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An Advanced Cold Moderator Using Solid Methane Pellets

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Abstract

This paper reports developments of the pellet formation and transport technologies required for producing a liquid helium or hydrogen cooled methane pellet moderator. The Phase I USDOE SBIR project, already completed, demonstrated the production of 3mm transparent pellets of frozen methane and ammonia and transport of the pellets into a 40cc observation cell cooled with liquid helium. The methane pellets, formed at 72K, stuck together during the loading of the cell. Ammonia pellets did not stick and fell readily under vibration into a packed bed with a 60% fill fraction. A 60% fill fraction should produce a very significant increase in long-wavelength neutron production and advantages in shorter pulse widths as compared to a liquid hydrogen moderator. The work also demonstrated a method of rapidly changing the pellets in the moderator cell. The Phase II project, just now underway, will develop a full-scale pellet source and transport system with a 1.5L "moderator" cell. The Phase II effort will also produce an apparatus to sub-cool the methane pellets to below 20K, which should prevent the methane pellets from sticking together. In addition to results of the phase I experiments, the presentation includes a short video of the pellets, and a description of plans for the Phase II project.

1. Introduction

Existing and planned DOE neutron sources, such as IPNS and SNS, generate pulses of cold neutrons for materials research. The efficiency of the components which convert the fast neutrons to a cold neutron beam determines the usefulness of the facility. The existing solid methane moderator at IPNS has a high efficiency, but the design cannot be scaled to the high power levels planned for the SNS. A cold moderator concept using solid methane pellets, which would be capable of high power operation, was proposed by Lucas in 1988[1]; however, the technologies of producing and transporting the solid pellets has not yet been developed. CAFI has previously developed equipment to produce and transport solid hydrogen pellets for the DOE Fusion program. This paper reports the results of a USDOE SBIR Grant #DE-FG02-99ER82772 to extend these technologies to produce packed beds of solid methane pellets suitable for use as a high power pulsed moderator.

During the phase I project an apparatus was constructed which produced batches of approximately 1,000 high quality 3mm pellets of solid methane. A small liquid helium cooled observation cell was constructed to collect and sub-cool the pellets. The methane pellets,

produced at 73K, stuck together in clumps in the cell, preventing them from forming a tightly packed bed. Ammonia pellets were also produced, which had no signs of sticking to each other and produced a packed bed of pellets which could be fluidized with a vibrator. The packing density of the ammonia pellets was measured to be 60% which is typical of a closely packed bed. A method of rapidly melting the pellets and emptying the test cell was developed which will allow the replacement of the pellets in an operating moderator to occur in less than one minute. A full scale apparatus capable of producing pellets to fill a 1.5 liter test moderator cell was designed for construction during the phase II project.

Spallation neutron facilities typically have several moderators located around a target which operate at different temperatures to produce neutron beams of different energies to suit the needs of different experiments. The longest wavelengths, which are highly desirable for materials research, are produced by cold moderators which are typically refrigerated by liquid hydrogen. The efficiency of these moderators is in large part determined by the density of the hydrogen atoms in the moderator. The so-called advanced moderator materials [2,3,4] are characterized by having a higher hydrogen density than pure liquid hydrogen. Molecules such as methane (CH_4) and ammonia (NH_3) are of comparable size as pure hydrogen (H_2) but contain more hydrogen atoms.

Another desirable feature of advanced moderator materials is to have large numbers of vibrational and rotational states in the low energy range [2,3] so as to more efficiently absorb energy from the neutrons. Methane has several rotational energy transitions below 5 meV which results in superior thermalization properties. The increased density and thermalization properties yield an increase in neutron flux for solid methane.

Because of their superior properties, a number of solid methane moderators have been put into service [5,6]; however, there have been significant operational problems which have occurred in their use. A major problem is related to the molecular breakdown and polymerization of the methane molecule caused by the neutron irradiation. This process produces long chain polymerization products which can build up as tar like deposits [7,8] in the moderator vessel. Another problem are the pressure bursts which result from the spontaneous exothermic recombination of free radicals which accumulate in the solid methane. At low temperatures, due to their low mobility in the solid, the hydrogen and CH_3 radicals produced during the neutron irradiation can accumulate in the solid and build up until a critical concentration is reached at which point a rapid exothermic re-polymerization occurs [9]. The rapid temperature rise produces a pressure rise in the solid methane containers which has caused rupturing of the moderator vessel. To prevent this the moderator is periodically increased in temperature, allowing a controlled reaction to occur. This process is referred to as a burp since it releases a burst of hydrogen gas from the solid methane. This problem will be aggravated in future high power spallation sources such as the Spallation Neutron Source (SNS) now being designed. At the higher neutron fluxes the present procedure of burping a solid block type moderator would have to occur approximately once per hour.

