STORED ENERGY IN IRRADIATED NATURAL ROCK SALT AS COMPARED TO SYNTHETIC HALITE OF DIFFERENT CHARACTERISTICS

H. Donker and A. García Celma

ABSTRACT

In this paper the results of stored energy measurements performed on irradiated, natural and synthetic rock salt samples are presented and discussed. The samples were irradiated in the GIF B irradiation facility of the Dutch Energy Research Foundation (ECN) at approximately constant dose rates of 4 and 15 kGy/h, at a temperature of 100 °C and total doses varying between 0.022 and 44 MGy. It is shown that in general the measured stored energy values for samples irradiated to the same total dose and at the same dose rate are approximately equal.

1. INTRODUCTION

One of the safety aspects that has to be considered for a radioactive waste repository in rock salt is the formation of radiation damage in the halite crystals. Most of the energy irradiated by the radioactive waste is dissipated in the rock salt as heat, but a small part of it is used to create various lattice defects in the salt crystals. Agglomeration of these defects leads to partial decomposition of the halite crystals into sodium and chlorine. Recombination of the sodium and chlorine will set free the chemical energy stored in the defects. It has to be investigated whether this stored energy may form a thread to the safety of a repository.

Experiments for the length of time during which gamma radiation above the natural background will be present in a repository are however, impossible to carry out. One therefore has to rely on computer simulations based on theoretical models to predict the behaviour of a repository. Since the conditions in a repository are so far away from those which can be reached in a laboratory, heavy demands have to be applied to these models. It is necessarry that the models

describe all the processes influencing the damage formation (and anneal) that can occur under repository conditions. Theory development is usually based on experiments performed on pure, undeformed single crystals irradiated at atmospheric pressure. These crystals are however, very different from the impure, polycrystalline and deformed rock salt at the lithostatic pressure of a repository. Therefore, many irradiation experiments, under various conditions and with different types of salt were needed and have been performed in the GIF B irradiation facility in the spent fuel basin of the High Flux Reactor at Petten, The Netherlands [García Celma et al., 1995].

The irradiation experiments performed in the GIF B facility were initially performed to monitor the HAW–field experiments [Rothfuchs et al., 1988]. The main objective of these experiments was to establish the links between long term in situ and short term laboratory results of irradiation experiments. Due to repeated delays and finally cancelation of the emplacement of the radio–active sources in the HAW–field, the laboratory experiments were steadily extended. The main objective of both the GIF B experiments and the planned HAW field experiments was to find a link between the existing theories and the conditions to be expected in a repository. To achieve this a great number of samples were irradiated together, each sample differing from the others in one or more of the following factors: microstructure, composition, pressure or amount of added brine. The irradiation experiments were performed at dose rates which were as close as possible to those expected for a radio–active waste repository i.e. as low as possible.

The starting material consisted of pure NaCl single crystals, pressed pure NaCl powder samples, synthetic rock salt samples and different kinds of natural rock salt: Speisesalz of the 800 meter level, Borehole anhydritic salt, Borehole polyhalitic salt and Polyhalitic salt (all provinient from the Asse mine, Remlingen, Germany), Potasas del Llobregat salt (from the Potasas del Llobregat mine, Cardona, Spain) and Dutch rock salt (origin unknown, somewhere in the Netherlands).

In this paper the result of the stored energy measurements performed on these samples are presented and discussed.

2. MATERIAL CHARACTERIZATION

2.1. Harshaw crystals (H)

Harshaw single crystals are frequently used as standards for stored energy measurements in salt. They are poor in OH^- content, have a very high purity and very low dislocation densities. They are produced by Harshaw Ltd. in the U.S.A., and are mainly used in optical instruments.

Stored energy determinations on several non–irradiated Harshaw crystals have been performed by Differential Thermal Analysis (DTA). The obtained results are not very reproducible, but some kind of general pattern could be observed. Below 500 K an endothermal effect is observed, while between 500 and 750 K an exothermal effect with a maximum around 600 K is observed. The magnitude of this exothermal effect varies between 0 and 15 J/g. Even samples taken from the same single crystal show large differences in thermal behaviour. No mass loss is observed during the DTA experiments. A full explanation for the observed features has not been found yet. Most probably they have to be ascribed to a rearrangement of dislocations in the crystals [García Celma, 1994; Schutjens, 1991].

At first these crystals were used as received in the irradiation experiments. Later when we knew that these non–irradiated crystals could contain considerable amounts of stored energy, they were annealed prior to irradiation in an open canister at 500°C for one hour in an Argon atmosphere. After anneal they were allowed to cool down slowly to room temperature. Stored energy measurements on these annealed crystals showed no significant endo– or exothermal ef–fects.

2.2. Pressed powder samples (PP)

Pressed powder samples are prepared by cold pressing NaCl powder (Merck, pro analysis) to which 0.2 weight% bi–distilled water has been added at 3 kbar. The NaCl powder was ana–lyzed by atomic emission spectroscopy (AES) using an inductively coupled plasma (ICP). Besides NaCl, only Fe (4.8 ppm) and Ca (13 ppm) were found in contents above the detection limit of the method. The average grain size of these samples is 66 μm. Most crystals present a cubic habitus.

The stored energy of these samples as measured with DTA is (4.2 ± 0.9) J/g. No endothermal decrepitation peaks are observed. It is therefore concluded that the pressed powder samples do not contain a significant amount of intragranular fluid inclusions.

2.3. Synthetic rock salt samples (SS)

The starting material used to produce these samples was the same as used for the pressed powder samples. Synthetic rock salt samples have been produced by:

a) forcing as much NaCl powder as possible into jackets;

b) vacuum emptying the jackets to extract the air from the pores;

c) pressing at 150°C and 1 kbar hydrostatic pressure for one day;

d) pressing at 150°C and 500 bar hydrostatic pressure for 30 days.

A detailed description of the method followed can be found in [García Celma et al., 1991].

Synthetic rock salt samples are real rock salt with respect to their microstructure, with real grain boundaries. In this they differ from pressed powder samples, which have more porosity and consist of loose grains.

The difference between synthetic rock salt and real (natural) rock salt is that the first is chemically pure and has a very perfect "foam microstructure", while the second is impure and has a granular microstructure. Foam microstructures are a special type of granular microstructure produced by grain boundary migration. Foam microstructures are special in that the grain boundaries present a sort of equilibrium: each grain boundary has the same tendency to intrude its neighbour as its neighbour has to intrude it. This produces grain shapes that resemble the shape of beer foam bubbles, with typical triple interferences of grain boundaries delineating three angles of 120 degrees.

Stored energy determinations of synthetic rock salt yielded (4.7 ± 0.5) J/g. During the DTA measurements a mass loss of 0.05 weight% was registered. This is assumed to correspond to the evaporation of water. Since no endothermal spikes are observed in the thermograms, this water is assumed to be intergranular water (grain boundary brine).

2.4. Asse Speisesalz of the 800–meter level (Sp–800)

The Sp–800 material consists of polycrystalline halite rock of a relatively high purity (> 99%), with a grain size of 3–10 mm. The main impurity phases are polyhalite ($K_2MgCa_2(SO_4)_4.2H_2O$) and minor anhydride. Besides the structurally bound water, the material contains about 0.05% intracrystalline H_2O, mainly in fluid inclusions at grain boundaries (i.e., halite–halite or halite–polyhalite) [Spiers et al., 1986].

As observed by Urai et al. [1986], original Asse Speisesalz samples have a granular microstructure produced by at least one episode of grain boundary migration in the mine. This was determined on the basis of grain overgrowths and substructure analyses. In a granular microstructure grain boundaries can have many different shapes.

The thermograms obtained by DTA characteristically consist of an exothermal peak between 485 and 705 K with a superimposed endothermal peak in the interval 565 to 635 K. During the DTA measurements a mass loss between 0.02 and 0.11 weight% was observed. The mass loss, which is assumed to be due to the loss of water, was observed to be proportional to the intensity of the endothermal peak. According to Jockwer [1981], polyhalite loses its crystal water between 235 and 350 °C. Therefore, the endothermal peak is ascribed to the dehydration of polyhalite. Mass losses less than 0.05 weight% are not reflected in endothermal peaks and are inferred to correspond to intergranular water.

In order to obtain the true stored energy in the halite of the Sp–800 samples, the observed exothermal effect is corrected for the endothermal dehydration peak of polyhalite. The shape of the true exothermal peak is estimated using the initial and final slope of this peak and the observed weight loss. Stored energy measurements of non–irradiated Sp–800 samples after performing the correction described above yielded 2.1 ± 0.7 J/g.

2.5. Borehole polyhalitic samples (Bhp)

Borehole polyhalitic samples are Asse samples from the same geological levels as the polyhalitic levels perforated by the HAW–test field boreholes. These samples present the same

type of microstructure as already discussed for the Asse Speisesalz, but contain more polyhalite.

The pre–irradiation stored energy of these samples is determined by correcting the exothermal signal for the endothermal dehydration of polyhalite in the same way as with the Asse Speisesalz samples. Due to the fact that more polyhalite is present in these samples, the corrected results are less accurate than those from the Sp–800 measurements. The corrected stored energy lies in the range between 4.4 and 1.9 J/g. The mass loss during the DTA experiments ranges between 0.01 and 0.32 weight% and is clearly related to the dehydration of polyhalite.

2.6. Borehole anhydritic samples (Bha)

Borehole anhydritic samples have also been taken from the boreholes of the HAW–test field. The difference with the borehole polyhalitic samples is that they contain anhydrite instead of polyhalite. From all the Asse samples, these are the most similar to the Potasas del Llobregat samples, although the borehole polyhalitic samples are more homogeneous at the mesoscale.

Pre–irradiation stored energy measurements yielded (2.6 ± 0.9) J/g. The mass loss during these measurements varied between 0.01 and 0.11 weight%. This mass loss is not accompanied by any endothermal peaks in the temperature interval where the stored energy is set free, as was the case with samples containing polyhalite.

2.7. Polyhalitic salt samples (PS)

Polyhalitic salt samples have also been taken from the boreholes of the HAW–test field. They contain extremely high amounts of polyhalite.

2.8. Potasas del Llobregat samples (PLL)

The solid phase of Potasas del Llobregat samples mainly consists of halite (85 to 99%) and anhydrite (1 to 15%). Clay, coelestine, an undetermined magnesium mineral and quartz are

present in minor proportions as determined by microprobe analyses [García Celma et al., 1991].

The amount of inherent brine was measured by us with TG–DTA and ranges between 0.1 and 0.9 weight%. For 175 thermogravimetric analyses (performed at the Barcelona University) where mass loss was measured up to 725 K, the mean content of brine was calculated to be 0.3 weight% with values ranging between 0.04 and 1.0 weight% [Pueyo et al., 1992]. This corresponds well with our measurements.

Observations of decorated microstructures in the irradiated Potasas del Llobregat samples revealed the presence of different subgrain microstructures, which points to at least two recrystallization periods in the starting material. After these recrystallization episodes, veins developed [García Celma et al., 1991]. Many intragranular fluid inclusions are found within hopper crystals. Intergranular fluid inclusions show the normal vermicular grain boundary structures [Urai et al., 1986].

In the temperature interval of 305 to 495 K several endothermal peaks are observed, which are ascribed to the evaporation of grain boundary water and production of CH_4. Due to these endothermal peaks the onset of the exothermal signal is difficult to determine and can vary from 395 to 505 K. The end of the exothermal signal is difficult to determine as well due to fluid inclusion decrepitation and can vary from 645 to 695 K. The endothermal effect of decrepitation does not usually represent more than 0.5 J/g. To avoid arbitrary interpretations the choice was made to integrate the thermal effect, assuming a base line as near as possible to the line where $\Delta H = 0$. The mean stored energy of non–irradiated Potasas del Llobregat samples determined in this way is (0.6 ± 2.2) J/g. This average has been established for samples containing low amounts of impurities. Low amounts of impurities are also reflected by the colour of the samples and the mass loss

2.9. Dutch salt samples (DS)

Dutch salt samples are samples of unknown composition and origin except that they were taken from somewhere in the Netherlands.

3. EXPERIMENTAL

3.1. Irradiation experiments

The samples mentioned above have been irradiated in the GIF B facility of the ECN at a temperature of 100 °C [García Celma et al., 1995]. They were irradiated at a low dose rate which was kept as constant as possible. To achieve this, old spent fuel elements which have a slow decay were used. Two different mean dose rates were applied in these experiments i.e. 15 and 4 kGy/h. In each experiment 16 samples were irradiated simultaneously. Twelve of these samples were irradiated under enhanced pressure, the other four at atmospheric pressure. To some of the samples an extra amount of brine was added previous to the irradiation experiment.

The first series of experiments (GIF B1) was performed at dose rates varying between 20 and 10 kGy/h . The average dose rate was 15 kGy/h. In these experiments the samples were wrapped in silver foil and then placed in an aluminum sample holder (in stead of the later used golden sample holders). The Harshaw crystals used in this series were not annealed prior to irradiation.

