be worth trying again and accepting the leak between the gas system and the brine system. Anyway, if we would continue this research we would introduce two more changes. First we would make all the pressure systems and casing from Inconel what also means that the sizes of the tubes would have to be changed to a diameter of 1/4 " (6.35 mm) because in Inconel these are easier to purchase than tubes (as the stainless steel tubes used now) with a diameter of 6 mm. And second, we would also have to heat the air instead of the aluminium plate to achieve a yet smaller temperature gradient.

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REFERENCES

J.L. URAI, 1983: *"Deformation of wet salt rocks"*. Ph.D. Thesis. University of Utrecht. 221 pp. Available at the University Library.

A. GARCÍA CELMA, J.L. URAI and C.J. SPIERS, 1988: " *A laboratory investigation into the interaction of recrystallization and radiation damage effects in polycrystalline salt rocks"* Commission of the European Communities, Nuclear Science and technology Series, EUR 11849 EN. 125 pp.

A. GARCÍA CELMA, A. and H. DONKER, 1995: *" Inter and Intracrystalline anneal processes in irradiated rock salt"*. Art. Nr.21, This volume.

METHODOLOGY OF IRRADIATION EXPERIMENTS WITH GROUND NATURAL ROCK SALT SAMPLES PERFORMED AT GSF-IFT

J. Mönig, N. Jockwer, H. Gies

ABSTRACT

The formation of radiation damage in natural rock salt samples from the Asse was investigated with special regard to the chlorine development and its correlation with both sodium colloid development and stored energy deposition in NaCl. In addition, the radiation-induced formation of gases and the release of gases from the rock salt was studied. The experimental set-up for performing these irradiations and the analytical methodologies used are presented.

1. INTRODUCTION

The emplacement of canisters containing vitrified reprocessed high level radioactive waste in boreholes in rock salt will result in an exposure of the host rock to temperatures up to 200 °C and gamma dose rates of 1000 Gy/h. The total dose in a repository is estimated to be in the order of 10^9 Gy. Apart from the formation of radiation damage in rock salt, gamma radiation leads to the formation and release of gases from the rock salt.

We determined the formation of radiation damage in natural rock salt samples from the Asse with special regard to the chlorine development and its correlation with both sodium colloid development and stored energy deposition in NaCl. Since these irradiations were carried out in sealed glass ampoules it seemed worthwhile, also to measure the radiation-induced gas formation in and gas release from these samples in order to allow comparison with previous data. The experimental set-up for performing the irradiations and the analytical methodologies used are described here in some detail. The results of these investigations are presented by Jockwer et al. (1995) [article 13 in this volume] and by Mönig et al. (1995) [article 16 in this volume], respectively.

2. EXPERIMENTAL METHODS

2.1. Irradiations

The irradiations were carried out in the cooling pool of the High Flux Reactor (HFR) at Petten. In order to be able to irradiate about 200 sample ampoules within two years, two special facilities were designed and build, so that the samples could be exposed to γ-radiation by placing them amongst spent fuel elements which had been used in previous reactor cycles [Nolten, 1994]. A schematic drawing of the irradiation facility is shown in Fig. 1. It consists of an aluminum container covered by a watertight lid with an O-ring and an aluminum sample holder housing five irradiation ampoules. The sample holder is equipped with an electrical heater and five thermocouples for measuring and controlling the temperature in the range between 80 and 250 °C.

Two of these irradiation containers were placed in a special fuel storage rack normally suitable for storing 42 spent fuel elements (Fig. 2). The space normally occupied by four fuel elements has been modified in two different places to allow positioning of the irradiation containers. The outside part of the irradiation containers consists of a cadmium tube which is necessary for the absorption of thermal neutrons (see Fig. 2).

As spent fuel elements are used as irradiation source, the gamma intensity decreases and the energy spectrum changes with time owing to the decay of the fuel elements. Figure 3 shows a typical curve for the decrease of γ-dose rate versus time inside the irradiator which decreases from about 400 to about 40 Gy/h within a period of 30 days. For irradiation periods longer than four weeks the fuel elements are changed every 28 days.