A more fundamental problem, which is exacerbated by the poor thermal conductivity of solid methane [10], will be the removal of the heat being deposited in the moderator by the intense neutron beam. In previous pulsed neutron sources the heat deposited in the solid methane by the fast neutrons could be removed by thermal conduction through the solid methane block. To improve the thermal conduction aluminum fins or an aluminum felt matrix was interspersed with

the solid methane. However these methods will not be sufficient to remove the heat deposition of high power spallation sources.

In order to solve many of these problems, Lucas has proposed a moderator consisting of a bed of solid methane pellets [11] which are cooled by passing the refrigerant, such as supercritical hydrogen, directly through the pellet matrix. His calculations indicate that pellets smaller than 5mm radius could be adequately cooled at the power levels of the SNS. Furthermore by transporting the methane pellets in and out of the moderator, the methane could be externally processed, to continuously remove the free radicals and polymerization products. This work is focused on developing the enabling technologies required to produce and transport solid methane pellets for a pellet based cold moderator. In addition the research will also develop the feasibility of using ammonia pellets as a cold moderator system. While much more work has been done on the use of solid methane as an advanced cold moderator, ammonia does have several characteristics which could lead to a good moderator system. First, the neutron thermalization characteristics of ammonia [4] may be comparable to methane since it has a higher hydrogen density and also has low energy rotational modes. Second it has a higher melting point and a higher thermal conductivity, making the cooling characteristics better. Finally, the irradiation products [12] end with hydrazine (N_2H_4) so that the buildup of tar products may be eliminated.

A major drawback is that nitrogen 14 has a large neutron absorption cross section which would require the substitution of nitrogen 15 ammonia. Although expensive, N-15 ammonia at 99.9% purity is commercially produced. The present cost of the material to fill a moderator would presently be about \$50,000. Total recovery and recycling of the ammonia and catalytic conversion of the hydrazine back to ammonia could make a system feasible.

Phase I Results

Cryogenic Applications F, Inc. specializes in the development of technologies for freezing and handling cryogenic solids. Under a previous DOE SBIR (DE-FG05-94ER81734), a method of continuously producing high quality cryogenic pellets of frozen deuterium was developed as part of a low tritium inventory pumping and fueling system for fusion reactors. Machines capable of producing 6mm and 10mm diameter deuterium pellets were developed using both a closed cycle G-M refrigeration system and liquid helium as refrigerants. This pellet production technology was extended to the efficient production of frozen dry ice pellets for use in commercial refrigeration applications and as a pellet source for dry ice blasting machines. A machine capable of producing 30 kilograms per hour of 3mm diameter clear dry ice pellets was constructed using a cascade refrigeration system.

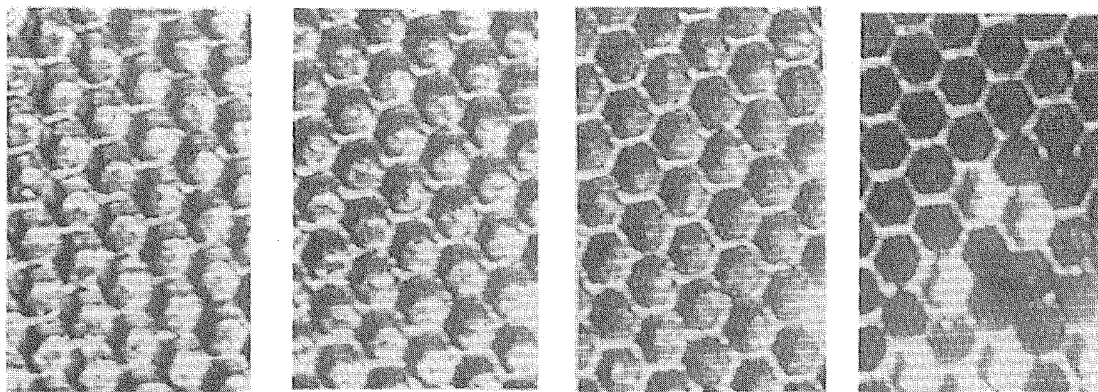
The process developed by CAFI (U.S. Patent # 6,000,332) produces high-density clear cryogenic ice by freezing gas directly to solid by reverse sublimation. The feedstock gaseous material is introduced to the freezing chamber below the triple pressure. The gas then freezes out onto a refrigerated surface maintained at a temperature below the equilibrium-vapor-pressure-temperature of the gas in the chamber. The gas thus condenses directly to solid on the cold surface. If the temperatures are far below the equilibrium point the ice forms as frost. However, by controlling the temperature of the cold surface close to the equilibrium temperature, the ice forms as a clear dense solid. The clarity of cryogenic ice is indicative of a defect free solid. An additional benefit is that since the ice forms directly into the solid phase, the voids formed in the process of freezing liquids (due to the density change of the liquid to solid transition) are eliminated.

