# DEVELOPMENT OF OPTIMUM PROCESS FOR ELECTRON BEAM CROSS-LINKING OF HIGH DENSITY POLYETHYLENE THERMAL ENERGY STORAGE PELLETS, PROCESS SCALE-UP AND PRODUCTION OF APPLICATION QUANTITIES OF MATERIAL

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## PROJECT OUTLINE

Project Title: Development of an Optimum Process for EB Crosslinking of HDPE TES Pellets

Principal Investigator: I. O. Salyer

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Project Goals: Develop a thermal energy storage system based on thermally form-stable pellets of crosslinked high-density polyethylene (HDPE) prepared by electron beam (EB) irradiation.

The optimum EB irradiation conditions for HDPE having the highest possible heat of fusion will be identified. A 250-lb batch of the optimum material will be prepared and evaluated in a 12,000-BTU pilot storage unit. If the evaluation proves promising, a 15,000-lb batch will be prepared, tested, and delivered to DOE (ORNL) for full-scale application tests.

Project Status: DuPont 7040 and 8 megarads have been selected as the optimum HDPE and dose, respectively. The 250-lb batch has been prepared.

Contract Number: Union Carbide Contract No. 7641

Contract Period: January 1979 - January 1980

Funding Level: $55,000

Funding Source: Oak Ridge National Laboratory

PROJECT SUMMARY

Project Title: Development of Optimum Process for Electron Beam Crosslinking of High Density Polyethylene Thermal Energy Storage Pellets, Process Scale-up and Production of Application Quantities of Material.

Principal Investigator: Ival O. Salyer

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Project Goals: The objective of this project is to define the electron beam irradiation conditions for preparing thermally form stable polyethylene pellets for a thermal energy storage application in the temperature interval of 120-140° Celsius.

Project Status: The objective of preparing thermally form stable crosslinked polyethylene has been achieved by electron beam irradiation. The irradiated polyethylene pellets have retained their initial physical form and heat of fusion after more than 100 melt-freeze cycles in ethylene glycol. Although the pellets adhere to one another at their points of contact, the pellet bed has remained porous to the free flow of the heat exchange fluid. Tests of the polyethylene pellet bed have been completed in the five pound thermal energy storage test unit. Sufficient polyethylene has been processed by electron beam irradiation to complete the planned tests in the 250 pound prototype thermal energy storage unit. We plan to complete these tests in the 250 pound unit and issue a final report in January 1980.

Contract Number: 9641

Contract Period: 5 January 1979 - 4 January 1980

Funding Level: $54,585

Funding Source: Department of Energy, Division of Energy Storage Systems, Oak Ridge National Laboratory

## INTRODUCTION

The University of Dayton is conducting a program whose purpose is to investigate the crosslinking of high density polyethylene by electron beam irradiation. The objective of the program is to define the conditions required to prepare thermally form stable high density polyethylene by electron beam irradiation. High density polyethylene has a melting point in the temperature interval of 125-140° Celsius and values for the latent heat of fusion has been reported as high as 49 calories per gram. At its melting point, the high density polyethylene changes from a white opaque crystalline solid to a clear transparent visco-elastic liquid phase. This property was especially useful in visual observations of the pellet bed in the thermal energy storage test column. The melting temperature of polyethylene makes it especially suited for solar absorption air conditioning. Further, polyethylene melts congruently and can be cycled repeatedly through its melting point with no decrease in the value of the heat of fusion. Although solar air conditioning provides an important application and supplied the initial impetus for this investigation, the thermal storage capability of high density polyethylene should be considered for applications which will utilize the off-peak electric generating capacity and/or solar heating applications.

In a previous investigation crosslinking of polyethylene by chemical methods were investigated. The crosslinked polyethylene products were found to have excellent thermal form stability and retained their initial value of the heat of fusion after more than 400 cycles through the melting point. These chemical methods are at least as effective as the polyethylene products crosslinked by electron beam irradiation but only at much higher costs per pound of finished product. The cost for preparing polyethylene cross-linked by electron beam irradiation are estimated to add between 0.5 and 1.0 cents per pound to the cost of the polyethylene. In comparison to other materials being considered for thermal energy storage, polyethylene will require a significantly smaller volume and weight than systems which utilize only sensible heat as the storage mechanism. Importantly, polyethylene can deliver this heat energy which is stored in the change of phase at temperatures between 125° and 140° Celsius.