A second series of experiments (GIF B2) was performed at dose rates varying between 8 an 1 kGy/h. The average dose rate was 4 kGy/h. In these experiments the golden sample holders were used and the Harshaw crystals were annealed prior to irradiation.

Finally a third series of experiments (GIF B3) with a limited number of sample types was performed at dose rates varying between 21 and 12 kGy/h. The average dose rate was 15 kGy/h. This to check some controversial results obtained in the GIF B1 experiments and also to check the effect of annealing prior to irradiation on the radiation damage development. To achieve this annealed and non–annealed Harshaw crystals were irradiated simultaneously in each experiment of this series. For these experiments also golden sample holders were used.

3.3. Stored Energy Measurements

The stored energy measurements were carried out by means of differential thermal analysis on a SETARAM DSC–111. Calibrations were performed by melting Indium metal. Anneals took place in "closed" Pt capsules with a small capillary hole to allow gases to escape in order to avoid explosion of the capsule when pressure builds up. The heating rate used for these measurements was either 5 (GIF B1) or 10 (GIF B2 and B3) K/min. In a first run the sample is measured against an empty reference sample holder up to a temperature of 750 K. Then the sample and reference are allowed to cool down and a background signal is measured in a second run. The result of the second run is subtracted from that of the first. The area closed by the resulting curve and the base line is then integrated to obtain the released stored energy. Due to the difference in heating rate the stored energy peaks for the samples measured with a rate of 10 K/min will be observed at slightly higher temperatures than the peaks observed for the samples measured with a rate of 5 K/min.

For the stored energy measurements, parts of the irradiated samples were cut in small pieces. From those pieces, the darkest i.e. free from secondary minerals and recrystallized material were selected with the naked eye. Small portions of secondary minerals and recrystallized material may however, still have been present in the analyzed material. This procedure worked quite well for most of the samples, except for the pressed powder and synthetic salt samples. For these materials the grains were so small that it was impossible to separate dark and light material. Therefore the stored energy values given for these samples represent the bulk stored energy

According to the measurements of Jockwer [1981], polyhalite loses its crystal water between 235 and 350 °C. As already discussed in section 2 our analysis showed that the dehydration of polyhalite takes place in the same temperature interval as the release of stored energy. This results in the presence of an endothermal peak superposed on the exothermal release of stored energy. When necesarry our results have therefore, been corrected for the dehydration of polyhalite.

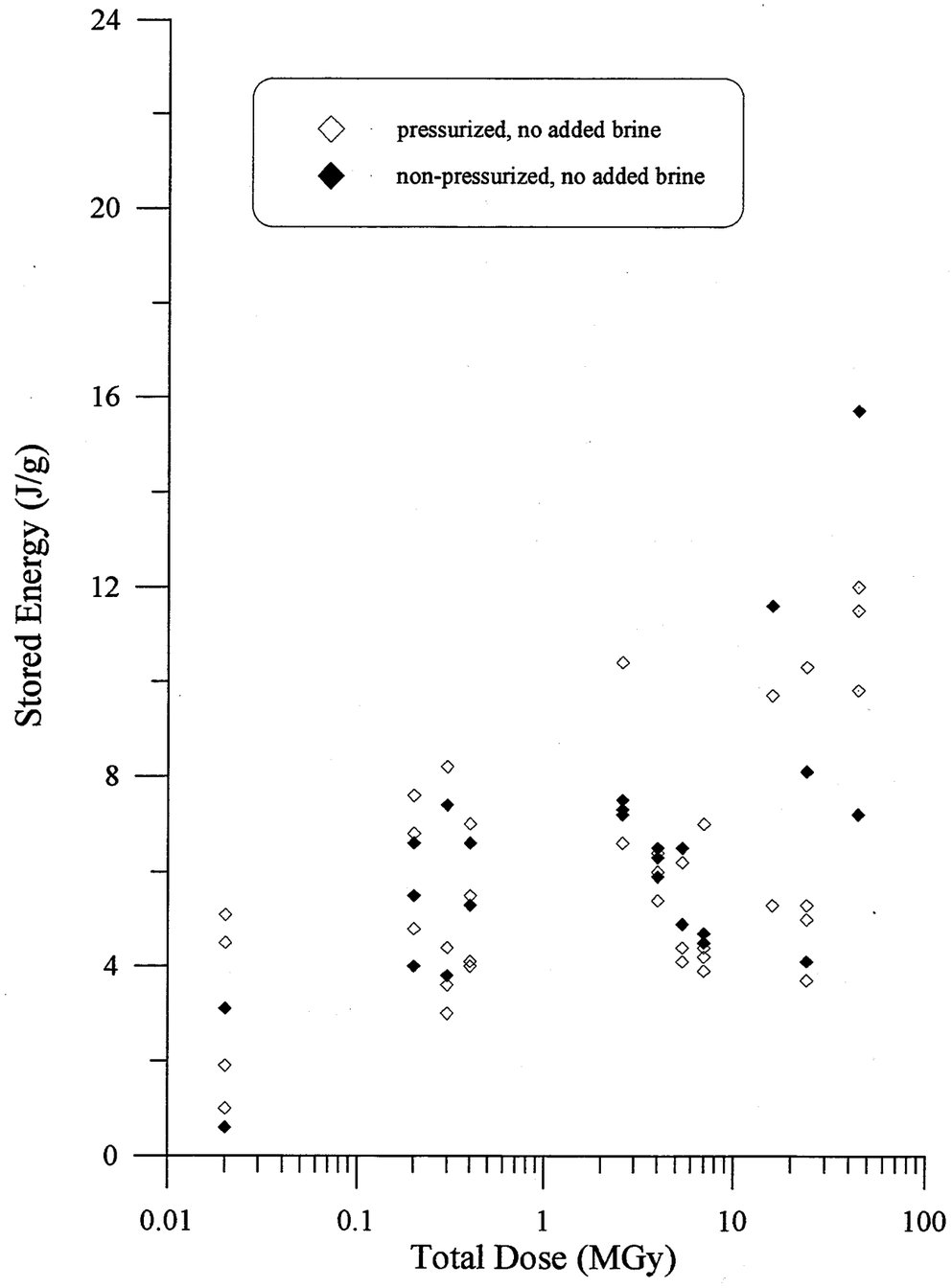

Figure 1a: *Stored energy of salt samples of various composition irradiated in GIF B1 (15 kGy/h, 100 °C)*

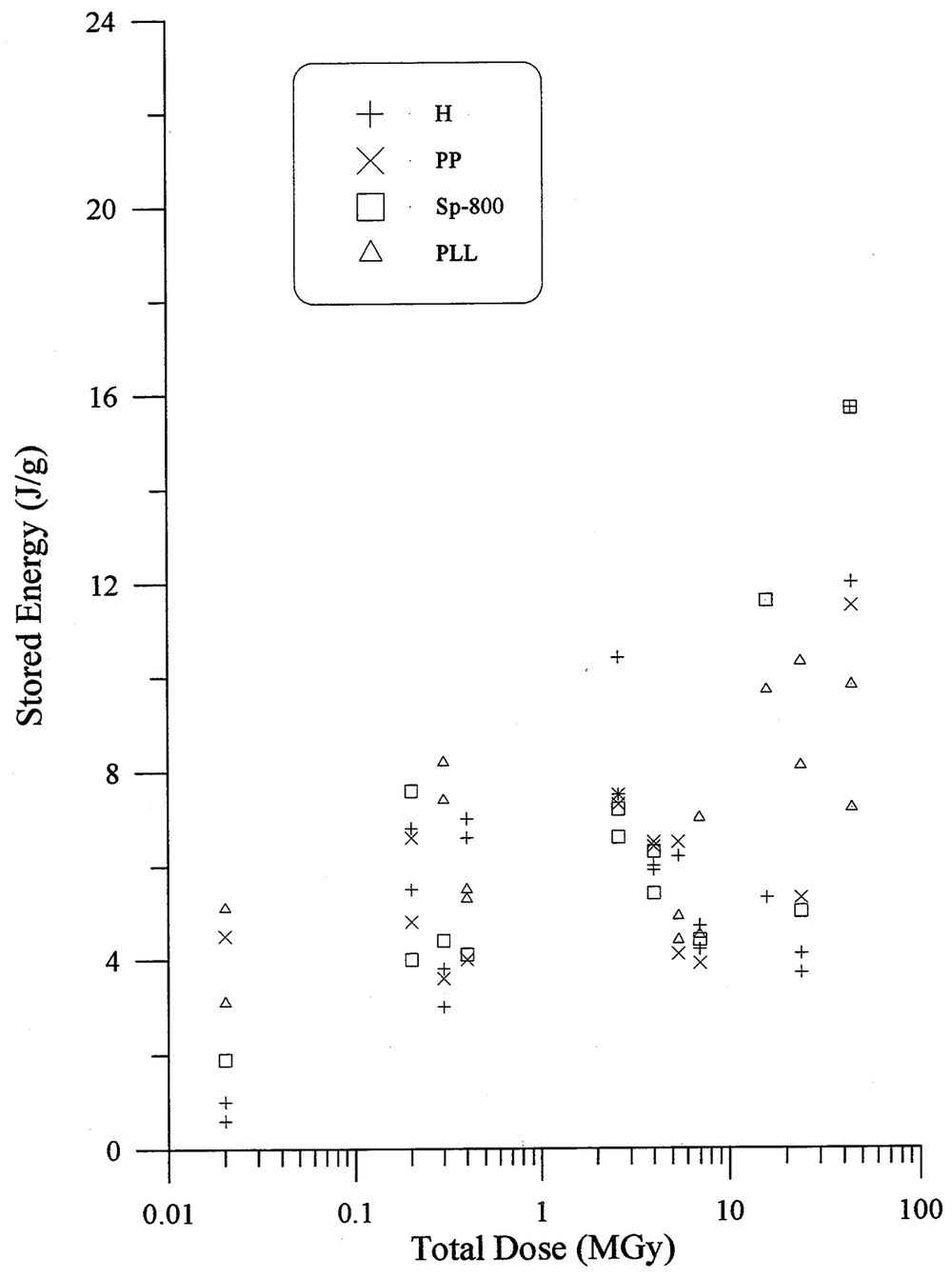

Figure 1b: *Stored energy of salt samples, pressurized and non-pressurized, with and without added brine, irradiated in GIF B1 (15 kGy/h, 100 °C)*

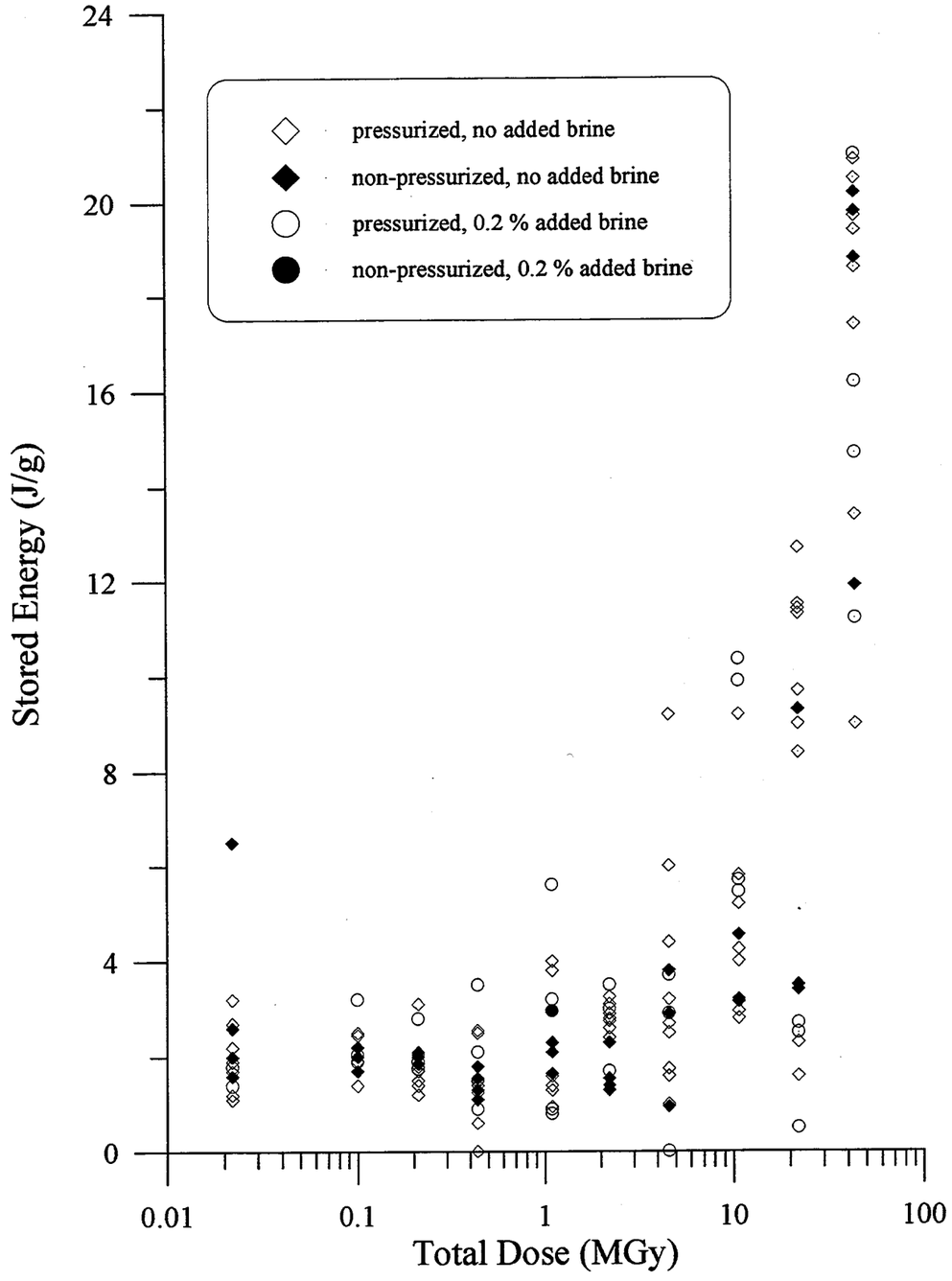

Figure 2a: *Stored energy of salt samples of various composition irradiated in GIF B2 (4 kGy/h, 100 °C)*