To make pellets of the desired shape and size, the freezing surface is formed into an array of freezing cells similar to an ice cube tray so that the pellets are molded to shape. To prevent the ice in individual cells from growing together, the freezing cell array is engineered to have low conductivity barriers between the cells. The freezing cells are also positioned so that they are facing downward, so that the pellets grow upside down. The pellets are released from the freezing cells by warming the cells, causing the ice to detach and fall down and out of the cell. This process can be done either by warming the entire array, releasing a batch of pellets, or by heating and releasing individual cells. The process thus freezes and releases high quality pellets with no moving parts. The 6mm deuterium pellet machine previously constructed for fusion applications had an array of 127 freezing cells attached to a G-M refrigerator. This machine, which had the capability of individual pellet release, continuously produced 0.3 pellets/s at a temperature of 14K. A larger machine was produced to manufacture dry ice pellets which had approximately 500,000 freezing cells on 45 square feet of honeycomb freezing panels. This machine produced 30 kilograms of 3mm dry ice pellets per hour at a freezing temperature of 205K. For a flat-panel-honeycomb-array, the freezing time for 3mm methane pellet at a 5K temperature differential is about 25 minutes. A machine to produce 1 kilogram batches of 3mm diameter methane pellets would consist of about 6 square feet of honeycomb panels. It would require about 10L of liquid nitrogen to freeze a 1 kilogram batch of methane pellets.

A test apparatus to produce 3mm hexagonal cylindrical pellets in a stainless steel honeycomb array was constructed. A 10cmX10cm SS honeycomb with 3mm cell size was soldered to a 6mm copper plate flange. The copper plate was thermally connected to the first stage of a Gifford McMahon (GM) refrigerator by a flexible short copper cable. A set of resistance heaters were attached to both the copper plate and the GM first stage to allow for accurate temperature regulation of the copper plate. The GM refrigerator was chosen for use in the phase I project over a liquid nitrogen cooling system due to its flexibility in operating at a broad range of temperatures, especially for producing methane at low pressures.

The methane pellets were formed from high purity gas. A 20 liter SS gas storage vessel instrumented with a high accuracy 5000 Torr capacitance manometer (MKS Baratron) was filled with the gas to be condensed in the honeycomb. An MKS gas flow-controller was used to meter the gas into the pellet growing chamber. A 100Torr capacitance manometer monitored the pressure in the growing chamber. The pellets were grown, by controlling the gas feed rate to obtain a relatively constant growing pressure and adjusting the refrigeration system to maintain the copper plate at a temperature slightly below the equilibrium condensing temperature. The pellet length could be controlled by adjusting the dose of gas supplied during the growth phase. The methane pellets were grown in 28 minutes. The release of the pellets from the honeycomb is achieved by warming the copper plate while maintaining sub triple point pressure in the growing chamber with a vacuum pump. The defrost cycle for the 3mm methane pellets was completed in 10 minutes, resulting in a complete grow-defrost cycle of 38 minutes. Figure 1 shows a time sequence of the pellets growing in and releasing from the honeycomb. The pellets sublime at the metal/solid interface and fall down and out of the honeycomb. The methane pellets were well formed and transparent, which is indicative of high quality ice, however the pellets were very sticky at the formation and release pressures tested, which were as low as 6 Torr and 70K which is well below the triple point of 90 Torr and 89K.

