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COLLOID FORMATION AND STORED ENERGY DEPOSITION IN IRRADIATED NATURAL ROCK SALT SAMPLES

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ABSTRACT

The temperature dependence of the radiation-induced formation of colloidal sodium, molecular chlorine gas and the associated deposition of energy in rock salt was determined between 100 °C and 250 °C. At each temperature the irradiation dose was varied between 10^6 and 10^8 Gy. After irradiation, the colloidal sodium content was measured via hydrogen evolution upon dissolving the salt in water. The amounts of chlorine gas were determined both in the gas phase above the salt and in the bulk of the sample. Stored energy was determined by DSC on selected halite specimens. The present study confirms the equivalence of the radiation-induced formation of the different products, i.e. colloidal sodium, molecular chlorine, and stored energy, over a substantial dose range and temperature range. The chosen range is of interest for radioactive waste repositories. From the data obtained it is concluded, that at temperatures above 150 °C, colloid formation starts to saturate with increasing dose. At 100 °C about 0.7 mol % sodium were detected for 10^8 Gy but no saturation was indicated. Most of the molecular chlorine is found, after irradiation, inside the salt crystals of the bulk sample, but chlorine evaporation from the salt increases with increasing temperature. The stored energy follows the trends outlined for the molecular radiation products, i.e. it increases with dose. A conversion factor of about 70 J/g per mol % colloidal sodium in the rock salt is found by us. This value is lower than that proposed by Groote and Weerkamp of 125 J/g per mol % colloidal sodium [Groote and Weerkamp, 1990]. The reason for this difference is explained by Donker et al. [Donker et al., 1995 (article nr. 19, this volume)]. They obtained a value for the equivalence of stored energy and colloid content that is much nearer to one obtained by us than to that of Groote and Weerkamp. The influence of sulfate-containing minerals as anhydrite and polyhalite on the formation of radiation damage and stored energy was investigated but the present data do not allow to derive any final conclusion.

1. INTRODUCTION

Gamma irradiation of rock salt leads via a complex reaction scheme to radiation damage with accumulation of colloidal sodium and chlorine gas in the sodium chloride lattice (see for example [Hughes, 1983, Hobbs, 1973]). The formation of the irradiation products is associated with the storage of energy. In order to evaluate the long-term safety of a radioactive waste repository in rock salt, among other things quantitative information regarding the amount of radiation damage is required.

The formation of radiation defects depends on the following parameters: total dose, dose rate, temperature, microstructure of the salt, and the level of impurities. This has been the subject of numerous studies in the past (for an overview see [Gies et al., 1994]). In most of these studies, however, the radiation-induced formation of only one of the irradiation products was determined. Exceptions are the investigations of Jenks et al. [Jenks and Bopp, 1974, 1977, Jenks et al., 1975] and of Groote and Weerkamp [Groote and Weerkamp, 1990], but in these studies the temperatures were below 150 °C. Also, in many studies only fairly low radiation doses were employed at which the coagulation of radiation products has just begun. Extrapolation from these values to the conditions in a repository is, at its best, questionable.

There was a lack of data regarding chlorine development and its correlation with both sodium colloid development and stored energy deposition in NaCl, at least for the temperatures and total doses relevant for radioactive waste repositories. We have filled in this gap by irradiating samples in the temperature region above 150 °C, measuring the stored energy deposited and determining chemically the amounts of molecular chlorine and of sodium colloids in the same samples. Moreover, in order to allow comparison with previous research, the same experiments and measurements have also been performed at temperatures lower than 150 °C. The results of these investigations are presented here. The experimental methodologies are described in detail elsewhere [Mönig et al., 1995 (article nr. 8, this volume)].

2. RESULTS

The γ -radiation-induced generation of colloidal sodium depends strongly both on dose and temperature. This is shown in Fig. 1, which presents the data obtained for irradiations at temperatures of 100 °C, 150 °C, 200 °C, and 250 °C, respectively. The data points obtained from high dose irradiations have all been set to 100 MGy. This dose value was estimated from recorded decay curves for the gamma intensity of the spent fuel elements, since the solid state

dosimeters were not calibrated for such high dose ranges at the temperatures being used. Therefore, the deviations of the dose values from 100 MGy are not exactly known, but are expected to be within 30% of this value.