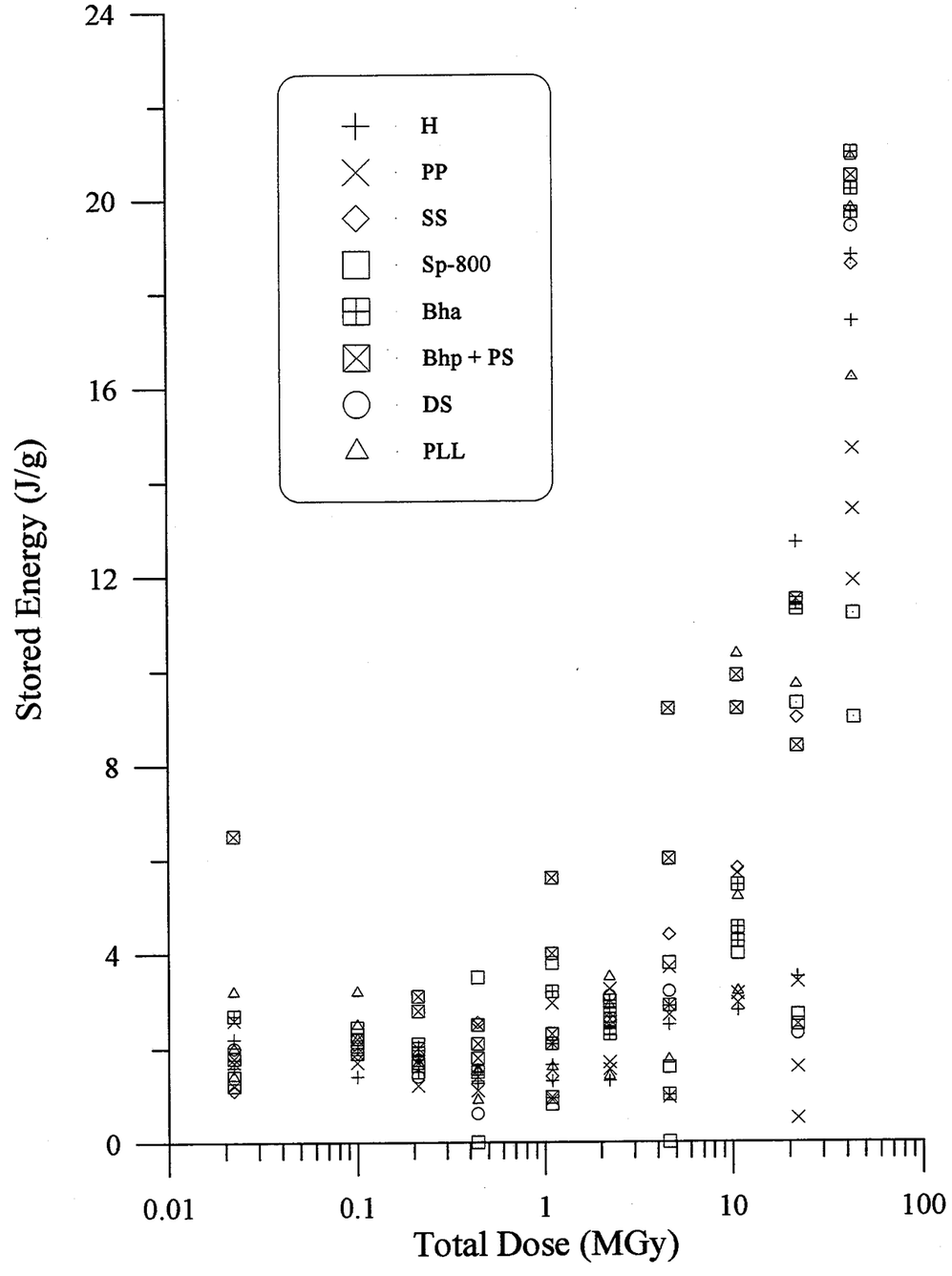

Figure 2b: *Stored energy of salt samples, pressurized and non-pressurized, with and without added brine, irradiated in GIF B2 (4 kGy/h, 100 °C)*

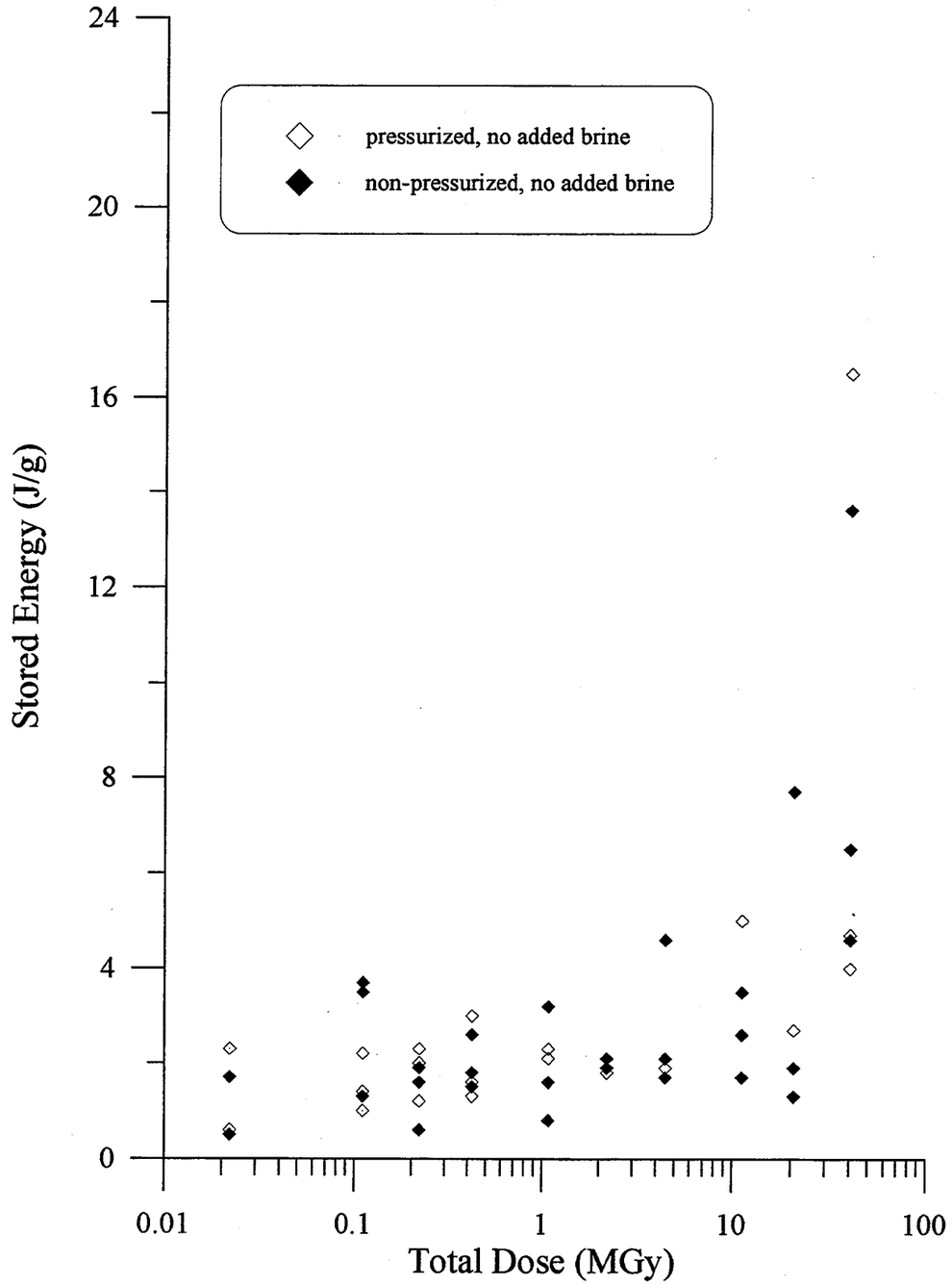

Figure 3a: *Stored energy of salt samples of various composition irradiated in GIF B3 (15 kGy/h, 100 °C)*

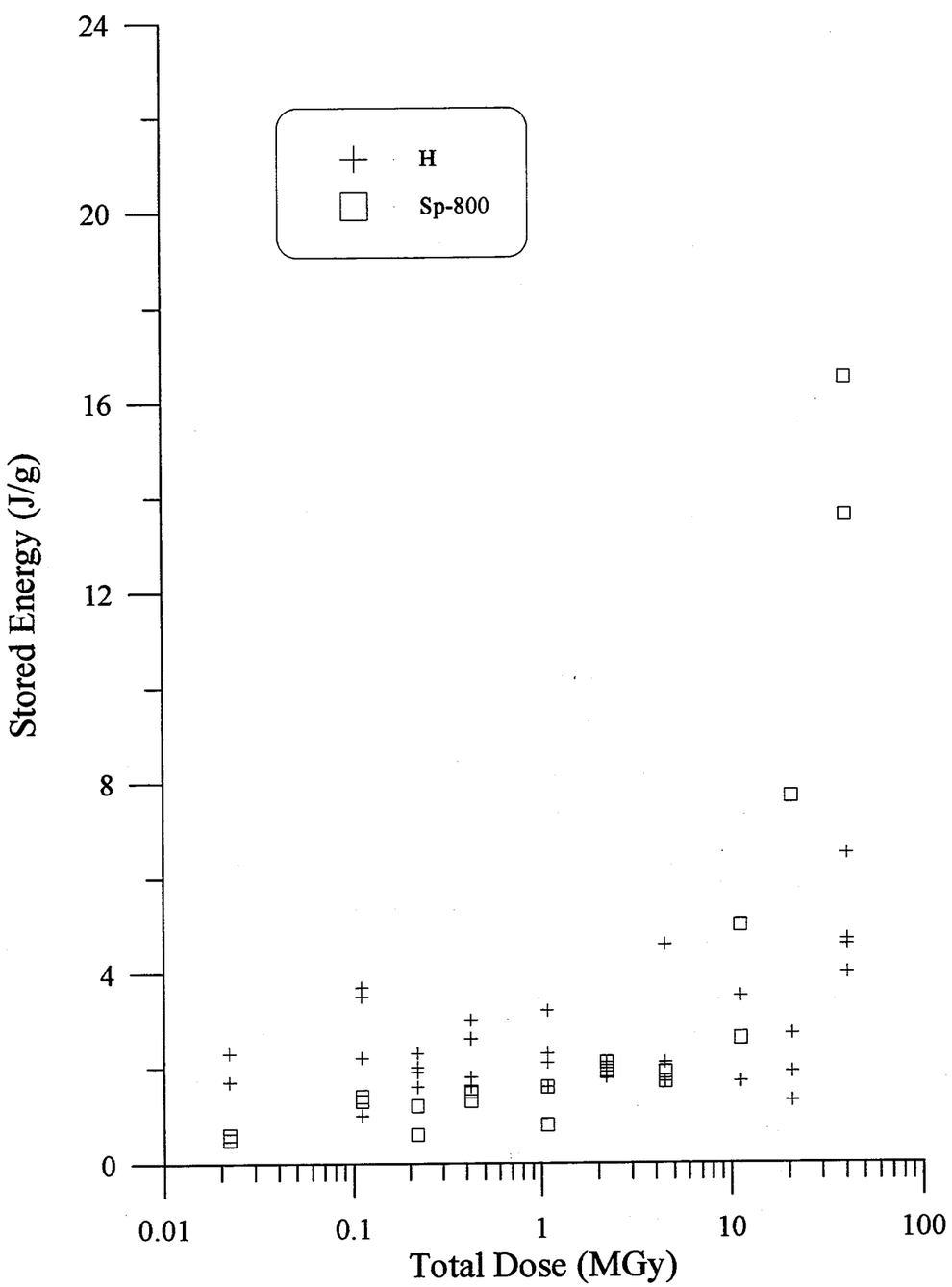

Figure 3b: *Stored energy of salt samples, pressurized and non-pressurized, without added brine, irradiated in GIF B3 (15 kGy/h, 100 °C)*

4. RESULTS AND DISCUSSION

4.1. General

The measured stored energy values for all samples irradiated in the three series of experiments in GIF B are shown in Fig. 1 to 3. In these figures no clear tendencies resulting from pressurizing the samples or adding extra brine to the samples can be observed. Also no clear distinction of some kind of sample developing systematically more or less damage than the others can be made, except maybe for the pressed powder samples irradiated in the GIF B2 experiments. At high total doses, low stored energy values have been systematically observed for these samples. Note, however, that for these samples bulk stored energy values have been measured whereas for the natural samples the darkest i.e. most damaged parts of the irradiated samples have been selected for stored energy measurements. The large variation in stored energy values observed for the different samples irradiated to the same total doses is probably caused by differences in the samples at the microstructural (or even submicrostructural) level.