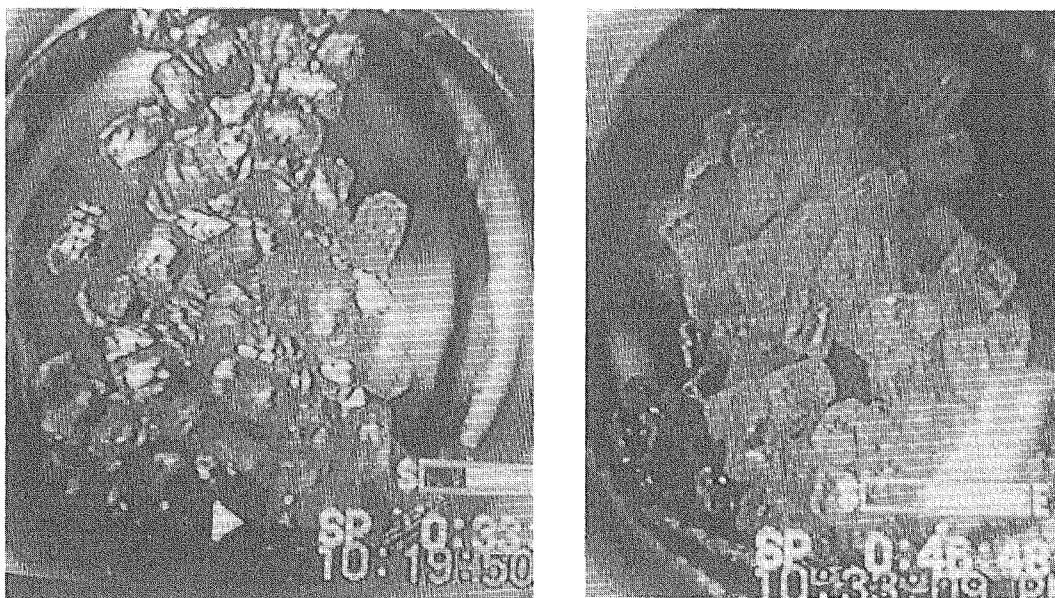
Figure 1. Methane pellets growing in a 3mm SS honeycomb panel. From left: empty honeycomb; 20 minutes into the growth cycle; 30 minutes, at the start of defrost cycle; 35 minutes, near the end of the release cycle.



In order to test the capability of cooling the pellets to liquid helium temperatures and to determine the packing density of the pellets in a moderator, an apparatus was constructed to collect the pellets in a small cell. A 42cc cylindrical or drum shaped stainless steel chamber was fabricated with indium sealed Pyrex windows forming the drum faces which faced the sides of the apparatus. A pellet feed tube was welded to the top of the drum cylinder and a drain tube was welded to the bottom of the cylinder. The bottom of the cylinder was lined with a metal screen which prevented the pellets from exiting the cell. The cell attached to the feed tube was suspended in a 4" diameter tube with conflat room temperature windows in line with the indium sealed cryogenic windows so that the pellets could be viewed in the cell. A liquid helium transfer tube with a metering valve in the dewar end could be inserted into the feed tube to allow liquid helium to flow through the cell and out the drain tube. The pellets drop out of the honeycomb, are collected by a funnel, pass through a gate valve, down the feed tube into the observation cell. Due to the stickiness of the methane pellets, the pellets did not fill the cell, but stuck together forming a column up into the feed tube as shown in Figure 2.

Attempts at sub-cooling the pellets with liquid helium as they dropped through the 12" long feed tube failed since the pellets would then stick to the cold tube walls. An attempt to try to break up the pellet clump with a stirring stick also failed. However, the pellets which did collect in the cell were successfully cooled down to 4.3K by flowing liquid helium over and through them which is also shown in Figure 2. This experiment did however show that the pellets could be cooled without thermal fracturing. Also there were some pieces which were not stuck to the mass of pellets which remained free, indicating that the pellets were not sticky at liquid helium temperature.

Figure2. Left, methane pellets sticking together in the observation cell. Right methane pellets with liquid helium flowing through the observation cell.



Since the simple attempts at unsticking the pellets were not successful and since it became obvious that developing a sub-cooling apparatus was beyond the time scale of the Phase I project, further attempts were abandoned in favor of the production of ammonia pellets.

The ammonia pellets were produced with the same apparatus operating at around 180K. A dramatic difference in the ammonia pellets was the total lack of the stickiness, as compared to the methane pellets, even though they were produced closer to the triple pressure than the methane pellets. The ammonia pellets behaved fluidically, filling the test cell. A vibrator, attached to the apparatus was used to settle the pellets and produce a well packed fluidized bed. Figure 3 shows a batch of ammonia pellets just prior to and after turning on the vibrator. Once the vibrator was turned on the pellets immediately flowed, filling the cell as a fluid would.