The ground rock salt samples were irradiated in glass ampoules having a length of 250 mm and a diameter of 49.9 ± 0.1 mm. A break seal and a connector were located at the top of the ampoule (see Fig. 4), in order to be able to take gas samples from the head space of the ampoule, i.e. the residual gas phase volume above the salt. Via a glass tube of 8 mm inner diameter the ampoules were filled with 300 grams of ground salt. In total 250 ampoules were prepared. In order to remove the residual air, the ampoules were evacuated to about 1 mbar and then re-filled to atmospheric pressure by adding either helium or a synthetic air-mixture (oxygen/nitrogen 20:80 v/v), respectively. This process was repeated three times. The ampoules were then sealed gastight by a glass blower.
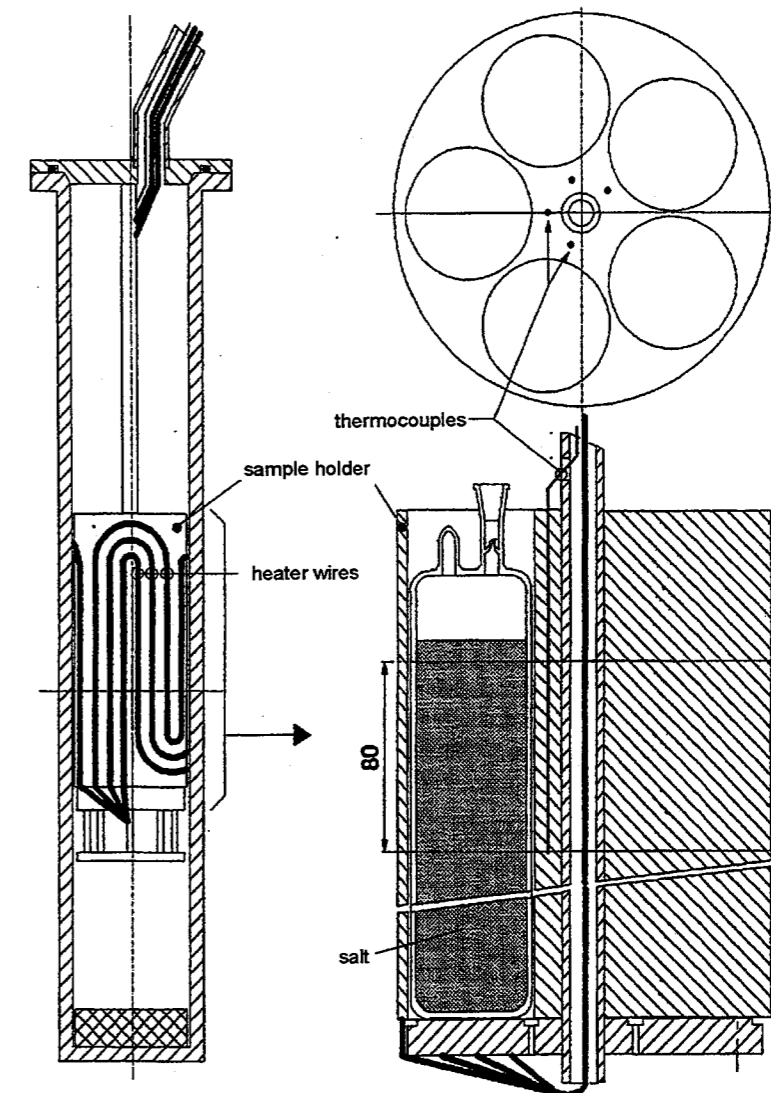

Figure 1: *Schematic drawing of irradiation facility at ECN Petten*

Throughout this study the salt samples used had a homogeneous composition and consisted of ground rock salt with mineralogical contents representative of those of the salt diapirs in northern German (see as well Gies, 1995, [article 11 of this volume]). Briefly, its mineralogical composition is

