A PELLETIZED SOLID METHANE MODERATOR FOR A MEDIUM-TO-HIGH POWER NEUTRON SOURCE

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ABSTRACT

Solid methane has been an elusive neutron moderator medium for some years. Good physics has been done using frozen blocks of methane and innovative ways have been found to compensate for its low thermal conductivity. Annealing techniques have been evolved to release chemical energy by polymerization, but the use of solid methane remains limited to low power applications. This paper describes a possible way of using solid methane for very much higher energy applications. It presents some ideas on how mobile solid methane in the form of pellets might be employed. Initial feasibility calculations are included along with a possible configuration for a practical moderator. Well-developed techniques, like those used in fusion reactor systems have been explored for the production of pellets.

1. Introduction

Methane has long been known as one of the most desirable moderator materials, in particular for pulsed spallation neutron sources. It excells by the following properties (see e.g. ref [1]):

• Methane has a relatively rich spectrum of low energy rotational modes with strong transition lines at 1,2,3 meV and up. As a consequence, neutrons can still lose energy when already very cold and slowing-down occurs to very low energies. This means that the narrow line width of the slowing-down spectrum can extend down below 20 meV and excellent time-of-flight resolution can be obtained.

• Methane has a high density of hydrogen atoms which means that the time between collisions is short and the energy transfer per collision is high. This leads to a very narrow time distribution in the slowing-down regime. The product of neutron velocity v and pulse width Δt_s is of the order of 1 cm, 25% better than for H_2O!

The most desireable temperature to use methane is around 25 K, because this avoids possible complications that might arise from the phase transitions at 14 - 15 and 20 K and provides some margin to cool with liquid hydrogen. This gives an effective moderator temperature of

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about 40 K and extends the slowing down regime below 20 meV. Solid methane as a block can, however, be cooled only at very low beam power sources such as KENS (5 kW).

Furthermore, while liquid methane tends to form oily and tar-like polymerization products already under moderate radiation levels [2], solid methane stores CH_3-radicals up to a certain level due to the low mobility of the radicals. However, since polymerization of the radicals is an exothermal process it can be set off at a certain temperature and concentration and then proceed like an avalanche. While potentially dangerous if left uncontrolled, this "burping" can be induced by a gentle temperature increase without causing damage to the container [1], [3]. Depending on the radiation load, this may have to be done rather frequently and may becoem quite impractical at high power sources.

In an attempt to bypass these difficulties, we examine in the present paper the possibility of using solid methane in the form of spheres. This is an extension from a paper presented at ICANS-X [4] with emphasis on avoiding polymerization in the system at points where it could give rise to clogging or hamper the performance of the moderator in some other manner.

Our main goal is thus threefold:

a) devise a system with the highest practical moderator efficiency, i.e. the highest possible hydrogen content in the moderator volume at the lowest possible temperature

b) devise a system where the polymerization products can be safely and continuously removed and which can be operated at spallation sources with several MW of beam power

c) devise a system where "burping" can be allowed to occur spontaneously without affecting the whole moderator or large parts of it at the same time.

2. Function and Operation

Using the solid methane in pellet form enables it to be handled as a semi-fluid. The principle objective described in this paper is to allow the pellets to pass across a moderator under gravity at a rate designed to suit the specific application. As they cross the moderator vessel the pellets are heated volumetrically and they also suffer from radiation damage, releasing hydrogen and leading to stored radicals which, at some point, can polymerize in an exothermal reaction. The required transport rate across the moderator vessel is governed by the dominant of these two factors. In an extreme case, radiation damage could completely transform pellets to a carbon-like consitency [2]. It is unlikely that this would be a serious problem, nor would the melting of a few individual pellets. Both situations are a real possibility since some pellets will almost certainly be irradiated more than others. The development program discussed later includes an investigation into the rate of spontaneous energy release within pellets of different sizes. Together with an understanding of the heat transfer mechanisms involved, this would enable good estimates of the transport rate to be calculated.