The test cell apparatus was designed to be able to measure the packing density by capturing the gas evaporating from the pellets into the 20 liter gas tank. This was done by first evacuating the tank, then valving the test cell from the growing chamber into the gas tank. After the system equilibrated to room temperature, the gas tank Baratron gauge could determine the number of moles of gas in the system. The pellet bed volume was determined by the dimensions of the test cell and by determining the filling fraction of the cell from the videos of the pellet bed. Two measurements were done, a run producing 3mm long pellets had a 62% filling fraction and a run with 4mm long pellets had 58%. While these may be within the experimental error, the 3 mm pellets seemed to pack better since their length matched the diameter. Figure 4 shows three batches of ammonia pellets grown to different lengths.

Figure 3. 3mm Ammonia pellets before(left) and after(right) turning on the vibrator.

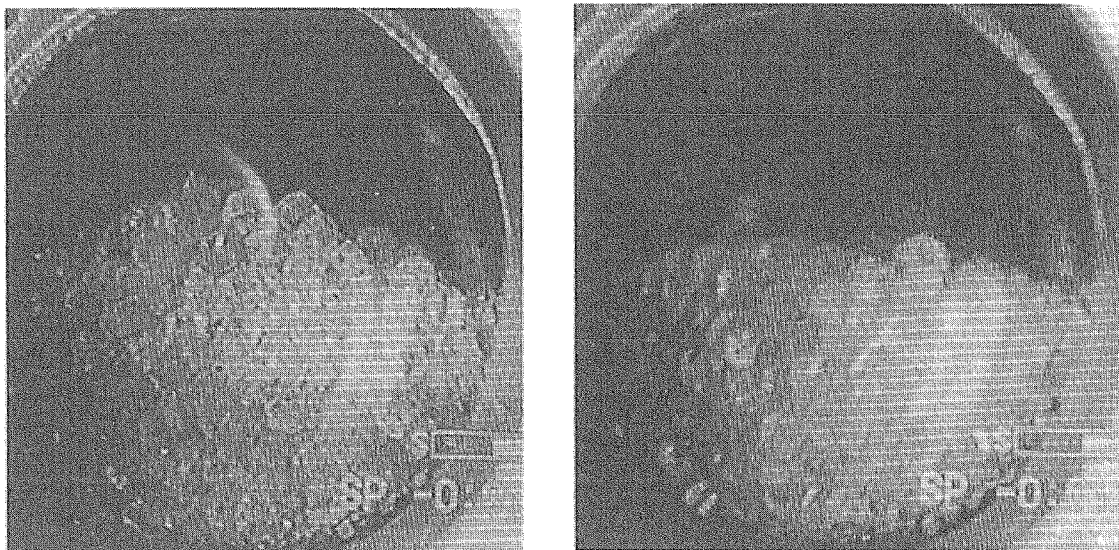
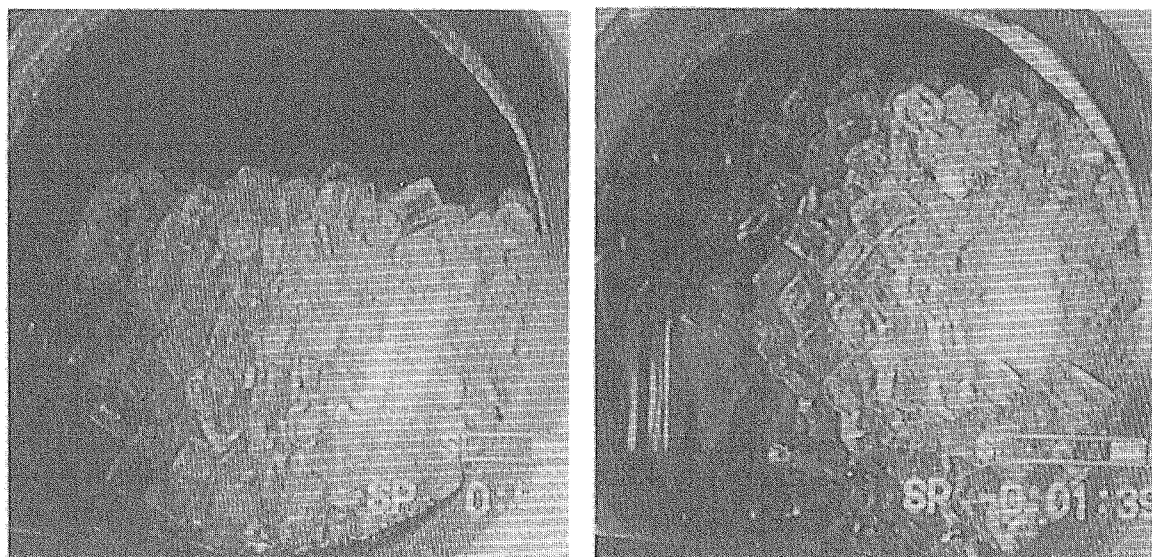