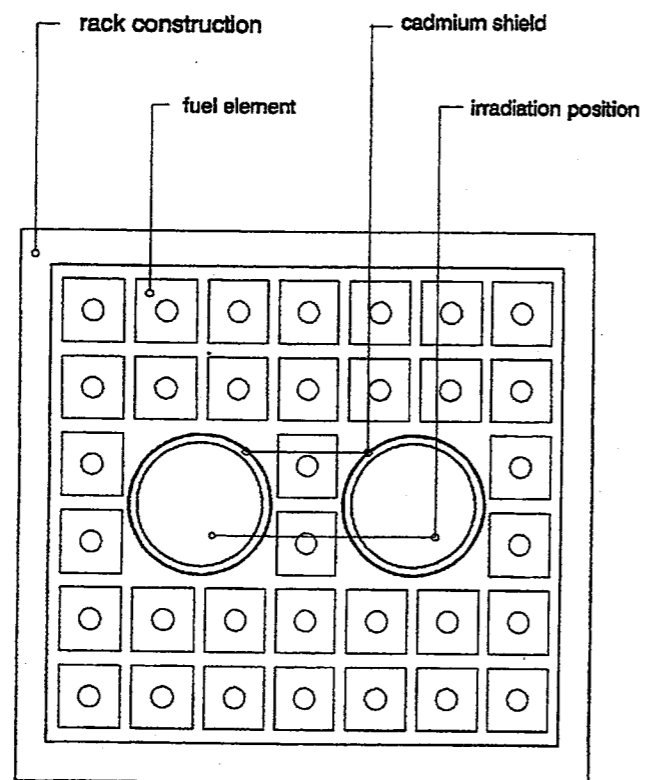|		
halite	97.7	wt%
anhydrite	1.84	wt%
polyhalite	0.47	wt%
total water content	0.04	wt%

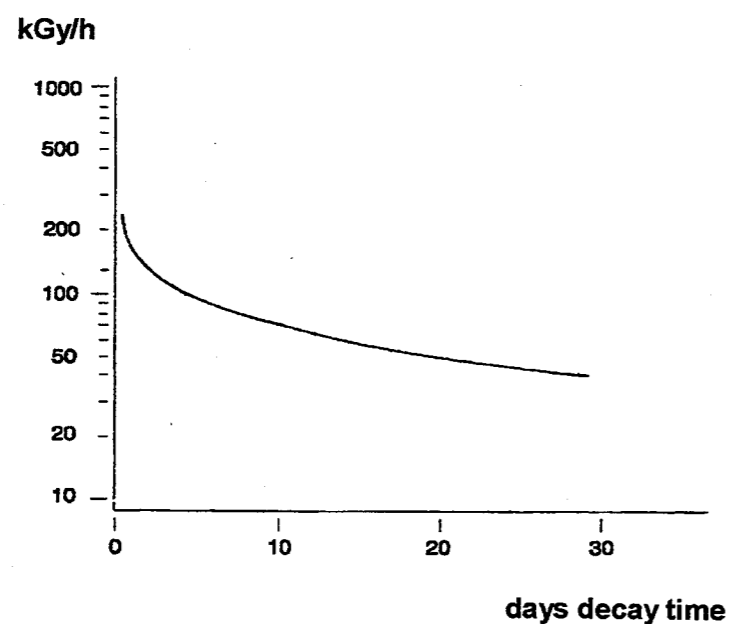Figure 2:   *Irradiation facility at ECN Petten*