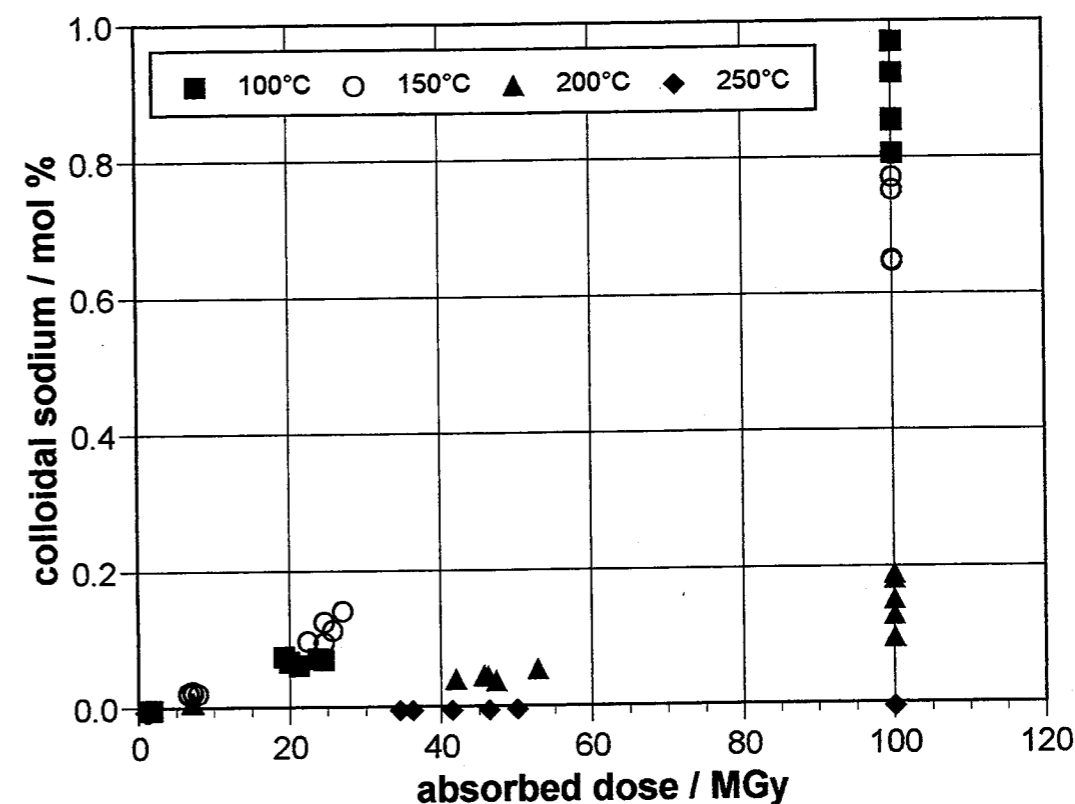


Figure 1: Yield of colloidal sodium vs. irradiation dose in rock salt samples γ -irradiated at various temperatures

Significant colloid formation is observed at temperatures of 100°C and 150°C, while only small amounts of colloids are produced at 200°C and hardly any colloid formation is found at 250°C (less than 0,003 mol % Na). At the latter temperature saturation in radiation damage is clearly observed. However, no saturation is indicated at 100°C and 150°C, while intermediate behavior is seen for 200°C.