3. Pellet Preparation

Frozen pellets made from a variety of materials, including hydrogen, are used routinely in fusion experiments. Although this application does not place particular importance on pellet size and shape, it has been demonstrated that repeatable spheres can be produced using the

same techniques. A development program would be required to optimize a moderator bed which might have a practical packing density of up to 68%.

4. Preliminary Feasibility Calculations

In order to examine some of the possible problems involved in manufacturing methane spheres for use in a pelletized cold source, several preliminary scoping calculations have been carried out. The thermophysical properties for methane at its freezing point of 90.67 K are collected in Table 1 as obtained from the literature [4-6] for use in the analysis.

Table 1: Thermophysical Properties of Methane [4-6]

Freezing point	90.67 K
Liquid density ρ_l	453.0 kg/m^3
Solid density, ρ_s	522.0 kg/m^3
Liquid thermal conductivity, k_l	0.216 W/ m · K
Solid thermal conductivity, k_s	0.26 W/ m · K
Liquid specific heat, $c_{p,l}$	3348.8 J/kg · K
Solid specific heat, $c_{p,s}$	2737.6 J/kg · K
Latent heat of fusion, h_{fs}	58680 J/kg

The first question that needed to be addressed was how large the methane spheres could be before internal heat generation would lead to melting inside the pellets while they were within the moderator vessel. Although some cracking or radiation damage to the solid methane might occur before the center of a sphere reached the melting point, onset of melting serves as a useful thermal limit for preliminary analysis. Since the pellets are assumed to be surrounded by liquid hydrogen during operation, they would enter the moderator vessel at a uniform temperature of 20 K and their outer surfaces would be maintained at approximately 20 K while they were exposed to nuclear heat generation. The problem thus reduces to calculating the transient internal temperature profile of a sphere subjected to uniform heat generation. In addition, pellet temperatures throughout the transient heating process will be bounded by the final steady-state solution. From Incropera and DeWitt [7], the steady-state temperature difference between the center and surface of a sphere is given by

$$T_0 - T_s = \frac{qR^2}{6k_s}$$
(1)

where q is the volumetric heat generation and k_s is the solid thermal conductivity. Equation (1) can be used to solve for the pellet radius that corresponds to a particular temperature difference once the heat generation is specified.

Setting the surface temperature T_s = 20 K and using T_0 = 90 K to reflect the maximum permissible center temperature allows one to calculate the largest sized pellet for no melting at steady-state. To provide a representative calculation for this feasibility study, a value of 1 kW/l = 10^6 W/m^3 (corresponding to several MW of beam power in a spallation neutron source) was assumed for the nuclear internal heat generation. Although the source would operate in a pulse mode with a repetition rate of 25 to 50 Hz, steady state conditions are considered an appropriate approximation because, at 50 Hz and 10^6 W/m^3, heating during each pulse is of the order of 0.015 K, which obviously does not constitute a severe deviation

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from steady state heating. The estimated maximum radius predicted for the methane spheres under these conditions was R = 10.45 mm. Table 2 shows the pellet radii associated with several other values of T_0 -T_s ranging from 70 K down to 5 K with the same internal heat generation of 10^6 W/m^3. According to these calculations, it is clear that reasonably large methane spheres can be placed inside the moderator vessel with no danger of internal melting, even under steady-state conditions.

Table 2: Preliminary steady-state results for methane pellet heating in the moderator

Radius of methane spheres (mm)	Volumetric heat generation (W/m^3)	Steady-state temp. difference (T_0-T_s) (K)	Approximate time to establish the steady-state profile (s)
10.45	10^6	70*	350
6.84	10^6	30	150
3.95	10^6	10	45
2.79	10^6	5	20

* Maximum allowable temperature difference for no melting at steady state

Another important factor involved in optimizing pellet sizes is the time that would be required to establish the steady-state internal temperature profile in pellets that entered the moderator at a uniform temperature of 20 K. Calculations to answer this question were carried out using HEATING7 [8], a transient finite-difference code developed at Oak Ridge National Laboratory for solving heat conduction problems in up to three spatial dimensions. Results of the HEATING7 analysis are also included in Table 2 for each of the pellet sizes examined. Even for the largest pellet size of R = 10.45mm, only about 350 s are needed for internal temperatures to rise to their steady-state levels. Reducing R to 2.79mm so that T_0 -T_s = 5 K at steady state allows the final temperature profile to be reached in only 20 s. Given the rapid heat-up times reflected in Table 2, the pellets in a finalized design would probably be sized based on internal temperatures for optimum effective neutron temperature. There are, however, several other criteria that enter the final sizing decision such as ease of pellet frabrication, obtainable homogeneity, hydrogen release, heating upon radical recombination and ease of transport to and from the moderator vessel. Some of these are discussed below.