## EXPERIMENTAL

The principal objective of this project has been to define the irradiation conditions required to prepare thermally form stable high density polyethylene (HDPE). This objective has been achieved through the following experimental tasks.

1. Evaluate the heat of fusion and the melting temperature of several commercially available HDPE specimens as they are delivered by the manufacturer. It should be noted that HDPE products presently available have not been optimized on the basis of the value of their heat of fusion. Values as high as 58 calories per gram, or even higher, may be possible in HDPE which is more completely crystallizable.

2. Select HDPE specimens for electron beam irradiation exposures, and irradiate the selected materials to several different radiation dosage levels.

3. Evaluate the irradiated HDPE specimens for their thermal form stability, retained heat of fusion, and their melting temperature.

4. Select the irradiation conditions for which the HDPE specimens are thermally form stable, cycle irradiated HDPE samples through the melting point in a five pound thermal energy storage test column.

5. Evaluate the performance of the HDPE specimens in the five pound thermal energy storage test column.

6. Irradiate HDPE pellets for cyclic testing through the melting point in the 250 pound prototype thermal energy storage test unit.

7. Evaluate the performance of the irradiated HDPE specimens in the 250 pound test unit.

A total of 13 different commercially available high density polyethylene specimens were obtained from five different manufacturers. Listed in Table 1 are the names of the suppliers, the type of high density polyethylene, and the nominal physical property values supplied by the manufacturer. The polyethylene specimens were supplied in the form of pellets approximately 0.125 inches in diameter with the single exception of the Phillips Marlex TR-885 which was supplied in both pellet and powder forms.

We conducted experimental measurements of the melting temperature and the heat of fusion on each of these 13 specimens. These measurements were performed in our Perkin-Elmer Differential Scanning Calorimeter, Model DSC-2. The HDPE samples were contained in the standard Perkin-Elmer aluminum pans and a nitrogen atmosphere was maintained around the sample during the measurement. Measurements of the melting temperature and the heat of fusion were performed between 25 and 150 degrees Celsius at heating and cooling rates of 10 degrees Celsius per minute. The instrument was calibrated by measuring the area under the time-temperature scan during the melting of a measured quantity of high purity indium.

The melting and freezing of the polyethylene specimens were observed to occur over a range of temperatures. The results of these measurements are presented in Table 2. The values of the temperatures, $T_1$, $T_2$, and $T_3$, are the values respectively, at which the transition was observed to begin, the temperature at which the maximum displacement was observed in the time-temperature plot, and the temperature at the end of the transition. An analysis of the time-temperature scans showed that more than 90 percent of heat of the transformation occurred within ±2 degrees Celsius of the temperature, $T_2$, even though the heating and cooling rates were 10 degrees Celsius per minute.

Four of the commercial polyethylene products were selected for the electron beam irradiation experiments. These products were, the DuPont 7040 pellets, the Phillips TR-885 pellets, the U. S. Industrial Chemicals LS-630 pellets, and the Gulf 9606 pellets. The three variables associated with the electron beam irradiation which were studied in our tests were:

1. the total radiation dose received by the pellets,
2. the accelerating potential of the electron beam,
3. the electron beam current,
4. the irradiation in inert atmospheres, and
5. the effects of stirring the pellets during the irradiation.