The formation of molecular chlorine in these γ -irradiated rock salt samples depends also on dose and temperature (see Fig. 2). The total chlorine yields are given in Fig. 2. It was found that a small portion of the chlorine gas is released from the salt samples already during the irradiation and, thus, is found in the gas phase. The relative portion of chlorine gas released from the samples during irradiation increases with temperature. The corresponding data for

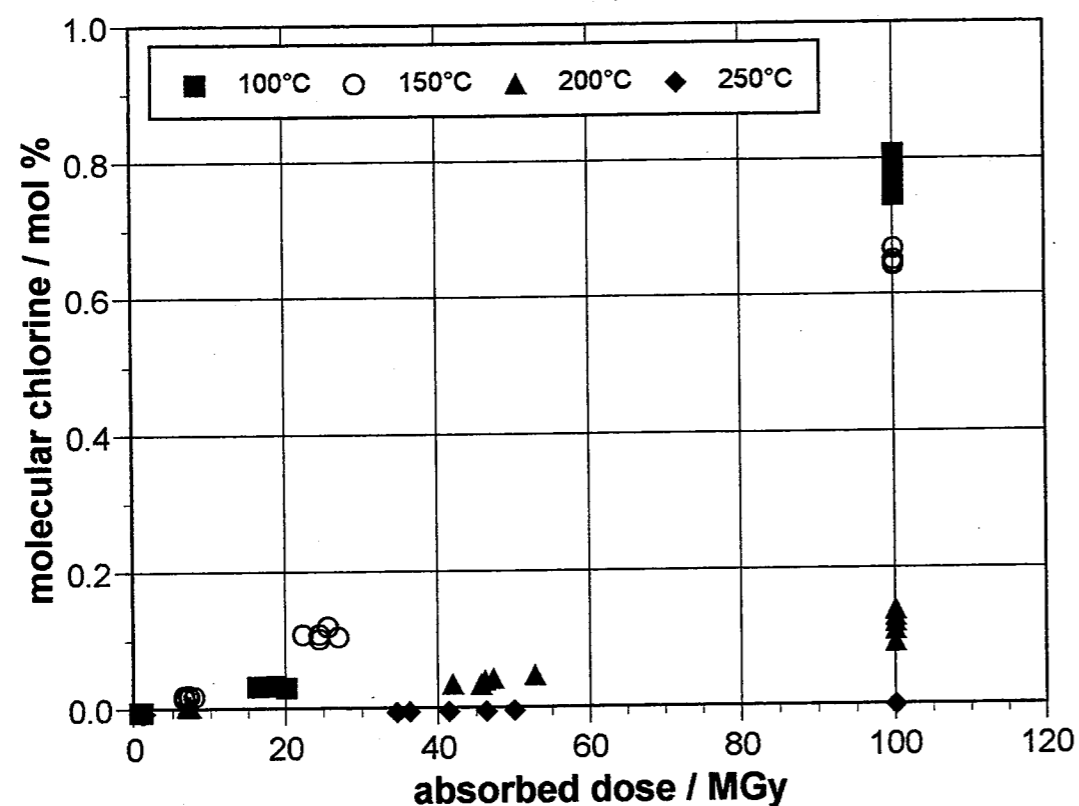


Figure 2: Yield of molecular chlorine vs. irradiation dose in rock salt samples γ -irradiated at various temperatures

high dose irradiations (duration 80 days, dose about 100 MGy) under helium are given in Table 1. At temperatures of 150 °C and lower, only insignificant amounts of chlorine were released during the experiment. However, it is conceivable, that the portion of chlorine gas being released from the salt increases with time. Since diffusion is slow and is often a temperature-activated process, at lower temperatures chlorine gas requires more time to diffuse through the crystal to the crystal's surface than at higher ones.

Table 1: Relative portion and absolute chlorine yield released from rock salt during irradiation (duration 80 days, dose about 100 MGy, helium atmosphere)

irradiation temperature [°C]	relative portion in gas phase [%]	absolute amount in gas phase [mol/kg]
100 °C	0.003	0.0045
150 °C	0.007	0.008
200 °C	0.16	0.04
250 °C	4.0	0.0045

As expected, the gas atmosphere during irradiation has neither an influence on the colloids yield nor on the chlorine yields. Identical results are obtained both for irradiations carried out in a nitrogen/oxygen (80/20 v/v) atmosphere and for irradiations carried out in a helium atmosphere (data not shown).