At least two approaches are available for making the pellets: Freezing in liquid nitrogen at 77 K followed by cooling to 20 K in liquid hydrogen, or direct freezing and cooling to 20 K in a liquid hydrogen bath. The first option has the advantage of using cheaper, non-explosive liquid nitrogen for much of the cooling process but would result in a somewhat more complex operating cycle. Several additional HEATING7 calculations were performed to investigate both these possible techniques of pellet formation for the sphere sizes from Table 2. The results are summarized in Table 3 for the liquid nitrogen/liquid hydrogen production cycle and in Table 4 for the cycle using only liquid hydrogen. All these HEATING7 runs started from uniform liquid methane spheres at 95 K and first calculated the time necessary for a one-dimensional freezing front to propagate inward all the way to the center, assuming a high heat transfer coefficient so that the sphere surface temperature T_s was essentially equal to the bath temperature. Once the solidification phase change part of the process was completed, cooling was allowed to continue in liquid nitrogen or liquid hydrogen to produce uniform methane spheres at 20 K. Freezing and cooling times were combined to yield the total pellet production times found in the last column of Table 3 and Table 4.

Table 3. Preliminary results for methane pellet production in liquid N_2 at 77K

Radius of methane spheres (mm)	Freezing time in liquid N_2 (s)	Total freezing & cooling time to 77 K in liquid N_2 (s)	Additional cooling time from 77 to 20 K in liquid H_2 (s)	Total production time (s)
10.45	300	540	450	990
6.84	120	270	210	480
3.95	45	90	70	160
2.79	20	40	35	75

Table 4. Preliminary results for direct methane pellet production in liquid H_2 at 20K

Radius of methane spheres (mm)	Freezing time in liquid H_2 (s)	Additional cooling time from 90 to 20 K (s)	Total production time (s)
10.45	120	360	480
6.84	45	195	240
3.95	15	75	90
2.79	8	32	40

Examination of Tables 3 and 4 shows several interesting features. Because of methane's relatively low heat of fusion, most of the pellet production time is consumed in cooling the frozen spheres from the solidification temperature of 90 K down to the working temperature of 20 K. This is particularly true when the cooling process is accomplished in two stages using both liquid nitrogen and liquid hydrogen. Furthermore, all the production times obtained are short enough to be incorporated into a realistic methane pellet system. Pellets near the smaller end of the size range described by the tables would probably be selected for use in an actual system because they would maximize fluidity for the moderator and keep the pellet internal temperature relatively low. For such pellet sizes, production times of 2-3 minutes are quite sufficient, even when a liquid nitrogen stage is used in the cooling process.

One factor that is not taken into account by HEATING is the increase in density that accompanies the freezing process. If solidification progresses from the outside of each sphere inward, the shrinkage associated with formation of the solid phase might be trapped as an internal void inside the pellet. The final void volume for this case is readily calculated based on the solidification shrinkage fraction, γ, for the material:

$$\gamma = \frac{V_{void}}{V_{total}} = 1 - \frac{\rho_l}{\rho_s} \qquad (2)$$

Using the available solid and liquid densities for methane yields a value of $\gamma = 13.2\%$ maximum void inside each pellet fabricated. It remains to be investigated whether this pellet void fraction represents an unavoidable reduction in moderator density or whether ways can be found to "grow" the pellets with a minimum void volume. For uniform-sized spheres, the

theoretical maximum packing density is already $(\pi/6)2^{1/2} = 74.05\%$ before considering the internal void fraction. These limitations on hydrogen atom density in a pelletized moderator compared to solid methane could be improved to some extent by using two different pellet diameters, with smaller pellets fitting into the interstitial spaces between the larger ones is a theoretical possibility. However, the pellet production system would then have to be considerably more complicated. Heat removal by liquid hydrogen flowing between the pelletes will also require some reasonable degree of "porosity" to avoid excessive pressure drops.