Figure 3:   *Typical dose rate decrease versus time in the irradiation facility at ECN Petten*
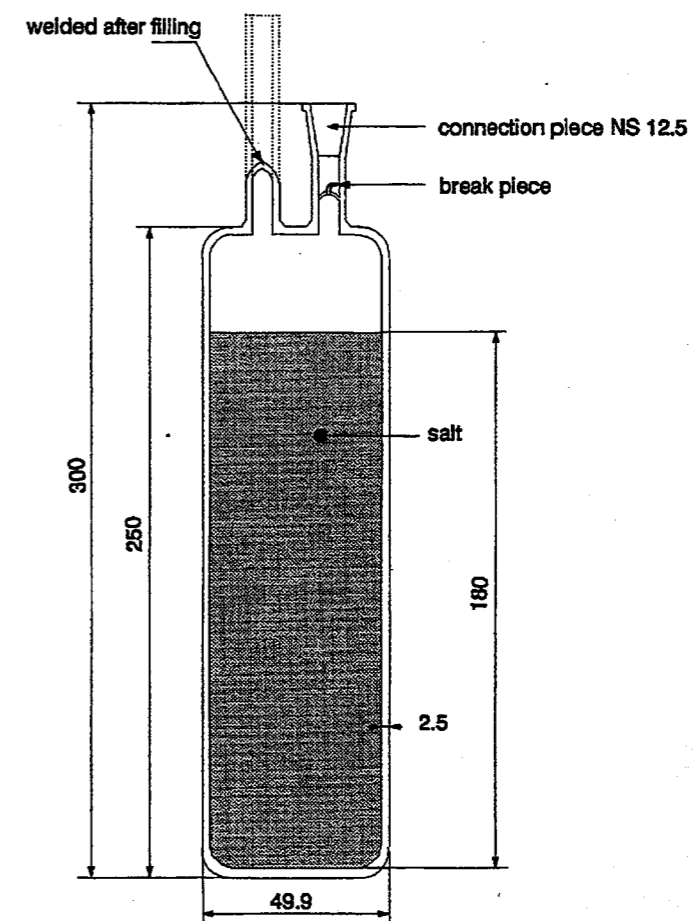

Figure 4:   *Schematic drawing of the glass ampoule used for irradiating the ground salt samples (all numbers are given in mm)*

Each experimental data point represents the average of the results obtained from five samples of identical composition that were irradiated in different irradiation exeriments using the same irradiation conditions. The duration of the irradiations varied between 1 to 80 days corresponding to a radiation dose between about 10^6 and 10^8 Gy. In order to distinguish between the effects of elevated temperature and the effects caused by irradiation, replicas of the ampoules used in the irradiation experiments, having the same salt composition and gas atmosphere, were heated for 8 days at the temperature of 100, 150, 200, and 250 °C.

The radiation doses absorbed in the salt samples were individually determined in each ampoule via two different solid state dosimeters. One type of dosimeter was based on a thermoluminescence measurement of LiF while quartz powder, which was analyzed by ESR, was used in the other dosimeter. The dosimeters were encapsulated in small glass vials (outer diameter 8 mm, length 35 mm) and placed inside the ground salt. Both types of dosimeters were especially developed to meet the temperature and dose rate requirements of the HAW in

situ irradiation experiments. After irradiation the dosimeters were analyzed at the GSF-Institut für Strahlenschutz (Neuherberg).

2.2. Quantitative Determination of Colloidal Sodium.

The amount of colloidal, metallic sodium in the crystal lattice was quantified chemically. About 10 g of salt were weighed into a teflon flask (volume about 250 ml) which was sealed with a screw cap that was equipped with two septa. The weighing in was carried out under nitrogen in a glove box in order to prevent any reaction between the metallic sodium and air humidity. Then 100 ml water were added through a septum and the salt was dissolved. The metallic sodium reacts with the water yielding hydrogen according to

$$Na_{met.} + H_2O \rightarrow Na^+ \ OH^- + \frac{1}{2} H_2 \uparrow \qquad [1]$$

An aliquot of the gas phase in the teflon flask was withdrawn through a septum using a gastight syringe and analyzed by gas chromatography for hydrogen. For each irradiated ampoule three independent hydrogen measurements were performed. The standard deviation of these determinations was typically better than $\pm 10\%$.