From the current understanding of the interaction of ionizing radiation with sodium chloride follows, that the γ -radiation-induced formation of metallic (colloidal) sodium is accompanied by the formation of equal amounts (on a molar basis) of molecular chlorine. Thus, plotting the chlorine yields versus the colloidal sodium yields should give a straight line with slope 1, irrespective of irradiation temperature, dose, and dose rate. This has indeed been observed in all our experiments (Fig. 3). Nonetheless, a small deviation from the expected straight line is apparent. In most cases, slightly lower chlorine yields than colloid yields are obtained. The deviation from the straight line increases at lower absolute yields. However, this finding does not invalidate the theoretical picture of radiation damage formation. It is rather attributed to small chlorine losses during the detection procedure, which inevitably occur even though extreme care has been taken in handling and preparing the equipment used. The scatter at very low yields (i.e. data for low dose irradiations and/or high temperatures) is most likely due to a decrease in the measuring accuracy as the lower detection limits of the hydrogen and hypochloride detection are approached.

The stored energy was measured in some of the samples. The available data are shown in Fig. 4 versus the amount of colloidal sodium detected in the same samples. Interestingly, no stored energy could be measured in samples irradiated at 200°C (triangles in Fig. 4), even though both colloidal sodium and molecular chlorine were clearly detected. This could be due to the low heating rate of 1 K/min that was employed in the DSC-measurements. The energy release peak is very broad under these conditions and may not be discernible from the baseline with its noise. In order to test this hypothesis, some of these measurements are being repeated at much higher heating rates, but the data are not yet available.

The two lines in Fig. 4 represent conversion factors between stored energy and the amount of colloidal sodium, that are published in the literature. The upper line corresponds to a conversion factor of 125 J/g stored energy per mol % colloidal sodium in rock salt. This number was taken from Groote and Weerkamp [Groote and Weerkamp, 1990]. The lower line corresponds to a value of 70 J/g stored energy per mol % colloidal sodium, that was derived by Jenks et al. [Jenks et al., 1975]. Clearly all our data fall close to the latter value.