5. Radiation effects

The spontaneous recombination of radiation-induced radicals was first observed at the IPNS-moderator at Argonne [1], where it led to destruction of the moderator vessel. Subsequent investigations showed that the likely explanation is as follows:

The methane molecules dissociate into H^+ and CH_3^- under the effect of ionizing radiation. While the H is relatively mobile and most of it can diffuse out of the methane or accummulate in internal voids, diffusion of the CH_3^- is mainly by H^+-exchange with neighboring CH_4-molecules, and therefore slow. In this way a fair concentration of CH_3^- can accumulate before polymerization can occur. The CH_3^--diffusion is strongly temperature dependent and therefore polymerization can be triggered by even a gentle temperature increase. Once triggered, the effect is self-amplifying due to the exothermal nature of the reaction. The destructive effect observed at IPNS is explained by hydrogen still trapped in the methane reaching a high enough pressure during the "burp" to cause the container vessel to rupture. Carpenter [1] and Beljakov et al. [3] have investigated this problem using similar relations for the temperature dependence. The one given by Beljakov et al. reads:

$$Q_R \cdot T_{act} \cdot a \cdot K(T) \, N^2/(\lambda \cdot T^2) \ = \ 0.88 \tag{3}$$

where Q_R is the energy of recombination, T_{act} the activation temperature, $K(T)$ an Arrhenius factor, λ is the thermal conductivity, a represents a linear dimension of the methane slug and N is the concentration of radicals in the methane.

This shows that one would expect "burping" to occur at higher radical concentration for smaller pellets. Also, pellets at different temperatures will behave differently.

In the moderator type considered here one would not expect burping to be a safety problem for the following reasons:

- The moderator vessel will always contain pellets exposed to different radiation levels and at different temperatures, so that simultaneous burping in a large number of pellets is unlikely.

- The pellets can be considered small enough not to accummulate significant amounts of hydrogen in voids, so no pressure increase is expected.

- Even if individual pellets should explode, this would not have a noticeable effect on the container walls.

- The pellets are sufficiently well cooled on their surface to prevent spreading of a temperature increase from one pellet to its neighbours.

It should therefore be possible to operate the moderator without intentionally triggering burping as has become a routine at IPNS. Note that, while at IPNS one "burp" per day is sufficient to release the radicals acummulated, the corresponding irradiation dose would be reached at a 5 MW source within about 2 min! It should also be noted that the performance of the methane as a moderator is expected to deteriorate only after a large number of "burps". According to Beljakov et al. [3], the CH_4-destruction occurs at a rate of roughly $0.2 \cdot 10^7$ mole/J. Using again our assumed energy deposition of 10^6 W/m^3, we find on average rate of CH_4-destruction of $6 \cdot 10^{-8}$ sec^{-1}, or 0.22% per hour. This shows that the residence time of the methane pellets in the moderator vessel is not a problem from this point of view.

Taken as a whole, all the preliminary calculations conducted indicate that a pelletized methane moderator system shows considerable promise. Solid methane has a high enough thermal conductivity that reasonably small pellets are in no danger of melting while in the moderator. In addition, methane's low heat of fusion and relatively high freezing point mean such pellets can be produced quickly and efficiently in either liquid nitrogen or liquid hydrogen. Although a great deal of work remains to be done to optimize such parameters as the pellet sizes, production rates, and moderator residence times, the project definitely appears feasible.