The amount of colloidal sodium in irradiated salt is typically given in mol-%. It was calculated from the measured gas phase concentration of H_2 as follows:

$$m_{col.sod.} = \frac{GPC \cdot GPV}{m_{NaCl}} \cdot \frac{2 \cdot MW_{NaCl} \cdot 100}{MV_{H_2}} \qquad (1)$$

with:

$m_{col.sod.}$ = yield of colloidal sodium [mol-%]
GPC = measured gas phase concentration [μl/ml]
GPV = free gas phase volume of teflon flask [ml]
m_{NaCl} = amount of dissolved rock salt [g]
2 = stoichiometry factor, since each colloidal sodium generates $\frac{1}{2}H_2$
MW_{NaCl} = molar weight of NaCl [58,44 g/mol]
MV_{H2} = ideal molar volume of H_2 at 298,15 K [24465 ml/mol]

2.3. Quantitative Determination of the Radiolytical Chlorine.

Molecular chlorine, Cl_2, was determined chemically as described below. First, it was reacted with sodium hydroxide or water, respectively, to yield hypochloride. The amount of hypochloride was subsequently measured by iodometric titration.

$$Cl_2 + 2\,NaOH \rightarrow NaCl + NaOCl + H_2O \qquad [2]$$

$$(Cl_2 + H_2O \rightarrow HCl + HOCl) \qquad [3]$$
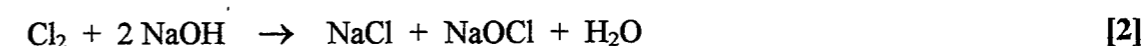
Hypochloride reacts with KI

$$OCl^- + 3\,I^- \rightarrow I_3^- + H_2O + Cl^- \qquad [4]$$

and the resulting ion I_3^- is titrated with thiosulfate.

$$I_3^- + 2\,S_2O_3^{2-} \rightarrow 3\,I^- + S_4O_6^{2-} \qquad [5]$$

The change in the redox potential is used to detect the equivalence point.

Chlorine is volatile and may already evaporate from the salt crystal during the irradiation. The measurement would produce an underdetermination, if the chlorine was only measured in the bulk. Therefore, chlorine was quantified both in the head space of the glass ampoule (see Fig. 4) and in the bulk of the salt.

2.3.1. Determination of Chlorine in the Gas Phase

All glass surfaces which come into contact with the gas sample were treated with hypochloride solution in order to destroy chlorine-consuming compounds (e.g. detergents). Afterwards, the flasks were rinsed thoroughly with Millipore-filtered water and dried.

After irradiation the ampoules were connected to a pump stand. It consisted of a glass transfer tube with several connectors to which four glass bulbs, each equipped with a stop-cock and a septum, were attached. At one end of the transfer tube a three-way stop-cock was

located to which two gas lines were attached, one for evacuating the whole system and the other for purging the system with nitrogen. The whole system was evacuated using an electrical pump and the three-way stock-cock was closed. Then the break seal at the irradiation ampoule was opened by dropping a small teflon-coated magnet on it, thus allowing the gas sample to enter the void volume. Nitrogen was added through the purge line to adjust the pressure inside the pump stand to 1.5 bar. All pressures, i.e. after evacuation, after opening the irradiation ampoule, and after adding the nitrogen, were recorded. While three of the glass bulbs were used to determine the radiation-induced gas release (see Jockwer et al., (1995) [article 13 in this volume]) by gas chromatography, one bulb was used for measuring chlorine gas.

Via the septum 5 ml of dilute sodium hydroxide solution (0,01 N) were injected into the glass bulb containing the gas sample. An aliquot of the solution was then withdrawn with a syringe and injected into the titration flask. The exact amount was determined by weighing. Afterwards 70 ml H_2O, 20 ml HCl (2 mol/l) and 1 ml KI-solution (300 g/l) were added and the solution was kept dark for 5 minutes. The solution was then titrated against a redox electrode using 0.01 N sodium thiosulfate solution.