The results of the GIF B1 experiments show that in most types of samples an initial increase of the stored energy with increasing total dose up to a maximum value at a total dose of about 2.6 MGy, is followed by a decrease of stored energy with increasing total dose. At a total dose between 5 and 15 MGy a minimum is reached after which the stored energy increases again with increasing total dose (see Fig. 1). Below integrated doses of 15 MGy a comparison of our stored energy results with the results of the Light Absorption measurements shows that the irradiated samples yield higher stored energy levels than could be attributed to colour centres [García Celma et al., 1992; García Celma and Donker, 1994a, García Celma, 1993; García Celma et al.,1993]. The initial increase and the ensuing decrease of stored energy was therefore ascribed to the development of dislocations and their anneal, also because the stored energy peaks were observed at a higher temperature than the colloid anneal peak in the thermograms of the Harshaw crystals irradiated to higher doses [García Celma and Donker, 1994a]. Moreover, the development of low energy dislocation arrangements has been shown by means of microstructural analysis [García Celma and Donker, 1994b]. However, the results of the GIF B3 experiments shed some doubts on this interpretation.

A comparison of Fig. 1 and 3 shows that for the samples of the GIF B3 experiments the measured stored energy values are systematically lower than for the samples of the GIF B1 experiments, while the experimental conditions (dose rate, total doses, temperature, etc) under which these two series were performed were similar. Also the initial rise and ensuing decrease of stored energy as found in the GIF B1 experiments, is not observed for the samples of the GIF B3 (or GIF B2, see Fig. 2) experiments. In the GIF B3 experiments the stored energy observed for samples irradiated up to total doses of 11 MGy has an approximately constant value of about 2 J/g. The reason for these differences is not yet very clear but we think that they might be caused by surface effects. Jiménez de Castro and Álvarez Rivas [1990] have reported that samples cut from the surface of their irradiated samples show an enhanced stored energy. This additional stored energy, as compared to samples cut from the interior of the same irradiated crystal, is released in the temperature region above 300 °C. In the GIF B2 and GIF B3 experiments the samples for stored energy measurements were all selected from the interior of the irradiated samples while this was most probably not the case in the GIF B1 experiments. For all our samples irradiated up to total doses of 22 MGy the maximum of the stored energy peak in the DTA scans is found at about 600 K, i.e. in the same temperature region as the enhanced stored energy of Jiménez de Castro and Álvarez Rivas.

Since we do not know to what extent surface effects have played a role in each individual stored energy measurement for samples irradiated in GIF B1 we will only briefly discuss the results of these measurements in what follows and not really use them for the conclusions.

For the samples irradiated in the GIF B2 experiments, the results of the stored energy measurements at low total dose are similar to those obtained for the samples irradiated in the GIF B3 experiments. At low total doses there is an approximately constant stored energy at a value of about 2 J/g. Above a total dose of 10 MGy this stored energy starts to increase. The maximal stored energy value observed at 44 MGy total dose is approximately 22 J/g

Note that for the natural samples we measured the stored energy in the most damaged parts of these samples. Bulk stored energy values for these samples will be lower than the values discussed in this paper since the microstructural analysis of these samples showed that they contain considerable recrystallized areas with less or no damage.

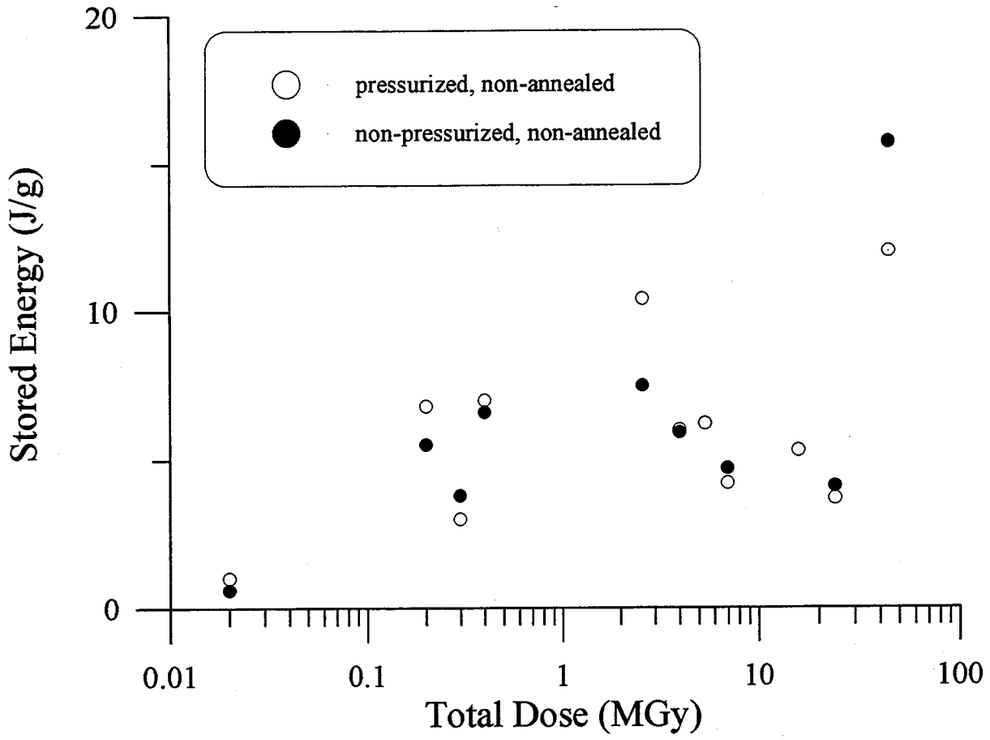

Figure 4: *Stored energy of Harshaw single NaCl crystals irradiated in GIF B1 (15 kGy/h, 100 °C)*

4.2. Harshaw crystals

In Fig. 4 the stored energy of the Harshaw crystals irradiated in GIF B1 is shown as a function of total dose. Below 2.6 MGy the stored energy increases rapidly with increasing total dose. Between 2.6 and 24 MGy a decrease in stored energy with increasing total dose is observed, while above 24 MGy it increases again although not as fast as in the interval between 0 and 2.6 MGy.

Of the Harshaw crystals irradiated in the GIF B1 experiments, those irradiated to integrated doses up to 24 MGy only show one exothermal peak with a maximum at about 600 K (see Fig. 5). At an integrated dose of 44.6 MGy two exothermal peaks are observed: the aforementioned peak at 600 K and another one at about 540 K (see Fig. 6). In previous reports we

have ascribed the 600 K stored energy peak to the anneal of dislocations, while the 540 K peak was ascribed to the anneal of colloids. In other (not Harshaw) samples we have observed only one stored energy peak with a maximum at a temperature of about 600 K. Also when these samples definitely contained a considerable amount of colloids. This means that in these samples the anneal of colloids takes place at a higher temperature than in the Harshaw crystals. The origin of this temperature shift is not yet clear. It does however indicate that there are possibly different kinds of colloids