The HDPE pellets were irradiated at the electron beam facility of the Radiation Dynamics Incorporated located in Plainview, New York. Samples of the HDPE pellets supplied by the four different manufacturers were irradiated with an electron beam accelerating potential of three million volts and at an electron beam current of 20 milliamperes to radiation doses of 2, 4, 6, 8, 10, or 12 megarads for a total of 24 irradiated samples. Tests were performed at electron beam currents of 10.3 milliamperes and 5.65 milliamperes. In these two tests the HDPE pellets were irradiated to a total dose of eight megarads in the three million volt facility. Tests were performed with accelerating potentials of 1.5 and 4.5 million volts. In these tests HDPE pellets were irradiated to a total dose of eight megarads in the 1.5 and 4.5 million volt facilities and to 12 megarads in the 1.5 million volt facility. The effect of stirring the pellets during the irradiation processing was studied at three million volts, 20 milliamperes, and at an eight megarad dose. Irradiation exposures were performed with the pellets under three different atmospheres, helium, nitrogen, and carbon dioxide. Two samples were irradiated under the carbon dioxide atmosphere. In one case the HDPE pellets were given a pre-irradiation heat treatment at 100° Celsius for 12 hours in the carbon dioxide atmosphere and in the other case they were irradiated without the benefit of the heat treatment.

The irradiated polyethylene pellets were evaluated for their thermal form stability; and the values for their melting points and their retained heats of fusion were measured in the Differential Scanning Calorimeter. The thermal form stability of the irradiated pellets was evaluated by placing a small quantity of the pellets, approximately 30 gram samples, in refluxing ethylene glycol, Prestone II. The pellets were maintained in the ethylene glycol at temperatures between 145° Celsius and 165° Celsius for extended time intervals. These tests showed that DuPont 7040 pellets maintain satisfactory thermal form stability at radiation dose levels of eight megarads. Stirring of the pellets during the irradiation process appeared to be beneficial. The thermal form stability of the irradiated pellets was unaffected by changes in either the electron beam current or the electron beam accelerating potential. There was some improvement in the pellets which were irradiated under the inert atmospheres. The pre-irradiation heat treatment at 100° Celsius under the carbon dioxide atmosphere minimized the adhesion of the pellets at their points of contact. Typical results of these tests are shown in Figure 1.

The values for the heats of fusion and melting temperatures which were measured on the irradiated pellets are presented in Table 3. No significant change was observed in the values of the melting temperature of the polyethylene pellets as a function of the radiation dose. All of the irradiated pellets show a trend toward slightly lower values for the heat of fusion with increasing radiation dose levels.

Three irradiated polyethylene materials were evaluated in the five pound thermal energy storage test column. The materials which were tested are the DuPont 7040 pellets, the U. S. Industrial Chemicals LS-630 pellets, and the Gulf 9606 pellets. All of the pellets had received an eight megarad dose in the electron beam. The temperatures of the ethylene glycol were measured as a function of time at the inlet and outlet ports of the thermal energy storage column, and the temperature within the polyethylene pellet bed was measured at a point which was located approximately six inches from the inlet port. This distance is one third of the length of the storage column. The five pound thermal energy storage test unit is shown in Figure 2. The polyethylene pellet bed was cycled between 100° Celsius and 145° Celsius through more than 100 complete cycles. The melting and freezing of the pellet bed was observed by the thermal arrest of the thermocouples. The melting and freezing of the pellet bed was confirmed by a visual observation of the pellet bed through an observation port in the side of the storage column. A typical plot during the cooling cycle of the temperatures at the inlet and outlet ports and within the pellet bed itself is presented in Figure 3. As shown in this figure the temperature of the ethylene glycol at the inlet port drops rapidly to 100° Celsius. The temperature measured within the

pellet bed shows the thermal arrest as the pellet bed freezes at that point, and the temperature of the ethylene glycol at the outlet port remains at the freezing temperature of the pellet bed until the solidification of the polyethylene is completed. The completion of the freezing of the pellet bed is observed by the rapid drop in temperature of the ethylene glycol at the outlet port of the storage column. The time-temperature plots of the storage column after more than 100 cycles were compared to the time-temperature plots which were measured before the accumulation of the heating and cooling cycles. This comparison of the performance of the storage column before and after the cycling tests did not show any significant differences. The condition of the pellets after their removal from the storage column is shown in Figure 4. Although the pellets had adhered to one another at their points of contact, the pellet bed had maintained an open porous structure throughout the thermal cycling tests. The pellet bed did not exhibit any increased resistance to the flow of the ethylene glycol as the number of heating and cooling cycles increased.