6. Alternative Design Configurations

Fig. 1 shows the scheme postulated in a previous paper [4]. The pellets are produced at the top of the moderator by pulsing liquid methane through nozzles into a flowing hydrogen matrix. The liquid hydrogen is subcooled and mechanically circulated at a flowrate sufficient to prevent boiling under its own internal heat load and a portion of that generated within the pellet bed. A melting zone at the bottom of the moderator is warmed by circulated helium gas. The liquid pool created at the bottom is then removed, cleaned, and re-used or disposed of. The presence of the pool helps to prevent hydrogen from entering the methane system by forming a liquid barrier.
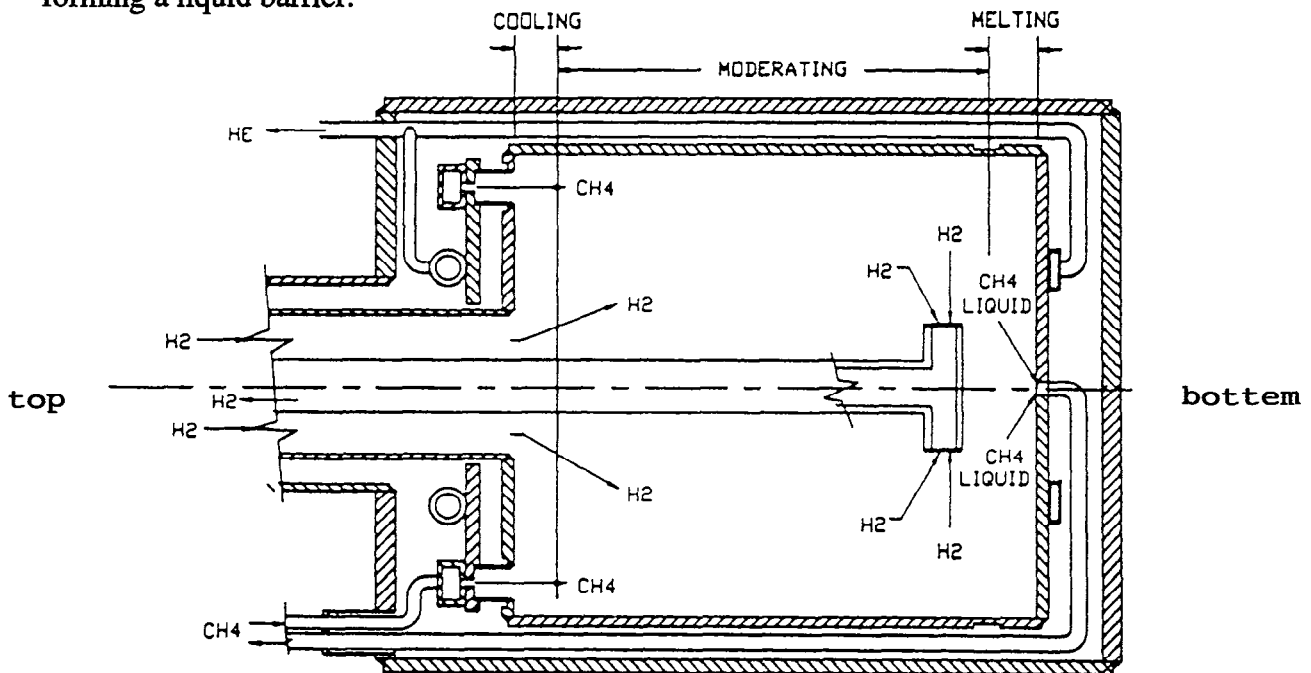

Figure 1: Pelletized methane moderator with pellet production through nozzles at the top and with melting zone at the bottom of the moderator canister as proposed in ref. [4].

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The principal advantage of this compact arrangement is its operational simplicity and compactness and the absence of mechanical transport systems. Also, the liquid hydrogen, in addition to acting as a coolant to extend the useful life of the pellets, helps improve the overall moderator flux.

Unfortunately, however, it requires considerable space which would be at the expense of reflector material, placing severe limitations on its application. Furthermore, it would be very difficult to monitor the many complex operational parameters in this highly fluent region and servicing would be extremely difficult, if not impossible, after a short operational period. Melting the spheres at the bottom of the moderator vessel also is likely to free the radicals and encourage polymerization and sticking to the walls.