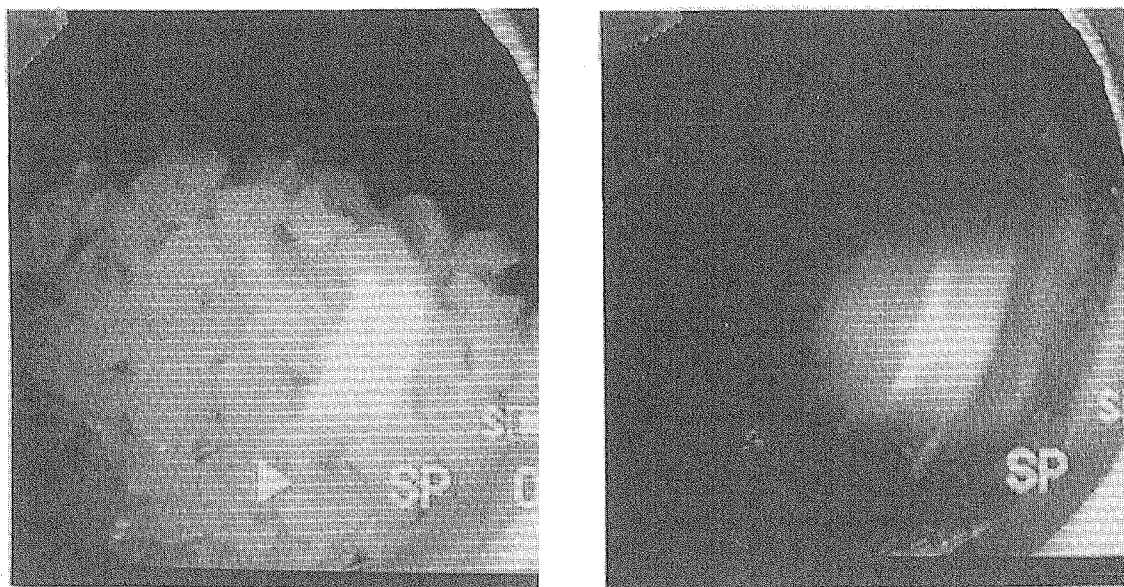
Figure 4. Left, 3X3.1mm ammonia pellets with 62% packing density. Right 3X3.6 mm ammonia pellets with 58% packing density.



Another test performed on the pellet bed was to determine the time it took to melt the pellets, blow out the test cell, and pump it back down. This procedure was first tried by blowing room temperature helium gas through the bed, however this tended to transfer the pellets mass downstream where it could freeze up the exhaust tube. A much faster and robust system was developed. Rather than helium gas, the pellet gas, i.e. ammonia gas for ammonia pellets, was injected into the cell raising the pressure above the triple point. This produced a near

instantaneous melt of the pellet bed since the heat transfer by condensation is very large and the heat of liquefaction is four times greater than the heat of solidification. Figure 5 shows the cell with ammonia pellets just prior to and 6 seconds after the admission of ammonia gas, during which the pellets have been melted and blown out of the cell.

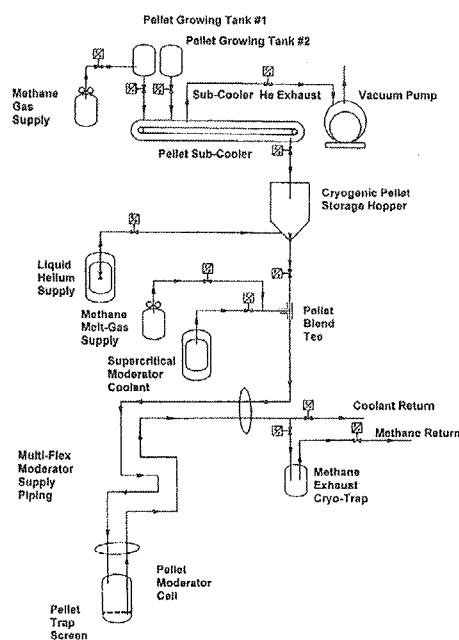
Figure 5. Flash Melt Process. Left, ammonia pellets just prior to the injection of ammonia gas. Right, The empty cell 6 seconds later, the pellets have melted and the liquid has blown out of the cell.