The DuPont 7040 pellets with a radiation dose of eight megarads were selected for evaluation in the 250 pound prototype thermal energy storage unit. This unit is shown in Figure 5. The apparatus has been installed and is ready for the scaled-up tests of the performance of the polyethylene pellet bed. A sufficient quantity of the DuPont 7040 pellets have been irradiated to a dose of eight megarads to completely fill the 250 pound unit. The irradiation of the pellets was accomplished at the Radiation Dynamics Incorporated electron beam facility. We expect to begin this series of thermal cycling tests this week.

## RESULTS

During the course of this project we have established:

1. that the crosslinking of the polyethylene is dependent primarily on the total radiation dose of the material and is not dependent either on the accelerating potential of the electrons or the electron beam current,

2. that polyethylene pellets irradiated to a dose of eight megarads have sufficient thermal form stability and retained heat of fusion to be utilized as a thermal energy storage material,

3. that the polyethylene pellets can be satisfactorily irradiated in air. Pellets irradiated in carbon dioxide or nitrogen atmospheres show less propensity to adhere together after being thermally cycled above their melting point,

4. that the heat of fusion of the irradiated pellets shows a trend toward slightly lower values with increasing value of the radiation dose,

5. no change was observed in the melting point of the pellets with increased radiation doses,

6. that the irradiated pellets will adhere at their points of contact in an unstirred pellet bed when heated above their melting point; in a stirred bed the pellets do not adhere together even when heated above their melting points for extended time periods, and

7. that pellets irradiated to a dose of eight megarads will maintain an open porous structure even after repeated thermal cycling through their melting point. Free flow of the heat transfer fluid through the pellet bed was observed after more than 100 cycles through the melting point of polyethylene.

Future Work: Based on the encouraging results we have obtained on the electron beam irradiation of high density polyethylene we recommend that Task 3 be implemented. The objective of Task 3 is the preparation of 15,000 pounds of electron beam crosslinked polyethylene pellets, the evaluation of the crosslinked material on a laboratory and pilot plant side, and the implementation of a full-scale applications test.

Acknowledgement: This work was performed at the University of Dayton under ORNL Sub 9641 by the following personnel: I. O. Salyer, J. E. Davison, R. Chartoff, and J. E. Minardi. The electron beam irradiation of the polyethylene pellets was performed in the facilities of the Radiation Dynamics Incorporated at Plainview, New York.

TABLE 1

HIGH DENSITY POLYETHYLENE SPECIMENS
RECEIVED FOR EVALUATION

| | Supplier | High Density Polyethylene | Melt Index* dg./min. | Density* g/cc |
|---|---|---|---|---|
| 1. | DuPont | Alathon 7040, Pellets | 6.0 | 0.96 |
| | | Alathon 7050, Pellets | 17.5 | 0.96 |
| 2. | Phillips Petroleum | Marlex TR-885, Powder | 30 | 0.964 |
| | | Marlex TR-885, Pellets | 30 | 0.964 |
| | | 6006, Pellets | 0.7 | 0.958 |
| | | 6030, Pellets | 3 | 0.960 |
| 3. | U. S. Industrial Chemicals Co. | LS-556, Pellets | 8 | 0.955 |
| | | LS-606, Pellets | 10 | 0.962 |
| | | LS-630, Pellets | 32 | 0.962 |
| 4. | Dow | 8064, Pellets | | |
| | | 1-12065, Pellets | | |
| | | 4-2060, Pellets | | |
| 5. | Gulf | 9606, Pellets | | |