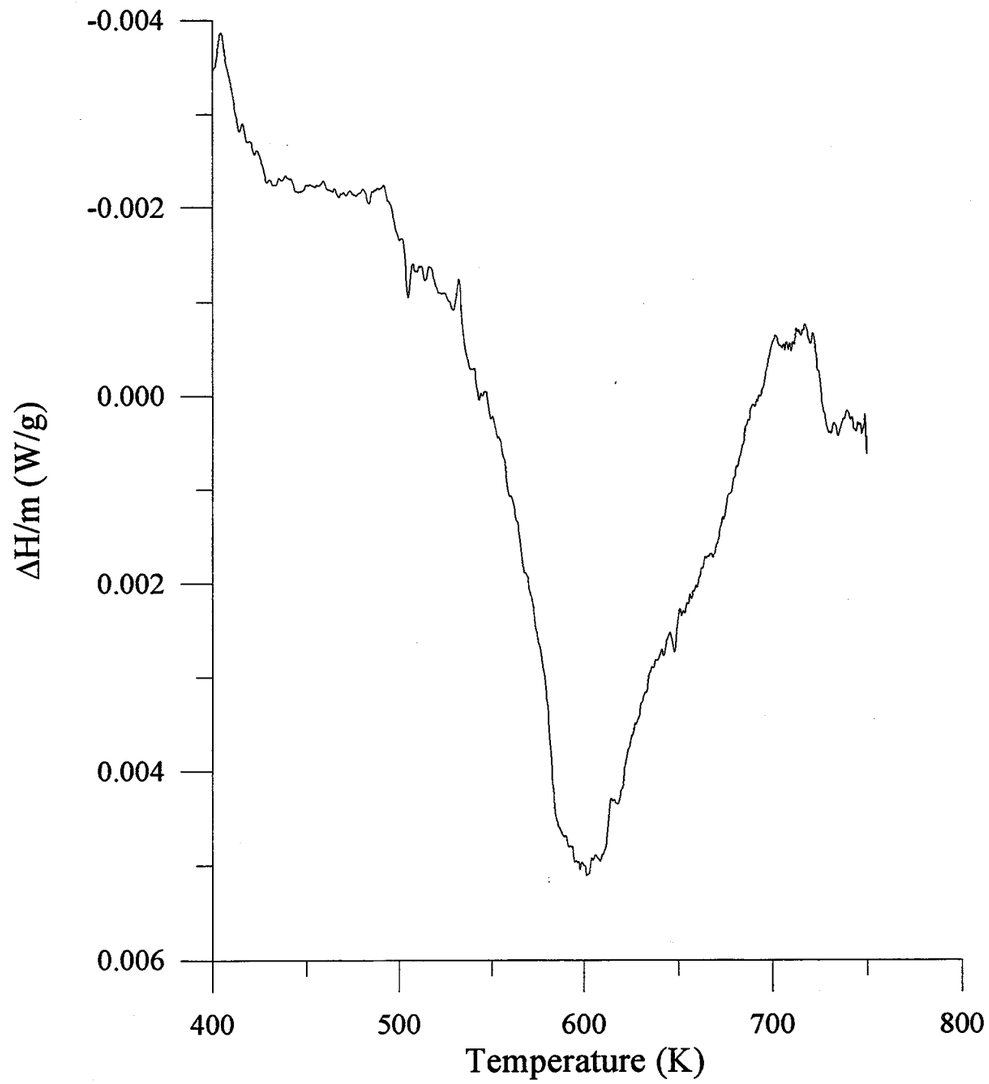

Figure 5: *DTA curve of sample 25 H (0.4 MGy, 15 kGy/h, 100 °C, 200 bar)*

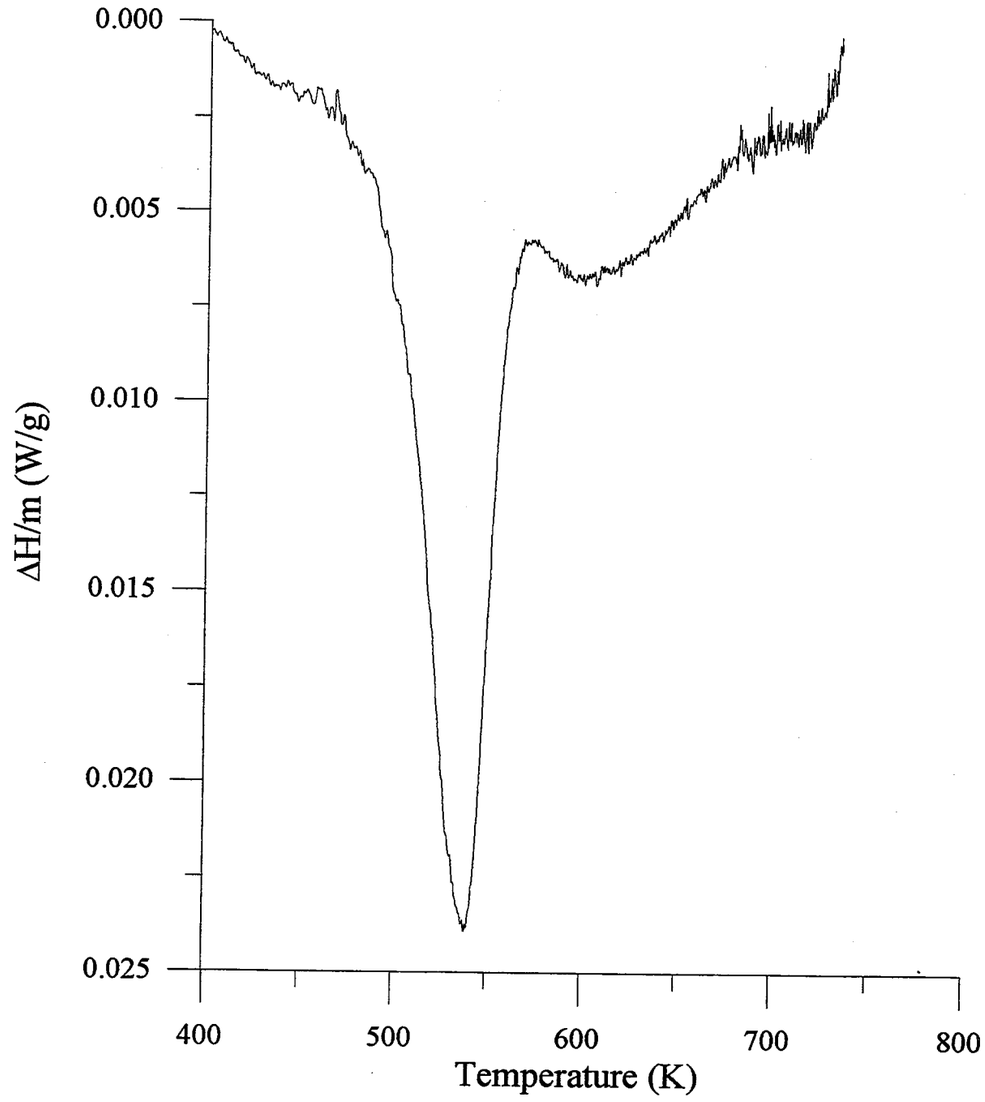

Figure 6 *DTA curve of sample 33 H (44.6 MGy, 15 kGy/h, 100 °C, 200 bar)*

In the GIF B2 experiments, performed at an average dose rate of 4 kGy/h, the samples irradiated up to a total dose of 4.4 MGy only show a weak exothermal peak at about 600 K similar to the one observed in the previous experiments. At 11 MGy the pressurized sample still only shows this peak, however, for the non–pressurized sample another much stronger exothermal peak at about 650 K is also observed. Also a small mass loss during the DTA measurement is observed for the non–pressurized sample. At 22 MGy the non–pressurized sample only shows

a weak exothermal peak at about 600 K again, while the pressurized sample shows a strong exothermal peak at about 560 K. According to our interpretation of the stored energy peaks, in the pressurized sample colloids have already nucleated while, in the non–pressurized sample they have not, at least not in significant amounts. This single observation, however is to little evidence to state that pressure enhances colloid nucleation. At 44 MGy both (pressurized and non–pressurized) irradiated Harshaw crystals only show an exothermal peak at about 570 K and their stored energy is approximately equal. Except for the mentioned sample none of the other samples show a significant mass change during the DTA measurement.

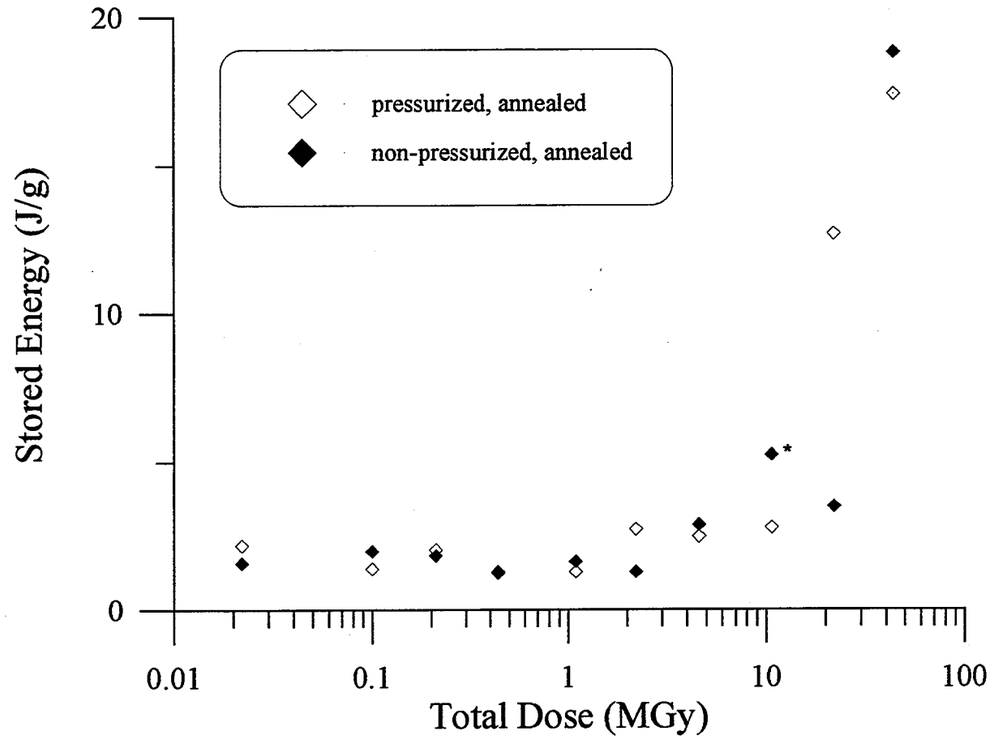

Figure 7: *Stored energy of Harshaw single NaCl crystals irradiated in GIF B2 (4 kGy/h, 100 °C)*

In Fig. 7 the stored energy of the Harshaw crystals irradiated in GIF B2 is shown as a function of total dose. The measured stored energy remains approximately constant for both pressurized and non–pressurized samples at about 2 J/g up to total doses of 1.1 MGy. Above 1.1 MGy the stored energy starts to increase with increasing total dose. Although, large differences

between the behaviour of pressurized and non–pressurized samples are observed, at 44 MGy the stored energy in both samples is again approximately equal and has reached a value of about 18 J/g.

Figure 8 shows the stored energy values obtained for the Harshaw crystals irradiated in the GIF B3 experiments. The generally observed tendency is the same as that observed in the 4 kGy/h experiments. At low total doses only a peak at about 600 K is observed in the DTA curves, while at high total doses a peak in the region between 525 and 570 K is observed. However, for some samples (marked with an asterisk in the figures) also an exothermal peak at about 650 K is observed.

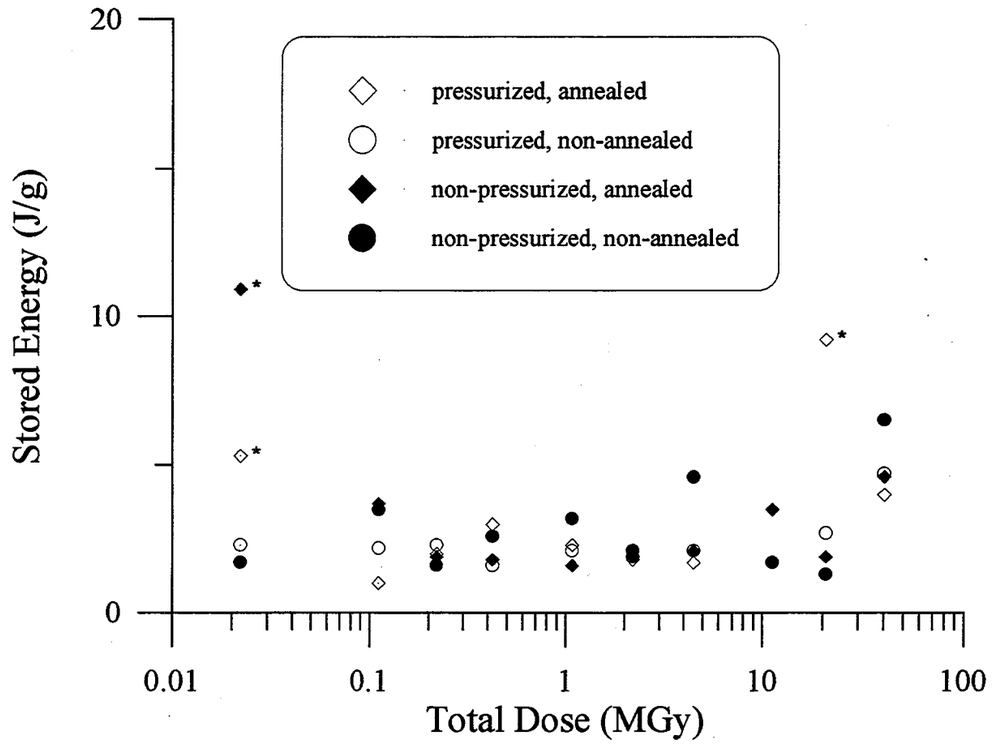

Figure 8: *Stored energy of Harshaw single NaCl crystals irradiated in GIF B3 (15 kGy/h, 100 °C)*

The occurrence of the peak at 650 K always goes accompanied by a considerable mass loss during the DTA measurement. Notice also that this 650 K peak is only observed for samples which have been annealed prior to irradiation. The Harshaw crystals were annealed in batches of four. Notice that altogether we have found exactly four Harshaw crystals in which the 650 K peak occurs. Although we have not kept record whether these Harshaw crystals were annealed simultaneously we do have this suspicion. Also we assume that during the anneal of these crystals something went wrong and that the 650 K peak has nothing to do with the irradiation experiments but is possibly due to a contamination of our samples.

As can be seen in Fig. 8, there are no systematic differences in stored energy values for either annealed or non–annealed and pressurized or non–pressurized Harshaw crystals. Although at 44 MGy total dose non–pressurized Harshaw crystals seem to contain more stored energy than the pressurized crystals. The differences are, however, within the experimental error.

As already discussed in section 4.1 comparison of Fig. 4 and 8 shows that for the Harshaw crystals irradiated in the GIF B3 experiments the obtained stored energy values are lower than those obtained in GIF B1. Also the trend of first an increasing and then a decreasing stored energy with increasing total dose in the total dose region up to 24 MGy as observed in GIF B1 is not found in GIF B3. As already explained in section 4.1 these differences are possibly due to surface effects.

Another remarkeble observation is that none of the irradiated non–annealed Harshaw crystals show any sign of the endo–and/or exothermal effects observed for the non–irradiated, non–annealed Harshaw crystals. Not even at total doses as low as 22 kGy. This means that the gamma radiation, at least at a temperature of 100 °C, is very effective in removing these effects.

Comparison of Fig. 7 and 8 shows that at total doses below 11 MGy the amounts of stored energy developed at 4 or 15 kGy/h are not very different. At higher total doses the amounts of stored energy developed at 4 kGy/h are much higher than at 15 kGy/h for the same total dose. At 44 MGy total dose the difference in stored energy is about a factor 3.

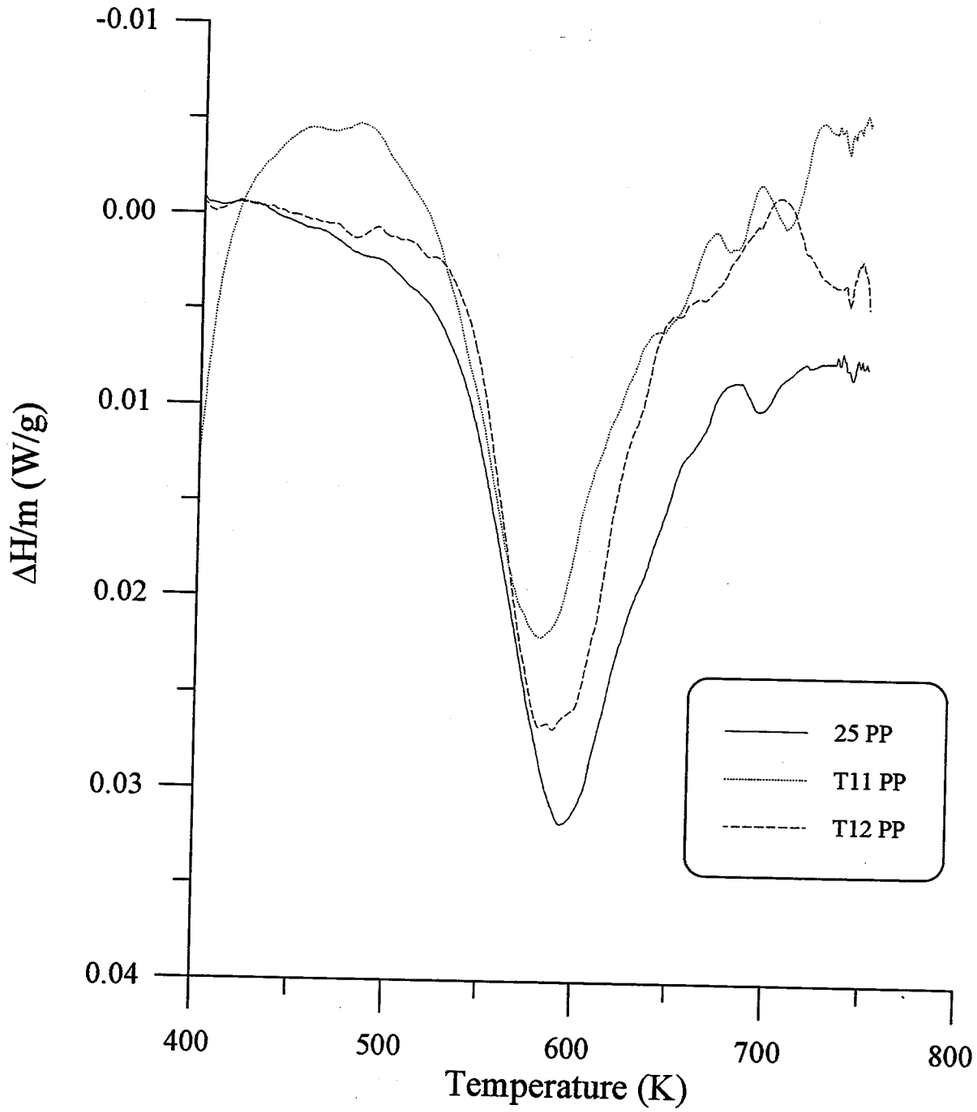

Figure 9: *DTA curves of Pressed Powder samples irradiated in GIF B2 (44 MGy, 4 kGy/h, 100 °C)*