Fig. 2 represents a slightly more complex system retaining the advantages and avoiding potential problems of the previous one. A liquid hydrogen loop is provided, but the pellet supply and removal operations are relocated to a low radiation area outside the reflector. The pellets are then removed in a solid state by a mechanical system. Removal of the trapped radicals or polymerization products from the spheres by melting is also relocated to an area where negative effects on the circuit can be avoided. This is accomplished by a separation of functions:
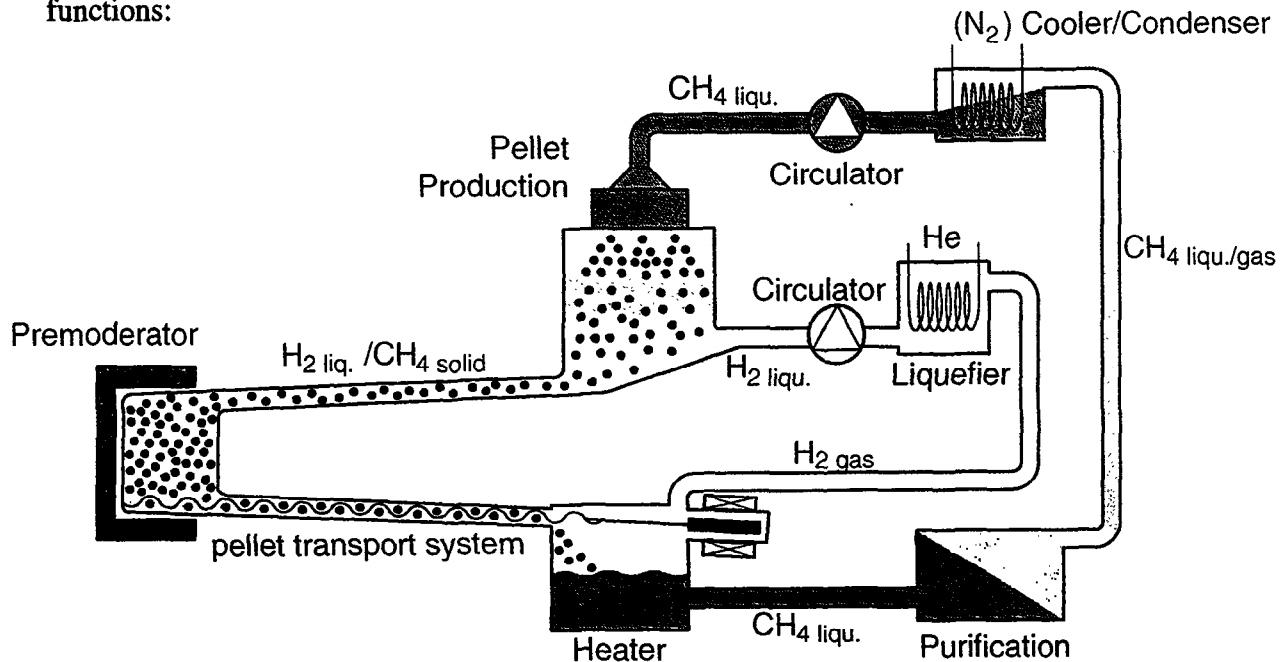

Figure 2: Pelletized methane moderator system with pellet production outside the radiation zone and pellet removal from the moderator canister by mechanical means. Melting of the pellets occurs outside the radiation zone, where also the hydorgen used to cool the pellets is separated. H_2 and CH_4 can be recirculated.

In the moderator vessel the pellets serve to slow the neutrons down, together with the liquid or supercritical hydrogen flowing between them. The heat deposited is removed by the flowing hydrogen. Hydrogen release from the pellets is not a concern because of the liquid hydrogen present. Radicals accummulated in the pellets may give rise to "burping" in individual pellets, but not in the whole system at the same time because

- the radiation load is not the same for all the pellets and

- the tempearture is not the same over the whole volume.

The pellets, together with the radicals and polymerization products trapped in them, are transported to a vessel outside the reflector. The rate of removal is controlled by a mechanical transport system. The methane is melted (polymerization of the radicals will proceed at this stage) and the H_2-gas is separated off by controlling the level of the melt in the vessel. The molten mixture of CH_4 and polymerization products is purified to obtain the remaining CH_4, which can be dumped or recirculated. CH_4 -gas is precooled (liquified) in a condenser and transported to the pellet-generating machine, where it is again immersed in the liquid hydrogen which is refrigerated in a separate circuit. The flow of liquid hydrogen is assumed to transport the pellets back to the moderator.