*nominal values supplied by vendor

TABLE 2

MELTING TEMPERATURE AND ENTHALPY OF FUSION
OF HIGH DENSITY POLYETHYLENE SPECIMENS

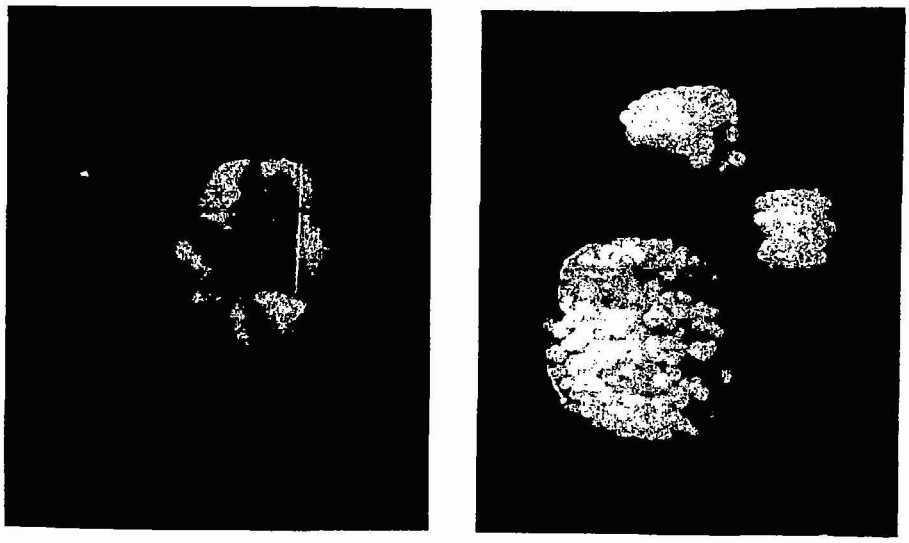
| Sample | Heating Cycle | | | | Cooling Cycle | | | |
|---|---|---|---|---|---|---|---|---|
| | Temp. °K | | | Enthalpy of fusion cal/g | Temp. °K | | | Enthalpy of fusion cal/g |
| | $T_1$ | $T_2$ | $T_3$ | | $T_1$ | $T_2$ | $T_3$ | |
| 7040 | 382 | 408 | 412 | 46.2 | 393 | 388 | 364 | 48.2 |
| 7050 | 385 | 406 | 410 | 47.3 | 393 | 387 | 370 | 44.2 |
| TR-855, Powder | 384 | 406 | 409 | 47.6 | 395 | 390 | 369 | 50.5 |
| TR-855, Pellets | 388 | 407 | 410 | 46.6 | 394 | 390 | 377 | 46.0 |
| 6006 | 384 | 411 | 420 | 47.1 | 398 | 392 | 365 | 49.1 |
| 6030 | 383 | 408 | 412 | 44.4 | 396 | 392 | 368 | 47.4 |
| LS-556 | 385 | 406 | 410 | 38.2 | 393 | 390 | 377 | 41.2 |
| LS-606 | 384 | 407 | 410 | 45.6 | 395 | 391 | 372 | 44.6 |
| LS-630 | 381 | 407 | 411 | 47.3 | 394 | 390 | 367 | 45.6 |
| 8064 | 390 | 407 | 411 | 43.7 | 394 | 389 | 375 | 43.2 |
| 1-12065 | 387 | 407 | 411 | 40.5 | 395 | 390 | 370 | 42.2 |
| 4-2060 | 389 | 406 | 410 | 42.4 | 393 | 386 | 372 | 43.4 |
| 9606 | 370 | 405 | 410 | 45.6 | 394 | 389 | 360 | 43.3 |