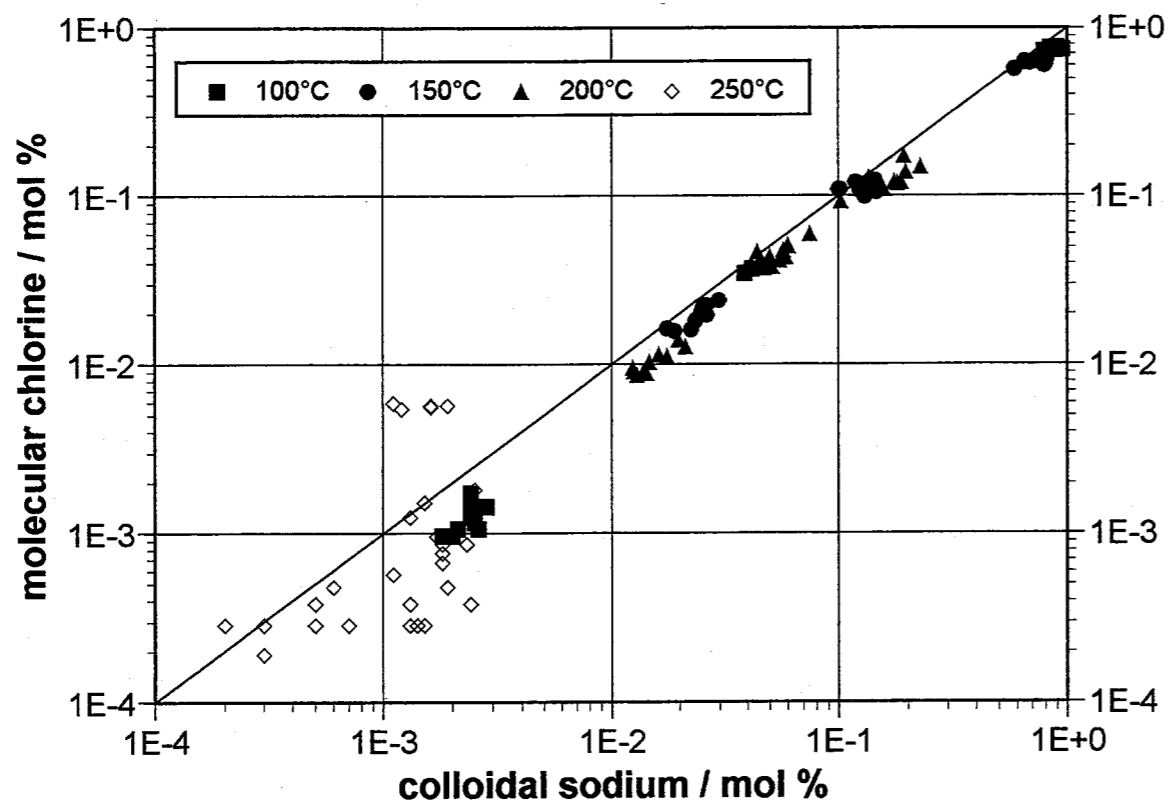


Figure 3: Yields of colloidal sodium vs. yields of molecular chlorine. Each data point corresponds to different irradiation conditions. The range of irradiation conditions was: temperatures 100 - 250 °C, dose 1 - 100 MGy, dose rate varied between 240 and 40 kGy/h during the irradiation.

Each data point in Fig. 4 represents the average of three independent DSC-measurements. In some cases it was observed that the individual results varied considerably (up to 40 %). Two reasons are conceivable for this finding:

Firstly, it could be due to the small rock salt specimens used in the DSC-measurements being different in their mineralogical composition from the bulk of the sample. As a rule, Asse rock salt consists of ~ 95 % halite and ~ 5 % of sulfates. Of the latter particularly the mineral anhydrite is known to be a very capable dosimeter material for ionizing radiation. It is expected, therefore, to contribute to the energy storage in rock salt, although it is not known to what extent. Generally, it is observed that the yield of the radiolysis mechanism in ionic crystals depends inversely on the charge of the ions. Thus, stored energy is expected to reach lower values in anhydrite and polyhalite than in halite. If the small specimens contain more sulfate minerals than the bulk, therefore, a lower value for the stored energy may be expected. Dehydration

of polyhalite is not the reason for these differences because the method used to determine the stored energy already takes it into account [Mönig et al., 1995 (article nr. 8, this volume)].

Secondly, the sample crystals being used in the measurements could have received significantly different radiation doses. The half-thickness of rock salt for γ -quanta from spent fuel elements (energy of several hundred keV) is about 30 - 40 mm. The diameter of the irradiation ampoule is 49.9 ± 0.1 mm. Therefore, crystals lying at the perimeter of the ampoule have received a dose which is about 50 - 60 per cent higher compared to crystals which are located near the middle axis. These differences in dose are averaged out in the determination of colloidal sodium and molecular chlorine, as big sample volumes are used in these measurements. For DSC-measurements, on the contrary, only a few crystals are used, so that it is quite possible that no representative subsample was taken. Unfortunately this situation can not easily be avoided.

