatic hydrocarbons, though the time of irradiation reached 45 h (dose up to 20 MGy). For higher temperatures of irradiation we expect neither spontaneous nor induced burps.

The maximal rate of energy accumulation in mesitylene (in phase I, "proton glass") is estimated to be <1 J/g (<0.02% of the absorbed dose rate) for 14 h of irradiation. It is the reason why no spontaneous burping is observed. In the other samples no stored energy was detected.

5. Conclusion

(1) Water ice at $T \leqslant 35$–40 K shows spontaneous burping at about $\geqslant 2$ kJ/g dose even for small samples (0.4 g).

(2) Spontaneous burps in solid methane occur less readily in such experiments. It occurred once at about 8.3 kJ/g whereas in the IBR-2 cold moderator and at IPNS such events happen at lower doses. The given experiments confirm the probabilistic character of spontaneous burps.

(3) Basing on the URAM-2 experiments it may be proposed to use mesitylene or a mixture of aromatic hydrocarbons as a moderating medium as very small concentrations of radicals, even in the case of operation at spallation sources, are expected to accumulate.

Acknowledgements

This work has been done under financial support of the Advanced Cold Moderator Collaboration (ACoM).

References

[1] E. Shabalin, S. Kulikov, V. Melikhov, Part. Nucl. Lett. 5 (2002) 82.
[2] E. Shabalin, E. Kulagin, S. Kulikov, V. Melikhov, Radiat. Phys. Chem. 67 (2003) 315.
[3] A.A. Beljakov, V.G. Ermilov, V.L. Lomidze, V.V. Melichov, E.P. Shabalin, in: Proceedings of the ICANS-XII, RAL Report 94-025, Vol. 2, 1994, p. 144.
[4] J. Carpenter, in: Proceedings of the International Workshop on Cold Neutron Sources LANCE, Los-Alamos, US, LA-12146-C, 1990, p. 131.
[5] S. Ikeda, N. Watanabe, S. Satoh, M. Furusaka, K. Inoue, in: Proceedings of International Collaboration of Advanced Neutron Sources (ICANS-IX), PSI, Willingen, Vol. II, 1986, p. 118.
[6] J. Carpenter, Nature 330 (1987) 358.
[7] V. Golikov, E. Kulagin, E. Shabalin, JINR Commun. (2002), E16-2002-79.
[8] E.P. Shabalin, V.V. Golikov, S.A. Kulikov, E.N. Kulagin, V.V. Melihov, A.A. Belyakov, L.B. Golovanov, Yu.T. Borzunov, V.I. Konstantinov, A.V. Androsov, JINR Commun. (2002), E13-2002-143. http://www1.jinr.ru/Preprints/2002/143(E13-2002-143).pdf.
[9] E.P. Shabalin, G.S. Bauer, V.V. Golikov, V.I. Konstantinov, H. Ullmaier, A.V. Androsov, L.B. Golovanov, E.N. Kulagin, ISSN 1433-559-X, ESS 99-92-T, 1999.
[10] E.P. Shabalin, in: Proceedings of the Workshop on Cold Moderators for Pulsed Neutron Sources, Argonne, IL, ANL-Report, ANL, 28 September–2 October 1998.
[11] E.P. Shabalin, in: Proceedings of the ICANS-XIV Meeting, Starved Rock, IL, USA, ANL-98/33, Vol. 2, 1998, p. 497.