TABLE 3

THE ENTHALPY OF FUSION AND THE MELTING TEMPERATURE OF HDPE PELLETS AS A FUNCTION OF ELECTRON BEAM IRRADIATION

| Sample | Radiation Level megarad | Heating Cycle Temp. °K $T_1$ | $T_2$ | $T_3$ | Enthalpy of Fusion cal/g | Cooling Cycle Temp. °K $T_1$ | $T_2$ | $T_3$ | Enthalpy of Fusion cal/g |
|---|---|---|---|---|---|---|---|---|---|
| 7040 | as received | 382 | 408 | 412 | 46.2 | 393 | 388 | 364 | 48.2 |
| | 2 | 373 | 408 | 412 | 42.8 | 393 | 388 | 362 | 40.5 |
| | 4 | 373 | 408 | 414 | 43.2 | 393 | 387 | 361 | 40.9 |
| | 6 | 371 | 406 | 411 | 39.9 | 393 | 387 | 362 | 38.8 |
| | 8 | 369 | 407 | 411 | 42.9 | 393 | 388 | 363 | 40.1 |
| | 10 | 373 | 405 | 410 | 40.4 | 393 | 387 | 361 | 40.0 |
| | 12 | 371 | 405 | 410 | 37.9 | 393 | 387 | 363 | 35.7 |
| | 8[1] | 373 | 406 | 412 | 38.0 | 393 | 387 | 368 | 36.6 |
| | 8[2] | 373 | 406 | 412 | 39.8 | 392 | 386 | 363 | 38.8 |
| | 8[3] | 373 | 404 | 409 | 37.9 | 393 | 387 | 364 | 36.4 |
| TR-885 | as received | 388 | 407 | 410 | 46.6 | 394 | 390 | 377 | 46.0 |
| | 2 | 376 | 406 | 409 | 48.7 | 394 | 390 | 360 | 48.8 |
| | 4 | 377 | 406 | 409 | 48.7 | 394 | 390 | 362 | 46.7 |
| | 6 | 373 | 407 | 410 | 51.0 | 394 | 390 | 360 | 50.2 |
| | 8 | 373 | 406 | 411 | 40.7 | 392 | 388 | 360 | 40.5 |
| | 10 | 373 | 406 | 411 | 40.2 | 393 | 388 | 362 | 40.2 |
| | 12 | 373 | 405 | 411 | 39.7 | 393 | 389 | 364 | 41.5 |
| LS-630 | as received | 381 | 407 | 411 | 47.3 | 394 | 390 | 367 | 45.6 |
| | 2 | 372 | 405 | 408 | 45.4 | 394 | 390 | 361 | 48.3 |
| | 4 | 373 | 406 | 409 | 47.8 | 393 | 389 | 361 | 45.3 |
| | 6 | 373 | 406 | 410 | 49.0 | 393 | 390 | 360 | 46.2 |
| | 8 | 373 | 406 | 411 | 43.6 | 392 | 390 | 360 | 40.4 |
| | 10 | 372 | 406 | 411 | 42.0 | 392 | 388 | 359 | 40.7 |
| | 12 | 373 | 405 | 409 | 42.9 | 393 | 390 | 360 | 38.9 |
| Gulf 9606 | as received | 370 | 405 | 410 | 45.6 | 394 | 389 | 360 | 43.3 |
| | 2 | 369 | 405 | 409 | 41.1 | 393 | 389 | 361 | 39.4 |
| | 4 | 368 | 405 | 410 | 41.8 | 393 | 388 | 360 | 36.3 |
| | 6 | 371 | 404 | 409 | 35.2 | 392 | 387 | 360 | 35.0 |
| | 8 | 367 | 403 | 407 | 35.5 | 392 | 388 | 360 | 33.0 |
| | 10 | 366 | 401 | 406 | 35.7 | 393 | 387 | 360 | 31.7 |
| | 12 | 367 | 401 | 406 | 37.0 | 395 | 387 | 360 | 34.3 |

NOTES:
1. electron beam current - 10.30 milliamperes
2. electron beam current - 5.65 milliamperes
3. HDPE stirred during radiation exposure