4.2. Pressed Powder Samples

The DTA curves obtained for irradiated pressed powder samples show only a single exothermal peak with a maximum at about 600 K. Some of the obtained DTA curves are shown

in Fig. 9. In Fig. 10 the stored energy values obtained for the samples irradiated in GIF B2 at a dose rate of 4 kGy/h are shown as a function of total dose. The dashed line indicates the average stored energy of non–irradiated pressed powder samples. At low total doses the stored energy of the irradiated samples is lower than that of non–irradiated samples At each total dose the stored energy values observed for the various samples are within experimental error equal to each other. Up to total doses of 22 MGy the measured stored energy is approximately constant at a level of about 2 J/g. Only at a total dose of 44 MGy a higher stored energy is observed i.e. about 14 J/g.

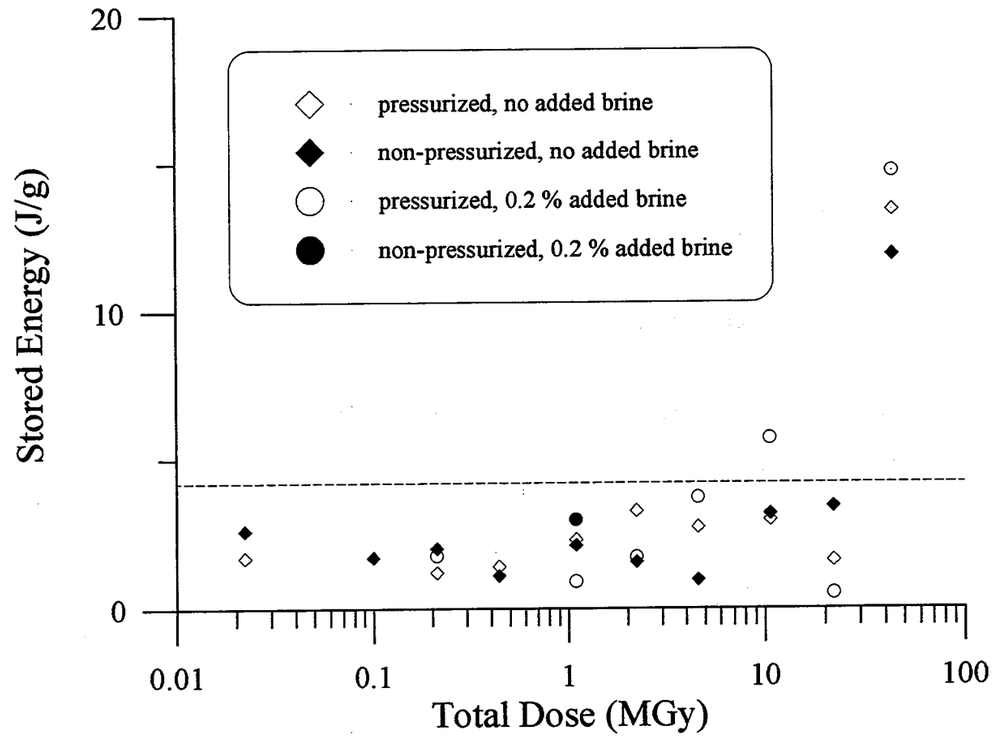

Figure 10: *Stored energy of Pressed Powder samples irradiated in GIF B2 (4 kGy/h, 100 °C)*

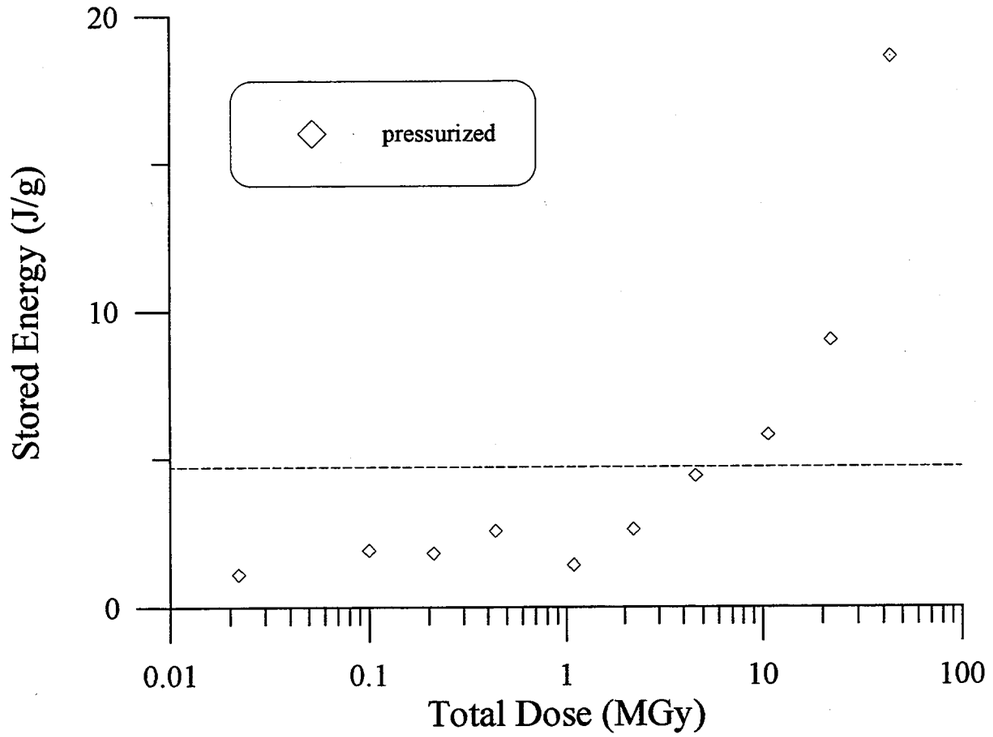

Figure 11: *Stored energy of Synthetic Salt samples irradiated in GIF B2 (4 kGy/h, 100 °C)*

4.3. Synthetic Rock Salt samples

For the synthetic rock salt samples we only have data from the GIF B2 experiments, i.e. only for samples irradiated at a dose rate of 4 kGy/h. Also only for pressurized samples. The DTA curves for these samples are similar to those observed for the pressed powder samples, i.e. only a broad exothermal peak at about 600 K. In Fig. 11 the stored energy observed for these samples is shown as a function of total dose. The observed dose dependence is similar to that observed for the Harshaw crystals i.e. a stored energy approximately constant at a level of about 2 J/g for total doses below 1.1 MGy and an increasing stored energy with increasing total dose above 1.1 MGy. For all studied total doses the measured stored energy values are approximately equal to those of the simultaneously irradiated Harshaw crystals.

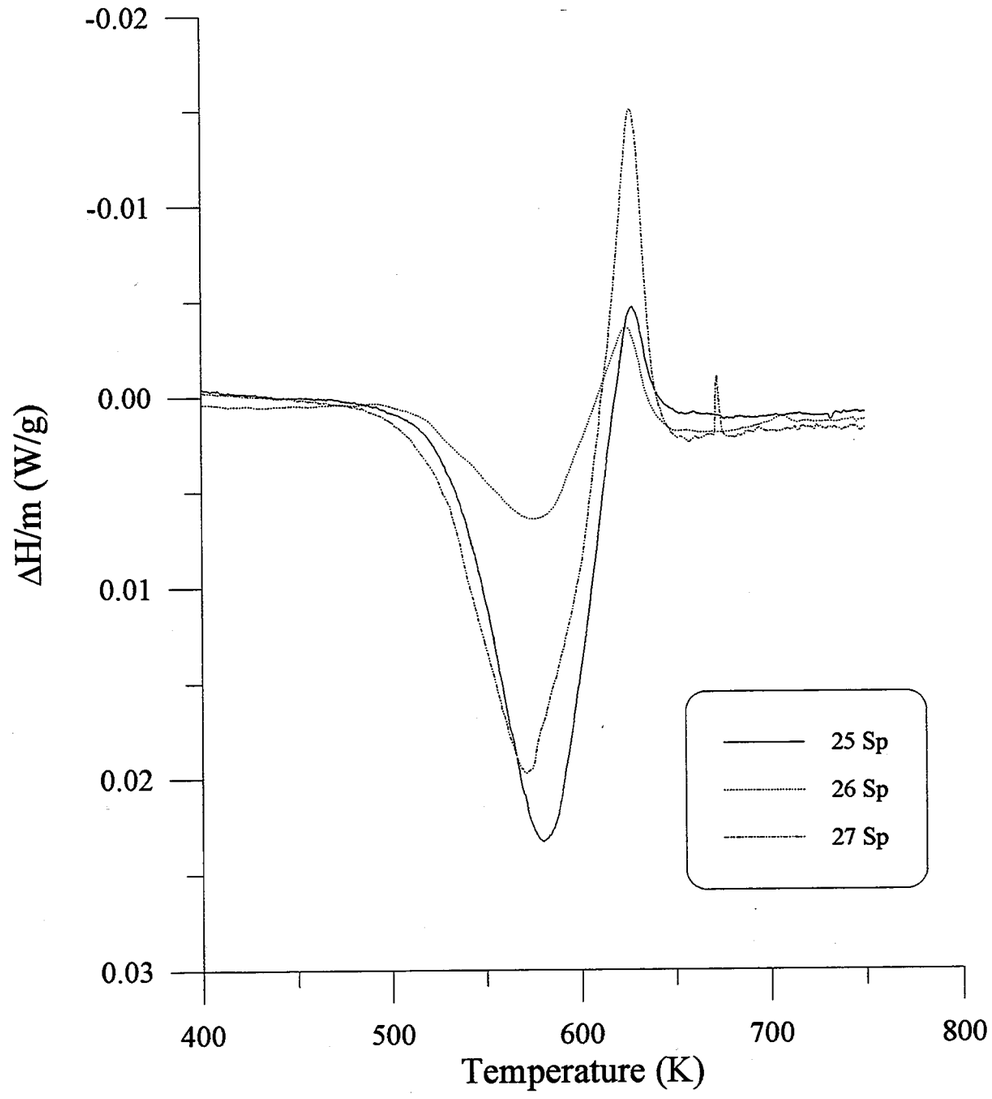

Figure 12: *DTA curves of Sp–800 samples irradiated in GIF B2 (22 MGy, 4 kGy/h, 100 °C)*

4.4. Asse Speisesalz of the 800 meter level (Sp–800) samples

The DTA curves obtained for irradiated Asse Speisesalz (Sp–800) samples show a similar pattern to those obtained for the non–irradiated Sp–800 samples: an exothermal peak between 485 and 705 K with a superimposed endothermal peak between 565 and 635 K due to the

dehydration of polyhalite. (see Fig. 12) Just as for the non–irradiated Sp–800 samples the stored energy values have been corrected for this endothermal effect.