As a final part of the phase I project a conceptual design of a full scale pellet moderator system which could be constructed and tested during the phase II program was developed. A schematic diagram of the proposed pellet moderator system is shown in Figures 6. It consists of :

1. A pelletizer to fabricate 3mm pellets of either methane or ammonia capable of producing 1.5 liters of pellets per hour. The pelletizer will have two growing chambers with a total of six square feet of honeycomb panels refrigerated with liquid nitrogen.
2. A pellet sub-cooler which will efficiently lower the temperature of the pellets from their formation temperature, near the triple point temperature, to below 20K. The sub-cooler is designed to prevent the methane pellets from sticking to each other during the cooling

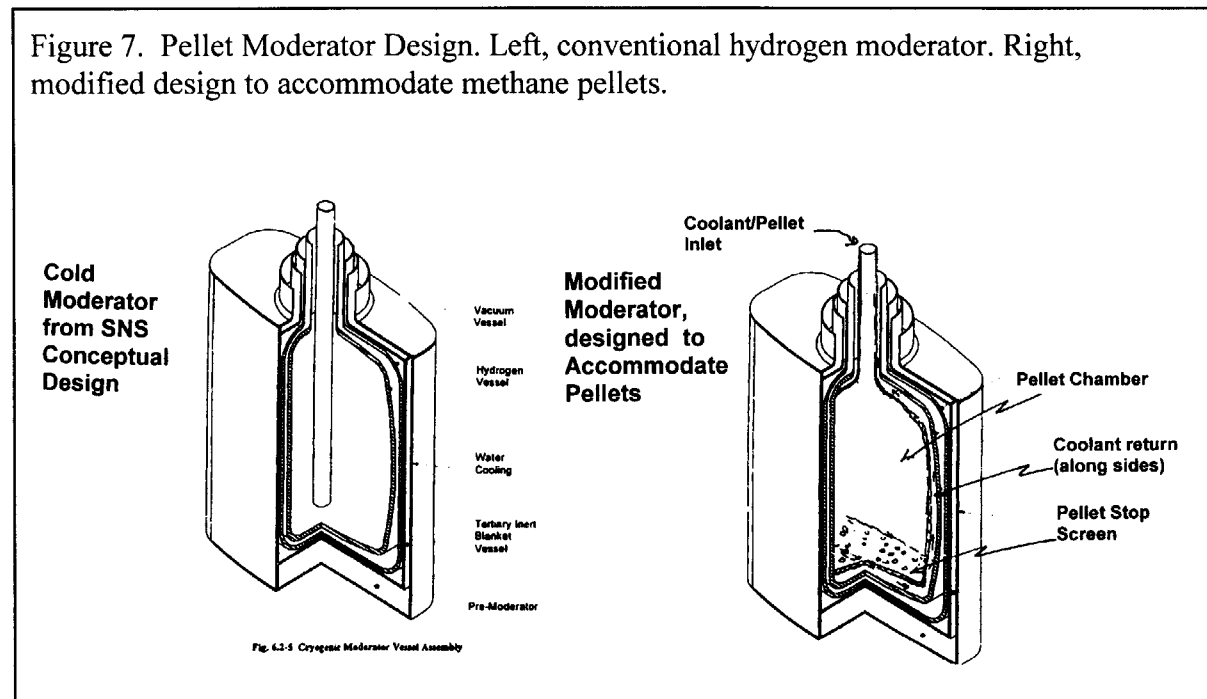
Figure 6. Methane Pellet Moderator Process Schematic.



process. At 20K, the sub-cooled pellets should be able to be stored and transported without sticking.

3.3 A liquid helium cooled cryogenic storage hopper which will accumulate and store 1.5 liters of pellets at a temperature below 20K.

3.4 A prototype moderator cell which will be of similar design and shape as those proposed for the SNS. The cell will be designed so that the pellets entering the cell entrained in the coolant will be trapped in the cell and will fill the cell uniformly, with a high packing density. The cell will further be designed to allow melted pellets to be blown out of the cell through the refrigerant return line. The test moderator cell is patterned after the cold moderator conceptual design of the SNS project. Since the pellets can be transported in a fluid like state, there are only a few relatively minor changes required to convert a conventional liquid hydrogen moderator to one that can accommodate pellets as shown in Figure 7.