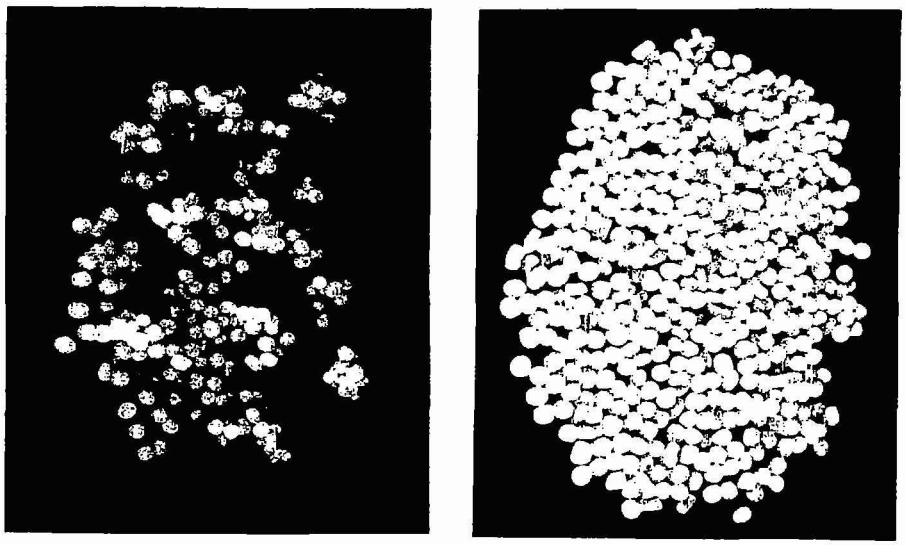


(a)

Condition: as received
Time: 2 hour exposure

(b)

Condition: 4 megarad dose
Time: 2 hour exposure



(c)

Condition: 8 megarad dose, unstirred
Time: 72 hour exposure

(d)

Condition: 8 megarad dose,
This sample was thoroughly stirred after each 2 megarad exposure during the electron beam processing
Time: 96 hour exposure

Figure 1. DuPont 7040 pellets after exposure in boiling ethylene glycol.

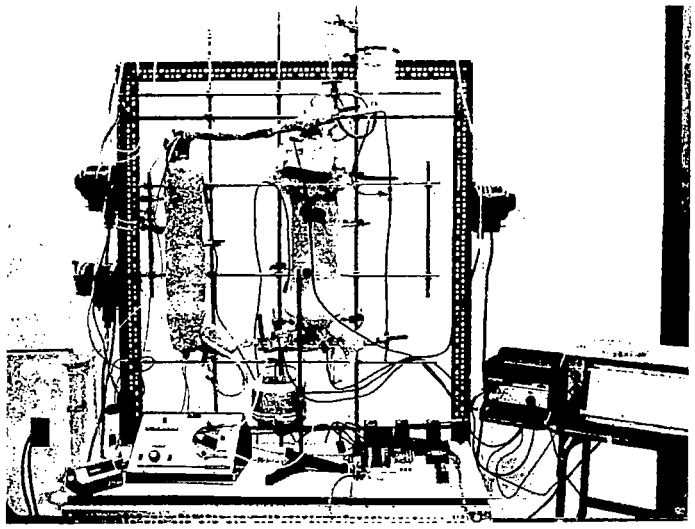


Figure 2. View of the five pound laboratory scale thermal energy storage test unit.