The mass of chlorine gas present in the head space of the irradiation ampoule is calculated as follows:

$$m_{Cl_2}(g.p.) = \frac{5 \cdot V_{Std} \cdot f_{Std} \cdot 0.01}{m_{NaOH}} \cdot \frac{GPV_{total}}{GPV_{bulb}} \cdot \frac{1000}{300} \qquad (2)$$

with:
$m_{Cl2}(g.p.)$ = mass of molecular chlorine in gas phase [mequiv/kg]
V_{Std} = consumption of standard solution [ml]
f_{Std} = titer of thiosulfate standard solution.
m_{NaOH} = amount of NaOH solution being redox titrated [g]
GPV_{total} = volume of gas phase in total system [ml]
GPV_{bulb} = volume of glass bulb [ml]

2.3.2. Determination of Chlorine in the Bulk of the Salt Crystals

The aqueous solution of irradiated salt, that was prepared for determining the amount of colloidal sodium (see above), was also employed for measuring the amount of molecular chlorine in irradiated solid rock salt. After the hydrogen measurement between 5 to 30 ml

were removed from this solution, weighed, and analyzed for its hypochloride content using the same recipe as described above. The mass of molecular chlorine present in the rock salt is calculated according to:

$$m_{Cl_2}(salt) = \frac{(100 + m_{NaCl}) \cdot V_{std} \cdot f_{std} \cdot 10}{m_{NaCl} \cdot m_{sol}} \qquad (3)$$

with:
$m_{Cl2}(salt)$ = mass of chlorine in rock salt [mequiv/kg]
V_{std} = consumption of standard solution [ml]
f_{std} = titer of thiosulfate standard solution.
m_{NaCl} = mass of dissolved rock salt [g]
m_{sol} = mass of solution being redox titrated [g]

The measurement was always carried out 30 minutes after adding the dilute sodium hydroxide/water to the salt sample. In preliminary tests it was verified that the hypochloride formed upon dissolution is stable within this time and does not disproportionate into chloride, Cl^-, and chlorate, ClO_3^-, a reaction that would result in an underdetermination of chlorine.

The total chlorine yield in irradiated rock salt is calculated via

$$m_{Cl_2}(total) = \frac{\left(m_{Cl_2}(salt) + m_{Cl_2}(g.p.)\right) \cdot MW_{NaCl}}{10000} \qquad (4)$$

with:
$m_{Cl2}(total)$ total mass of chlorine being produced upon irradiation [mol-%]

2.4. Calorimetric Measurements of the Energy Stored in Rock Salt

The determination of the energy storage in irradiated rock salt was carried out by differential scanning calorimetry (DSC) at the Institute for Physical and Theoretical Chemistry, Technical University Braunschweig. This thermoanalytical method allows the measurement of the heat taken up by the sample (endothermal) or, in case of irradiated halite, released to the environment (exothermal) while the sample and an inert reference are heated according to a given controlled temperature-program. The measured heat is assumed to be proportional to the area between the recorded DSC-curve and a straight line between the initial and the final

peak temperatures, ϑ_i and ϑ_f, which is called the interpolated baseline. In order to make an assignment of the heat measured by the calorimeter to the true heat taken up or released by the sample, a heat calibration (peak area calibration) was performed before the evaluation of other data.

For the determination of the energy storage the microcalorimeter SCERES B-900 S has been used which allows to use sample masses of several hundred milligrams. Halite samples of 260 - 290 mg were weighed into small glass ampoules and heated two times from 30 °C to 400 °C at a constant heating rate of 1 K min^{-1}. The reference ampoule contained pure sodium chloride (NaCl, suprapur) which had been heated for 3 weeks at 300 °C in order to recover defects in the crystalline structure. During the first heating the halite releases the stored energy and the colour of the sample changes from black to white. The second heating process is necessary to obtain a baseline under identical measurement conditions but without any reaction peak. In the following evaluation the baseline (second heating) is subtracted from the reaction curve (first heating). As a result of this procedure a 'corrected' exothermic peak without any twist in the baseline is obtained.