One change was to have the inlet tube feed the top of the moderator with the coolant exhaust flowing out the bottom and up the sides of the moderator. A second change was to install a false bottom in the liquid hydrogen portion of the cell which is designed to block the pellets from exiting the cell and also will be designed, by adjusting the hole pattern, to produce an even flow of coolant through the bed of pellets.

The filling of the moderator cell will occur by pneumatic conveyance of the pellets entrained in the coolant flow. At the start of the fill cycle the coolant flow will be on and the hopper plug valve opened allowing the pellets to stream out of the hopper down a vertical tube of similar size to the coolant hose. At a point downstream from the hopper the coolant gas flow will join the tube at a T provided with an aspirator collar so that the coolant enters the pellet flow coaxially. The pellets are then carried with the coolant and, depending on the gas flow velocity, can travel

around bends and actually uphill. The time to fill the moderator cell will be determined primarily by the time required to empty the hopper which we estimate, based on our experience with dry ice pellets, should take 18 seconds.

Emptying the pellets from the moderator cell will be demonstrated by the rapid melt process demonstrated in part during the phase 1 experiments. To accomplish this, the coolant flow will be interrupted by closing the inlet valve, allowing depressurization and then closing the exhaust valve. The pellet hopper will also be isolated by closing the outlet gate valve. Room temperature pressurized methane (ammonia for ammonia) gas will then be injected just below the closed coolant inlet valve through the moderator cell and allowed to exhaust through a valve located just upstream from the closed coolant return valve. Due to the large heat of liquefaction of the methane gas condensing on the cold pellets, the pellets will rapidly melt. This process took less than 5 seconds during the Phase 1 tests. At a methane gas flow rate of 0.26 kg/s the gas velocity in the coolant return line will be about 150m/s. At this velocity the liquid methane in the moderator cell will be blown out and carried with the methane gas through the coolant return line in the mist flow regime. In this regime the gas velocity is great enough to break the liquid into a fine mist and carry it through a vertical pipe in up-flow. When the exhaust temperature of the methane reaches significantly above the liquefaction point, the methane gas injection will be terminated and the residual methane gas will be evacuated with a vacuum pump. The helium coolant will then be valved back in recooling the moderator and inlet lines. Once the moderator reaches operating temperature, a new batch of pellets will be introduced from the hopper. The complete emptying and refilling cycle should be accomplished in about 43 seconds (5 second melt + 5 second blowout +3 second purge, +12 second cool-down + 18 second refill).

Summary

The purpose of the project is to establish the enabling technologies required to produce and transport solid methane pellets for an open-bed-pellet cold moderator. The phase I project has demonstrated the production of high quality methane and ammonia pellets which would be suitable for use in a pellet cold moderator. The phase I project has also shown that the methane pellets, at temperatures of 72K are sticky, causing them to stick to each other and to cold surfaces. The Phase I project demonstrated that ammonia pellets, which were not sticky, could be transported into a freezing cell and fluidized with a vibrator to form a bed of pellets with a packing density of up to 62%. This is equal to the packing density achieved in hoppers filled with fluidized uniform spheres. The phase I project demonstrated the sub-cooling of both the methane pellets and the ammonia pellets to temperatures below 20K with no apparent degradation of the pellets. The phase I project produced a design of a pellet apparatus which will be capable of producing either methane or ammonia pellets at a rate sufficient to supply a pellet moderator which is changed out every 90 minutes. The phase I project has designed an apparatus which will allow methane pellets to be cooled to temperatures below 20K while minimizing the pellets sticking together. This will allow methane pellets to be transported and fill a moderator at the packing densities obtained with ammonia. The sub-cooler will also efficiently cool both methane and ammonia pellets while minimizing liquid helium consumption. The phase I project has designed a cold moderator cell for use with pellets which has minimal changes to the supercritical hydrogen cold moderator cells planned for SNS. The phase I project has demonstrated a simple method of rapidly melting and blowing out the pellets in a moderator cell. The phase I project has designed a pellet transport system which will allow a pellet bed to be removed and replaced in a time of 43 seconds. Replacing the pellet bed every 90 minutes will allow a beamline availability of 99%. To these ends the Phase I project has demonstrated the

technical feasibility of the concept and has produced a design of a system, to be constructed and tested in the phase II project, which will demonstrate the operation of a full size pellet cold moderator.

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