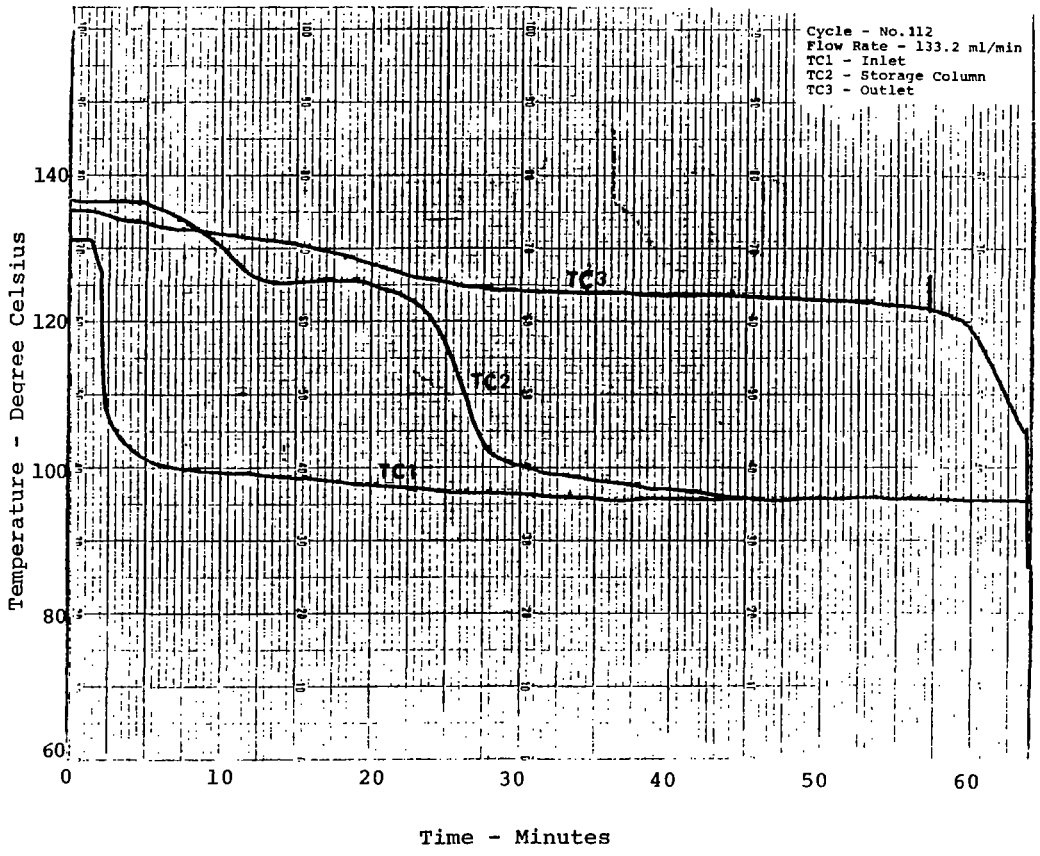



Figure 3. Temperature versus time plot for the 112th cooling cycle of the DuPont 7040 pellets in the five pound thermal energy storage test unit.

Figure 4. DuPont 7040 HDPE pellets after more than 100 complete melting and freezing cycles. The HDPE pellets had received an eight megarad dose of radiation.

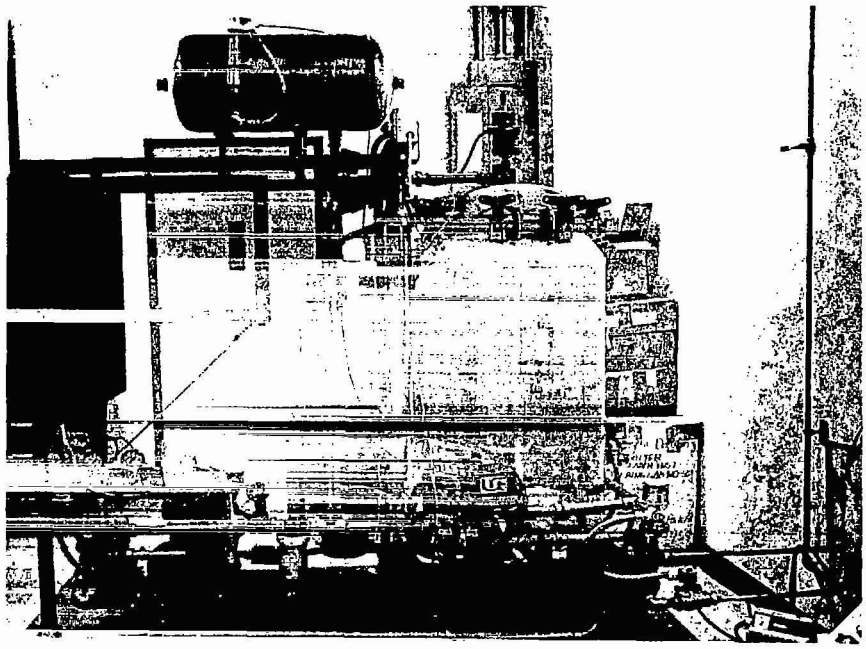


Figure 5. View of the 250 pound prototype thermal energy storage test unit.