The heat flux signal, which is normally recorded as a function of the temperature, contains several important points which are determined by an evaluation software. One of the characteristic temperatures of a DSC-peak is the extrapolated peak onset temperature, ϑ_e, that defines the temperature at which the observed reaction takes place. This temperature corresponds to the point in which the auxiliary line intersects the interpolated baseline. The auxiliary line is defined as the slope of the curve in the low-temperature side of the peak. To determine the temperature at which the salt sample releases the stored energy we make also use of the peak minimum temperature ϑ_p. This value depends on the sample mass. Therefore, the same sample mass was used in all the calorimetric measurements. Figure 5 shows a typical DSC-curve of irradiated halite.

Another thermal analysis technique is thermogravimetry (TG). TG allows to record the change of sample mass as a function of temperature. The resulting mass-change versus temperature curve (thermogram) provides information concerning the thermal stability and composition of the initial sample. Before performing calorimetric measurements, thermograms of the salt samples were recorded in order to determine the crystal water content of the salt. This procedure was necessary because of the high vapour pressure which may occur during the calorimetric measurements inside sealed crucibles or ampoules if the sample contains significant amounts of water. In addition, the evolution of water would manifest itself in an endothermal peak, which may superimpose with the exothermal peak of the back reaction of

radiation damage defects. The TG-measurements were carried out up to 500 °C at a heating rate of 5 K/min. This yielded a mass loss for polyhalite between 290 and 360 °C. This process caused a second double peak also in the DSC-measurements. The onset-temperature of water release is identical for DSC measurements and TG measurements: 276 ± 1 °C! Due to this process the enthalpy values are changing strongly and are not reproducible.
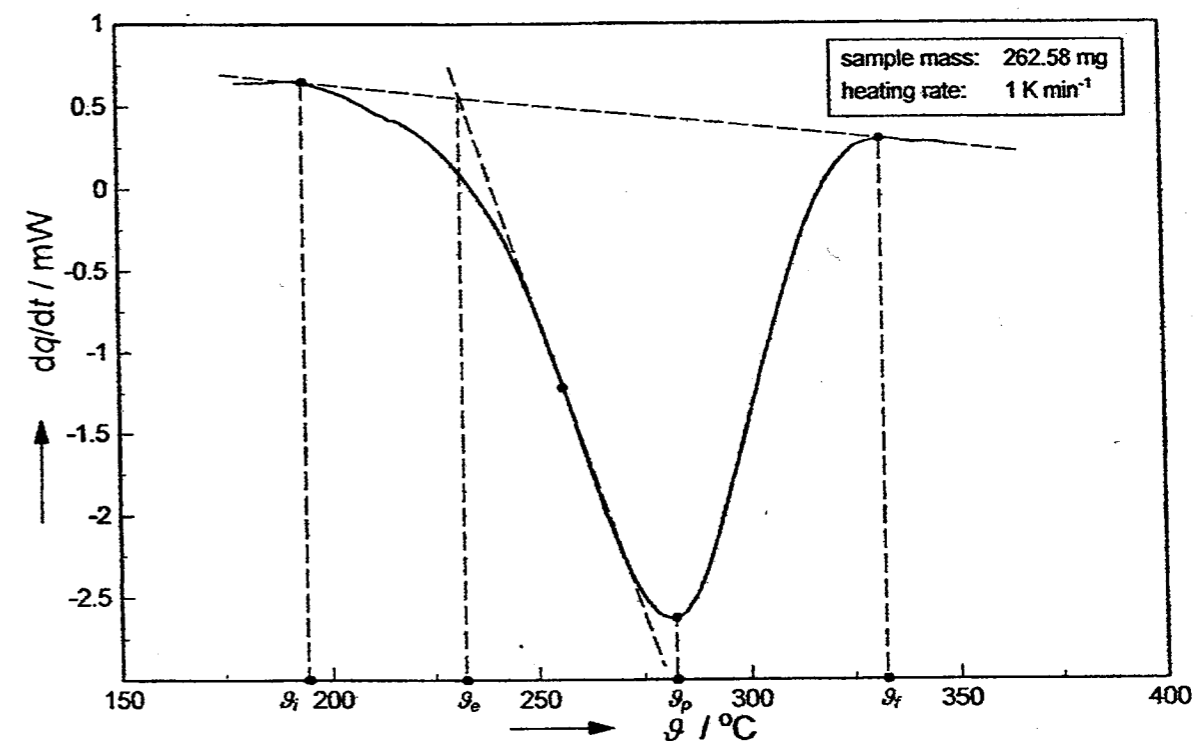