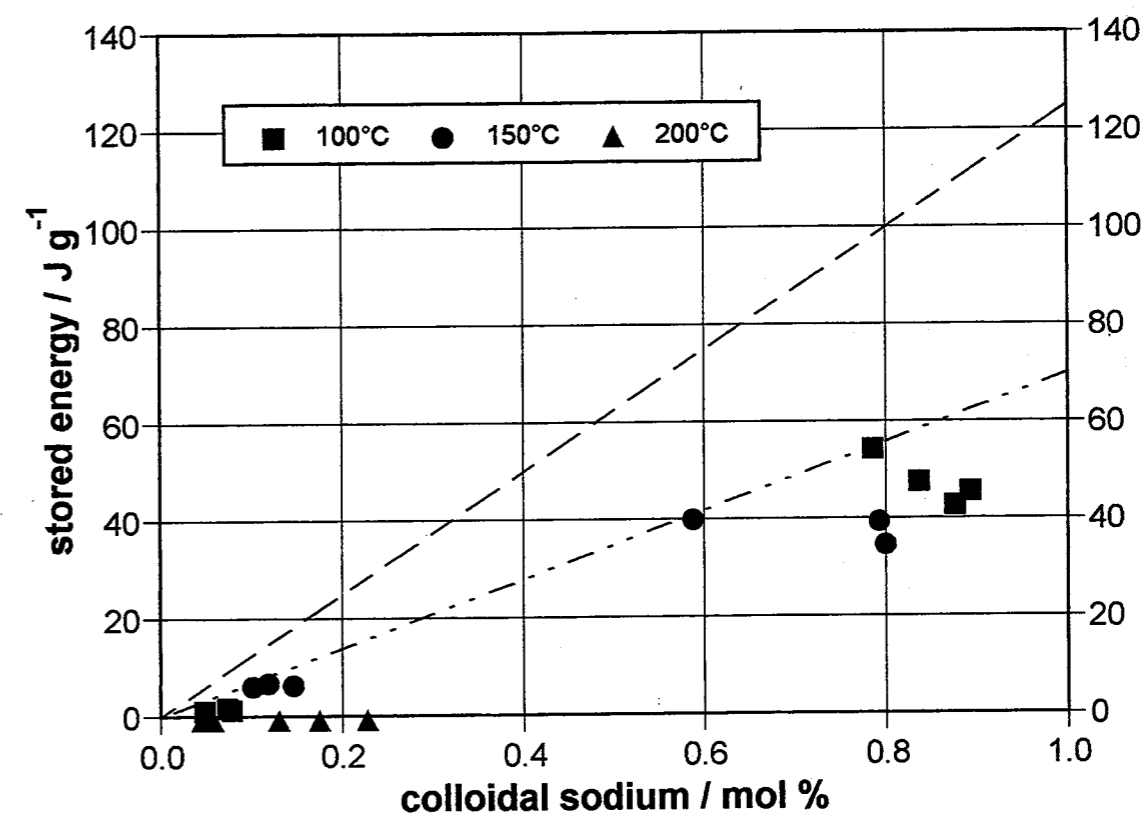


Figure 4: Yield of colloidal sodium vs. stored energy for different irradiation temperatures (the broken line (upper line) reflects a conversion factor of 125 J/g stored energy per mol % colloidal sodium, while the dashed one corresponds to 70 J/g per mol % Na).

The salt samples used in the DSC-measurements were chemically analyzed afterwards and their individual polyhalite and anhydrite content was calculated on the basis of elemental analyses. In order to find out whether the content of sulfate-containing minerals in the samples has an effect on the amount of stored energy, the individual results for two different sample series with identical irradiation history (100 MGy at 100°C and 100 MGy at 150°C) are listed in Table 2. Clearly, from these data no correlation between the amount of stored energy and the content of sulfate-containing minerals can be derived.

Table 2: *Results of the DSC measurements in individual subsamples and their respective anhydrite and polyhalite content.*

irradiation conditions	subsamples for DSC	anhydrite [mg / kg]	polyhalite [mg / kg]	stored energy [J / g]
sample 101 100°C, 100 MGy	subsample 1	5583	1205	84,1
	subsample 2	3870	2131	45,5
	subsample 3	6046	1884	35,6
sample 103 100°C, 100 MGy	subsample 1	3777	3441	45,2
	subsample 2	5067	2101	40,1
	subsample 3	5331	2731	45,3
sample 104 100°C, 100 MGy	subsample 1	2245	3161	45,7
	subsample 2	2206	2664	44,2
	subsample 3	2742	3243	49,4
sample 105 100°C, 100 MGy	subsample 1	1315	11692	37,0
	subsample 2	4378	9424	50,8
	subsample 3	2235	4930	57,5
sample 131 150°C, 100 MGy	subsample 1	2168	6727	42,4
	subsample 2	1044	8130	41,1
	subsample 3	1403	3206	38,6
sample 132 150°C, 100 MGy	subsample 1	1457	6746	37,2
	subsample 2	1957	3841	33,6
	subsample 3	1959	5490	49,9
sample 133 150°C, 100 MGy	subsample 1	1818	5281	32,2
	subsample 2	1356	2854	38,0
	subsample 3	1605	4674	36,1