While this scheme reflects our present way of thinking, it may well be possible that some simplifications can be introduced in the course of a practical development program.
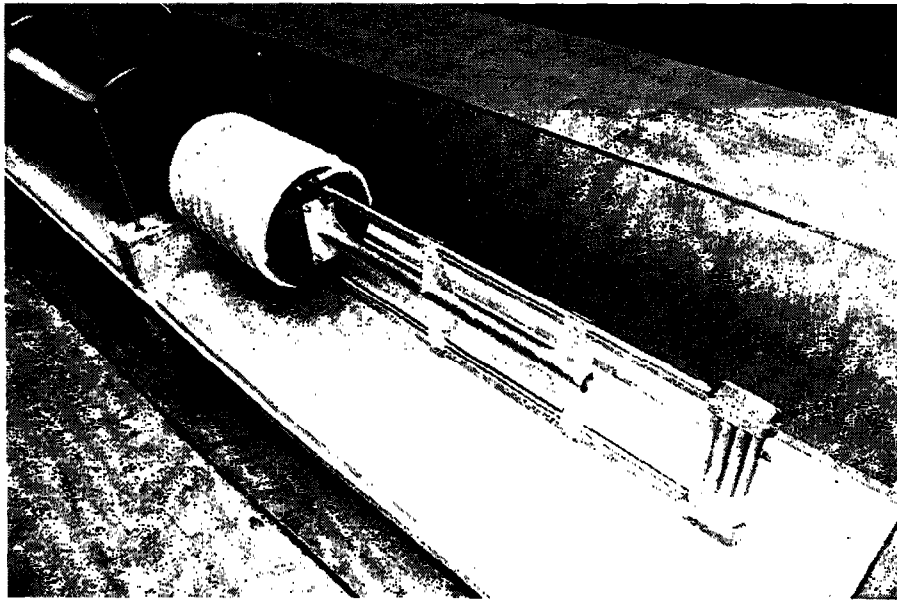

Figure 3: The water scatterer vessel at the PSI spallation neutron source SINQ. This vessel and holder plug can be replaced by a pelletized solid moderator as described.

7. Development Program

A practical working system would require a comprehensive, multidisziplinary R&D program involving computer modeling and analysis to examine the flow and heat transfer problems at various levels of the operation. It would also require a considerable experimentation and testing program together with an all-embracing safety and health physics involvement. It might be that such a work program could best be divided between two or more laboratories, each able to carry out tasks for which they are best qualified. A first-order task breakdown of the program would be as follows:

1) A basic study of the polymerization process using data from existing liquid and solid methane moderators. Possible radiation testing under controlled conditions might be considered. This would give a lead to the development of an optimum pellet size and residence time in the radiation field.

2) In parallel with the first task, a theoretical pellet size could be developed from the point of view of body heating and surface cooling. Practical aspects such as the initial forming and solidification, would have to be considered and an effort made to minimize internal voids.

3) Development of a reliable working system for producing the pellets continuously. In this regard, the very considerable work done by fusion groups might be applied. Pellet size and shape and some form of tolerance in each regard would be required before this task could be sensibly started.

4) Computer modeling of the loop systems would be used to examine the flow characteristics of a postulated configuration. This would include thermal and hydraulic considerations. A practical exercise of physical modeling using a surrogate fluid might be required.

5) Development of a final realistic model which would be designed for a specific operation in an existing facility. Suitable provisions have already been made in the SINQ spallation source now under construction at PSI. The water scatterer which would eventualle be replaced by a pelletized moderator system is shown in Fig. 3.

8. Conclusions

The practical feasibility of a system such as considered in this paper seems reasonable. Given sufficient time and effort, a working system based on these principles could be devised that would expand the capabilities of current cold neutron facilities. In light the of potential gains in neutron source performance with such a system, the development effort outlined above seems more than justified.

9. References

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