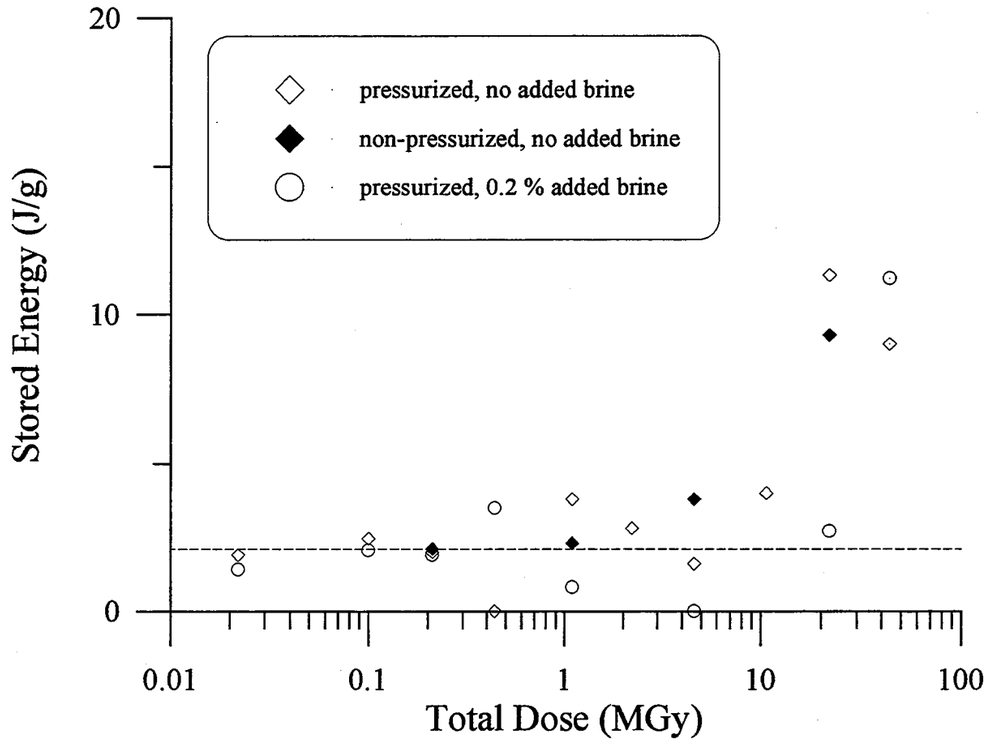

Figure 13: *Stored energy of Sp–800 samples irradiated in GIF B2 (4 kGy/h, 100 °C)*

Figure 13 shows the stored energy values obtained for the Sp–800 samples irradiated in GIF B2 at 4 kGy/h. At low total doses the stored energy values are approximately equal to those observed for the simultaneously irradiated Harshaw crystals. However the stored energy observed for the samples irradiated up to 44 MGy is much lower than that observed for the Harshaw crystals, i.e. 10 versus 18 J/g. A possible explanation for this observation is that for the stored energy measurements of the Sp–800 samples irradiated up to a total dose of 44 MGy, recrystallized and then redamaged material was selected.

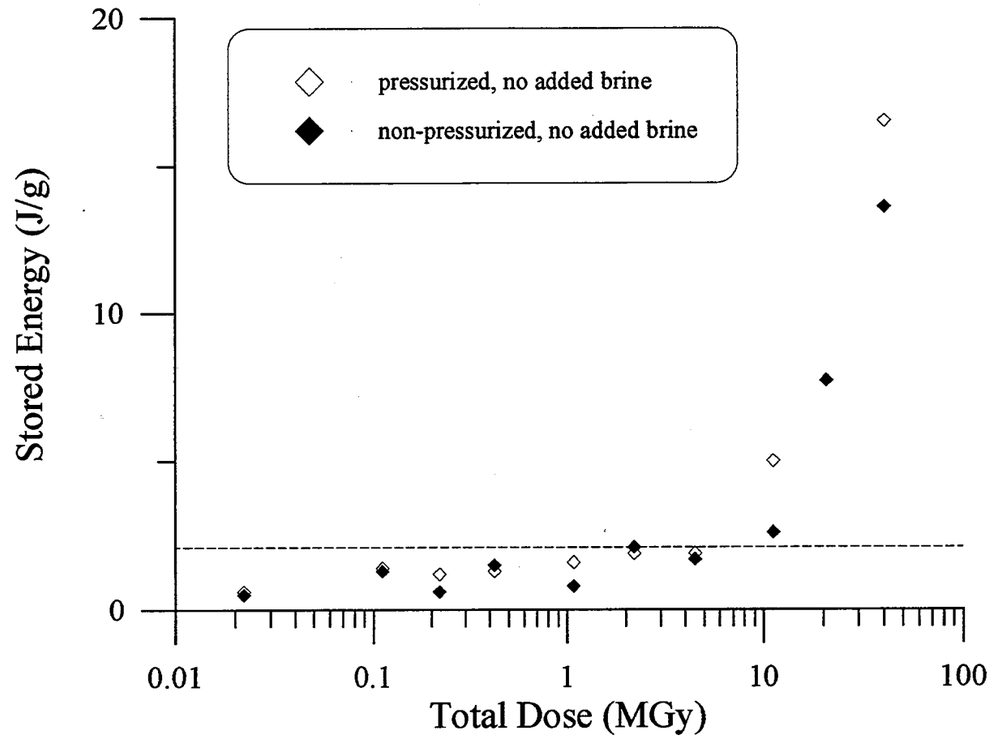

Figure 14: *Stored energy of Sp–800 samples irradiated in GIF B3 (15 kGy/h, 100 °C)*

The stored energy values obtained for the Sp–800 samples irradiated in the GIF B3 experiments are shown as a function of total dose in Fig. 14. The results obtained for the Sp–800 samples in the GIF B3 experiments are also similar to those obtained for the Harshaw single crystals, at least up to total doses of 11 MGy. At 22 and 40 MGy total dose, however, the stored energy values obtained for the Sp–800 samples are higher than those for the Harshaw crystals.

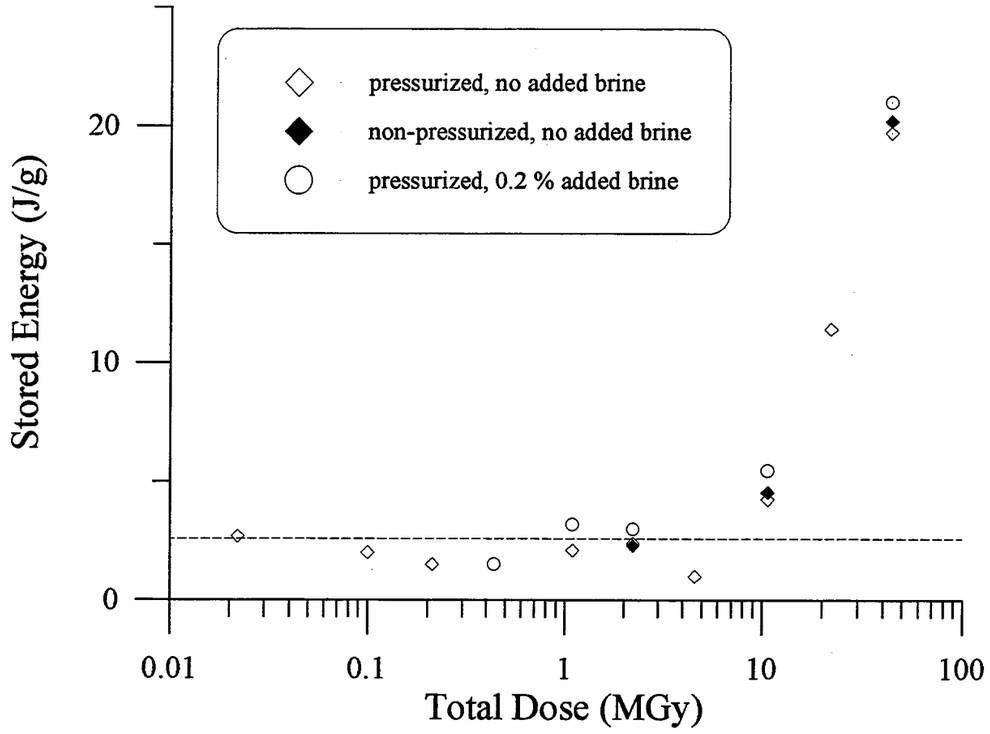

Figure 15: *Stored energy of Borehole Anhydritic samples irradiated in GIF B2 (4 kGy/h, 100 °C)*

4.5. Borehole Anhydritic Samples

For the borehole anhydritic samples we only have stored energy data from GIF B2, i.e. samples irradiated with a dose rate of 4 kGy/h. The DTA curves obtained for these samples only show an exothermal peak with a maximum at about 600 K. In Fig. 15 the dependence of the stored energy of these samples on total dose is shown. The observed dependence is similar to that for the Harshaw crystals irradiated in this experiment. The stored energy for the samples irradiated to 44 MGy total dose is a little higher than that of the simultaneously irradiated Harshaw crystals, 20 and 18 J/g respectively.

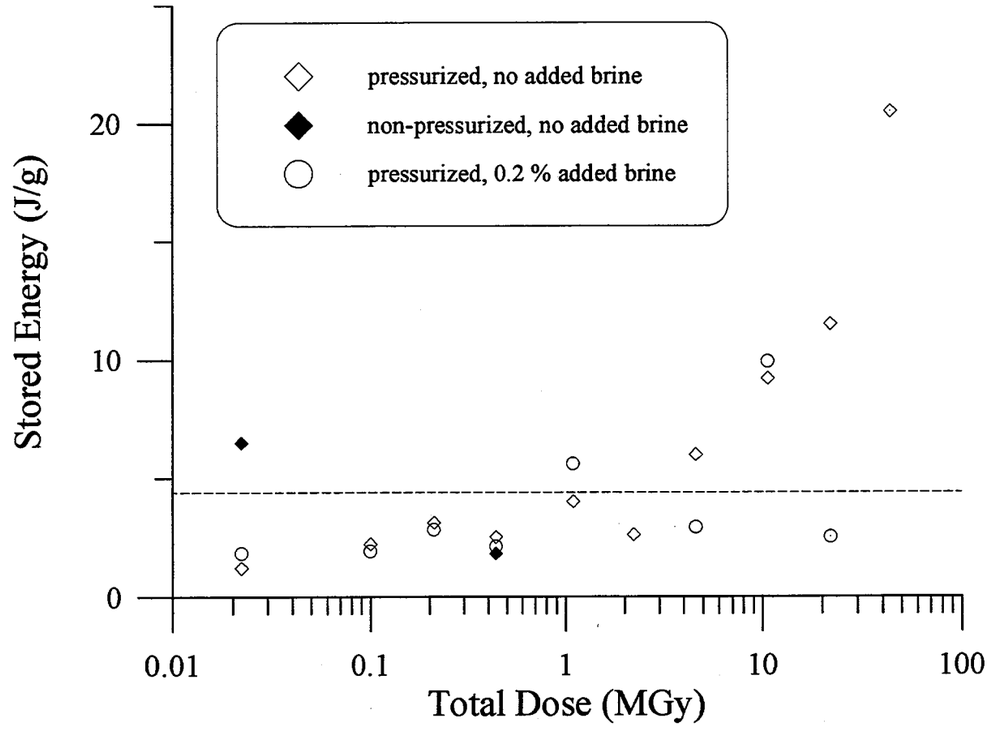

Figure 16: *Stored energy of Borehole Polyhalitic samples irradiated in GIF B2 (4 kGy/h, 100 °C)*

4.6. Borehole Polyhalitic Samples

The DTA curves obtained for these samples are similar to those observed for the Sp–800 samples, only the endothermal signal due to the dehydration of polyhalite is often a lot stronger. This makes it more difficult to estimate the stored energy. It is therefore not surprising that in Fig. 16, where the obtained stored energy values are shown as a function of total dose, the spread in the data points is much larger than that of the other samples. The dependence of the stored energy on total dose is however similar to that of the other samples.

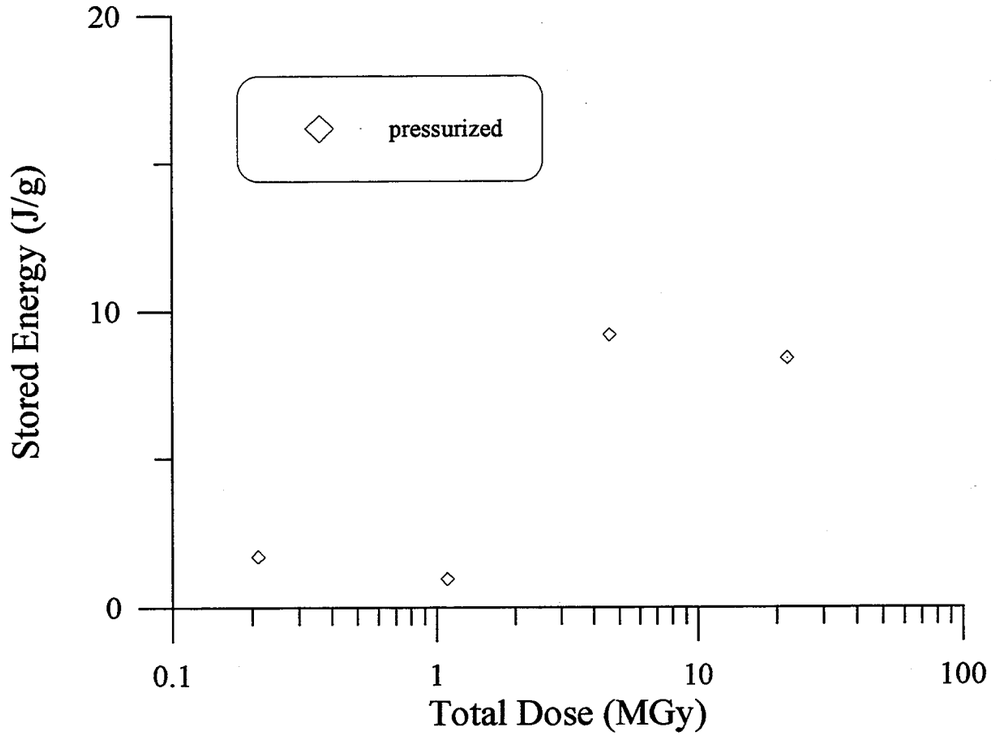

Figure 17: *Stored energy of Polyhalitic Salt samples irradiated in GIF B2 (4 kGy/h, 100 °C)*

4.7. Polyhalitic Salt samples

Only a few data points for these samples have been obtained and are shown in Fig. 17. The DTA curves for these samples are similar to those of the borehole polyhalitic samples.