3. DISCUSSION

The present study confirms clearly that the irradiation of rock salt leads to the formation of equal amounts (on a molar basis) of the molecular products colloidal sodium and

chlorine gas over a broad temperature and dose range. This is one of the few investigations, in which the various products have been determined for the same sample. Other investigations are those of Jenks and Bopp [Jenks and Bopp, 1974, 1977] and of Groote and Weerkamp [Groote and Weerkamp, 1990]. However, in these studies the irradiation temperature was restricted to a range below 150°C. In order to quantify the formation of molecular chlorine, both the amount present in the crystals and the amount released into the gas phase above the salt must be determined. This is particularly true for temperatures above 150°C. A time dependence for the chlorine release is conceivable but was not investigated in the present study.

The formation of radiation defects and of molecular products in NaCl depends, in a complex manner, on the parameters dose, dose rate, and temperature. Also the microstructure of the salt and the level of impurity were suggested to have an influence. In principle, three phases can be distinguished in which the formation of defects is related to radiation dose. In an induction phase the density of F- and H-centers increases, while no significant growth of sodium colloids or other molecular irradiation products occurs. This is followed by a phase in which a more or less linear relationship exists between the formation of molecular defects and dose. At even higher radiation doses saturation occurs under specific conditions. While the beginning of the saturation depends on dose, the amount of irradiation products becomes independent of dose once saturation is reached. When considering waste disposal, one of the aspects of importance is the extent of radiation damage to the salt. Therefore, the linear phase and the possible saturation level are of most significance. In the present study saturation is clearly observed at a temperature of 250°C (at a very low level of less than 0,003 mol % damage). At 200°C saturation seems to begin at about 100 MGy. No saturation occurs at 100°C and 150°C in the investigated dose range. This is in accord with the extended Jain-Lidiard (JL) theory [Jain and Lidiard, 1977, Lidiard, 1979, van Opbroek and den Hartog, 1985], which predicts that at a dose rate of 10⁴ Gy/h damage saturation begins above 300 MGy. Unfortunately, under the boundary conditions of our experiments this dose range is only accessible using prohibitively long irradiation times. The absolute yield of radiation damage observed in our experiments is also in accordance with the JL-theory. At a dose of about 100 MGy, a damage level of about 0.8±0.1 mol % was determined. For comparison, using the JL-theory values of 1,4 mol % and 0,6 mol % are estimated for dose rates of 10⁴ Gy/h and 10⁵ Gy/h, respectively, for 100 MGy. Our stored energy data are slightly higher than those of Garcia Celma and Donker [Garcia Celma and Donker, 1994], who determined the stored energy in halite samples (Speisesalz) from the Asse salt mine, which were irradiated at 100°C in the same irradiation facility at Petten. They observed a stored energy of about 15 J/g at 100 MGy and of 40 J/g at about 160-180 MGy. Possibly these differences can be accounted

for by the different dosimetry systems utilized. Our high dose values have been roughly estimated, but in fact may be higher than 100 MGy.

The amount of energy that is deposited in the salt due to the formation of molecular radiation products is of particular importance when the thermo-mechanical consequences of a spontaneous release of the energy is considered. Our data seem to indicate that one mol % colloidal sodium corresponds to a stored energy of about 70 J/g. This value agrees well with the one given by Jenks et al. [Jenks et al., 1975]. From their data Groote and Weerkamp [Groote and Weerkamp, 1990] concluded a value of 125 J/g. Donker et al. [Donker et al., 1995 (article nr. 19, this volume)] reviewed the available data and published calculations. They showed that the value of 125 J/g is based on erroneous assumptions. In their paper Donker et al. suggested to use a conversion factor between defect concentration and stored energy of 5 eV/defect, which corresponds to about 82 J/g. Our experimental value is very similar to this value and corroborates their conclusions.

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