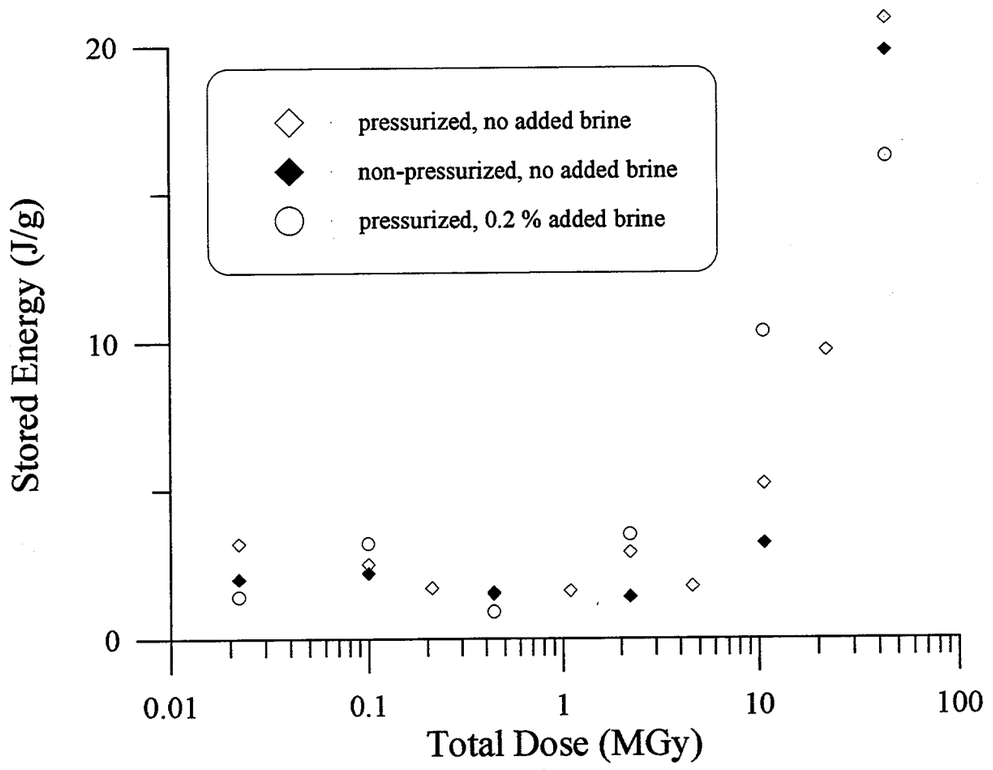

Figure 18: *Stored energy of Potassas de Llobregat samples irradiated in GIF B2 (4 kGy/h, 100 °C)*

4.8. Potasas de Llobregat samples

The measured stored energy values obtained for the irradiated Potasas del Llobregat samples irradiated in GIF B2 are shown in Fig. 18. The results obtained for these samples are similar to those of the other samples.

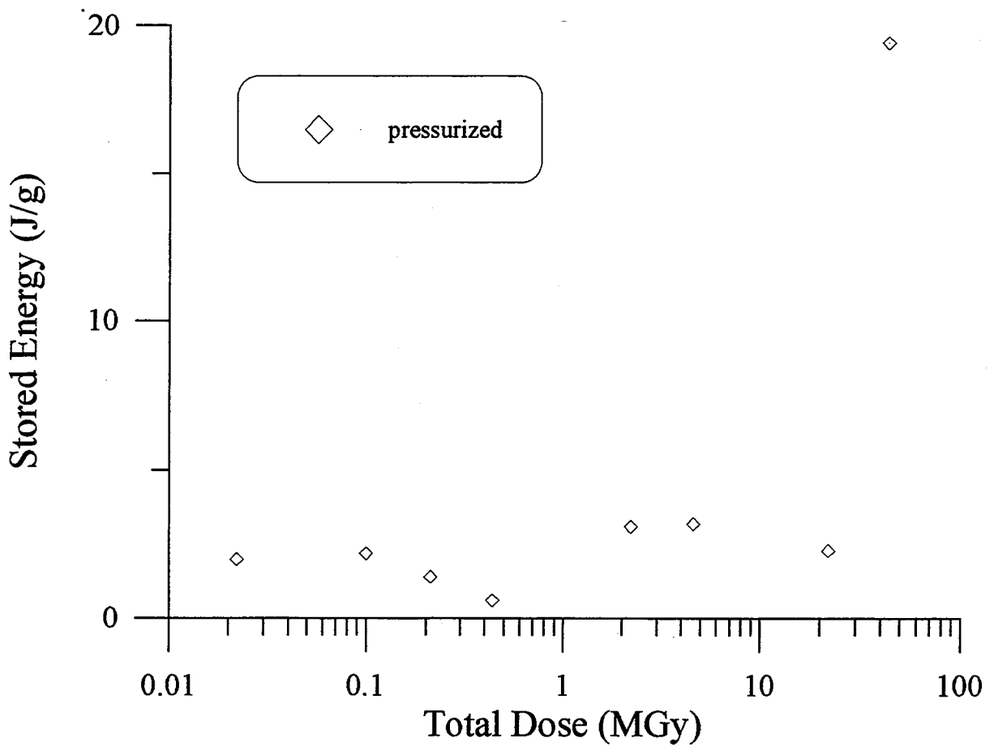

Figure 19: *Stored energy of Dutch Salt samples irradiated in GIF B2 (4 kGy/h, 100 °C)*

4. 9. Dutch Salt samples

The measured stored energy values obtained for the Dutch salt samples irradiated in GIF B2 are shown in Fig. 19. The results obtained for these samples are also similar to those of the other samples.

5. CONCLUSIONS

For total doses between 0.02 and 44 MGy, a temperature of 100 °C and dose rates of either 4 or 15 kGy/h it can be conluded that in general the stored energy developed in the most damaged parts of salt samples of different composition and microstructure, irradiated under the same conditions, is approximately equal

Hydrostatic pressure of 200 bar or less has no effect on the stored energy developed in pure NaCl single crystals during irradiation.

At a total dose of 44 MGy the stored energy developed in pure NaCl single crystals irradiated at 4 kGy/h is about a factor three higher then that developed at 15 kGy/h.

In most of the irradiated samples recrystallized material has been found. Since for the stored energy measurements presented in this article the most damaged material of the irradiated samples was selected, this means that in general bulk stored energy values will be lower than the values presented in this article.

We strongly suspect, stored energy at crystal boundaries to follow a different behaviour than at the crystal interior.

ACKNOWLEDGEMENT

We would like to thank Mr. A.C.G. van Genderen and Dr. P.J. van Ekeren of the Thermodynamics Centre Utrecht for performing the DTA measurements and calculating the stored energy values.

REFERENCES

A. GARCÍA CELMA, 1993: *"Radiation Damage in Natural and Synthetic Halite, Progress report December 1992 – February 1993"*, ECN–C––93–087, Netherlands Energy Research Foundation ECN, Petten, 99 p.

A. GARCÍA CELMA and H. DONKER, 1994a: *"Stored energy in irradiated salt samples"*, Nuclear Science and Technology series, EUR–14845, Commission of the European Communities, Luxembourg, 127 p.

A. GARCÍA CELMA and H. DONKER, 1994b: *"Radiation–Induced Creep of Confined NaCl"*, Rad. Eff. Def. Solids **132**, 223–247.

A. GARCÍA CELMA, H. VAN WEES and L. MIRALLES, 1991: *"Methodological developments and materials in salt–rock preparation for irradiation experiments"*, Nuclear Science and Technology Series, EUR 13266 EN, Commission of the European Communities, Luxembourg, 67 p.

A. GARCÍA CELMA, J.C. MAYOR, C. DE LAS CUEVAS and J.J. PUEYO, 1992: *"Radiation Damage in Salt"*, in: "Pilot Tests on Radioactive Waste Disposal in Underground Facilities", Ed. B. Haijtink, Nuclear Science and Technology Series, EUR 13985 EN, Commission of the European Communities, Luxembourg, p. 75–89.

A. GARCÍA CELMA, H. DONKER, W.J. SOPPE and L. MIRALLES, 1993: *"Development and Anneal of Radiation Damage in Salt: End Report August 1988 – August 1993"*, ECN–C––93–086, Netherlands Energy Research Foundation ECN, Petten, 77 p.

A. GARCÍA CELMA, A.J. NOLTEN, W.A. FELIKS and H. VAN WEES, 1995: *"Methodology of Irradiation Experiments on Non–Ground Salt Performed at the HFR in Petten"*, article 6 of this volume.

M. JIMÉNEZ DE CASTRO and J.L. ÁLVAREZ RIVAS, 1990: *"The Surface Effect on the Stored Energy in Gamma–Irradiated NaCl and LiF"*, J. Phys. Condens. Matter **2**, 1015–1019.

N. JOCKWER, 1981: *" Untersuchungen zur Art und Menge des im Steinsalz des Zechsteins enthaltenen Waser sowie dessen Freisetzung und Migration im Temperaturfeld endlagerter radioaktiver Abfälle"*, Ph.D. Thesis, Technische Universität Clausthal, 135 p.

J.J. PUEYO, C. DE LAS CUEVAS, J. GARCÍA, P. TEIXIDOR and L. MIRALLES, 1992: *"Geochemical Characterization"*, in "Textural and Fluid Phase Analysis of Rock Salt Subjected to the Combined Effects of Pressure, Heat and Gamma Radiation, Part A". Ed. F. Huertas, J.C. Mayor and C. Del Olmo, Nuclear Science and Technology Series, EUR 14169 EN, Commission of the European Communities, Luxembourg, p. 3–64.

T. ROTHFUCHS, K. DUIJVES and R. STIPPLER, 1988: *"Das HAW–projekt. Demonstrationseinlagerung Hochradioaktiver Abfälle im Salzbergwerk Asse"*, Nuclear Science and Technology Series, EUR–11875–DE/EN, Commission of the European Communities, Luxembourg, 227 p.

P. SCHUTJENS, 1991: *"Intergranular Pressure Solution in Halite Aggregates and Quartz Sands: an Experimental Investigation"*, Ph. D. Thesis, Utrecht University, p.123–124.

C.J. SPIERS, J.L. URAI, G.S. LISTER, J.N. BOLAND and H.J. ZWART, 1986: *"The Influence of Fluid–Rock Interaction on the Rheology of Salt Rock"*, Nuclear Science and Technology Series, EUR–10399, Commission of the European Communities, Luxembourg, 131 p.

J.L. URAI, C.J. SPIERS, H.J. ZWART and G.S. LISTER, 1986: *"Weakening of Rock Salt by Water During Long–Term Creep"*, Nature **324**, 554–557.

ON THE SATURATION OF RADIATION DAMAGE IN IRRADIATED NATURAL ROCK SALT

H. Donker and A. Garcia Celma

ABSTRACT

Natural rock salt samples of the 800 m. level from the Asse mine, Remlingen, Germany were gamma–irradiated at 100 °C with spent fuel elements from the High Flux Reactor at Petten, The Netherlands. Dose rates in the experiments varied between 200 and 20 kGy/h in monthly cycles. After irradiation the radiation induced stored energy was studied as a function of total dose. Total doses of up to 1200 MGy were reached. Initially there is an approximately linear increase of stored energy with increasing total dose, which levels of at higher doses until it reaches a saturation value of about 140 J/g. The results of the stored energy measurements were compared with those obtained by other scientists for irradiated pure and K–doped NaCl single crystals.

1. INTRODUCTION

One of the considered options for the disposal of radioactive waste consists of depositing the waste in deep rock salt formations. Rock salt however, is known to be very susceptible to radiation damage when exposed to ionizing radiation. Therefore, much research on radiation damage in rock salt and its safety aspects for repository concepts has been performed during the last decades.

The primary defects formed upon irradiation of alkali halides are F– and H–centres, which result from the radiation–less decay of excitons [Itoh, 1982]. Upon prolonged irradiation, depending on the temperature, the F–centres can aggregate forming colloidal metallic particles [Hughes, 1983; Hughes and Jain, 1979]. Also prismatic dislocation loops have been observed to develop during irradiation of alkali halides. According to Hobbs et al. [1973] these dislocation