Figure 5:   *Typical DSC-curve of irradiated halite, difference between reaction peak (first heating) and baseline (second heating), period of irradiation: 80 days (dose about 100 MGy), temperature during irradiation: 100 °C, $\vartheta_i = 193$ °C, $\vartheta_e = 235$ °C, $\vartheta_p = 283$ °C, $\vartheta_f = 332$ °C, released energy: 38.5 J g^{-1}*

The enthalpy-determination for anhydrite and polyhalite did not result in any useable signals, except for a 'noise' beyond 480 °C! This behaviour can be considered to offer a good basis for the measurement of the stored energy in the rock salt and particularly the halite, the amount of which is significantly lower.

Out of the entire series of 160 crushed rock salt samples irradiated at the HFR in Petten 22 subsamples were selected, as described above, for a first series of calorimetric measurements. Each sample was split into three subsamples and measured separately in order to obtain

a better verification of the energy quantities determined per sample. After performing the calorimetric measurements, the various annealed subsamples were analyzed chemically to determine their polyhalite and anhydrite content, respectively.

2.5. Head-space Gas Analysis

After irradiation the gas in the head space of the irradiation ampoules was transfered into various glass bulbs for analysis. The pump stand is described in section 2.3.1. The gas samples were analyzed gas chromatographically. The GC system consists of four independent GC channels, each of which is optimized for detecting a specific class of gases. Each channel is equipped with two chromatographic columns in series, a guard column and a separation column. The guard column is used only to remove compounds which may interfere with the detection, while the compounds of interest pass through this column quickly. After all analytes have travelled through the guard column, a multiposition valve is switched in order to back-flush the guard column. The analytes are then separated on the separation column. Details of the GC system are listed in Table 1. The measuring signals are recorded, analyzed and archived on a personal computer.

The gas samples were withdrawn from the glass bulbs via the septum with a gas-tight syringe and then injected into the chromatographic system using a sample loop and switching valve. Each channel was individually loaded with 10 to 20 ml gas, in order to ensure that the tubings and the sample loops are flushed with ten times their volume.

Calibration was performed using commercially available test gas mixtures, having a certified accuracy of ± 2 %. Usually, gas concentrations between 50 and 500 vol. ppm (i.e. cm^3 gas per m^3 gas phase) were employed. The gas phase concentrations were calculated via the rule of three, as the detector signals (peak areas) depend linearly on concentration in this concentration range. In contrast, the high nitrogen and oxygen concentrations occasionally resulted in column overloading, so that these results exhibit a slightly higher measuring error. For these two compounds calibration was performed using gas concentrations in the per cent range.

Table 1: *GC system used for the chromatographic gas analyses*

chromatographic channel	A	B	C	D
guard column	Porapak PS, aceton-washed 1.0 m 80-100 mesh	Porapak T + mol sieve 5Å 1.0 m + 1.0 m 80-100 mesh	Porapak T 1.0 m 80-100 mesh	Porapak QS 0.5 m, 80-100 mesh
separation column	Porapak PS, aceton-washed 2.0 m 80-100 mesh	mol sieve 5Å 5.0 m 80-100 mesh	mol sieve 5Å 2.5 m 80-100 mesh	Porapak N 2.5 m 80-100 mesh
carrier gas	N_2	N_2	He	N_2
detector*	FPD, TCD	TCD	TCD	FID
analyzed components	sulfur-containing gases, e.g. H_2S, SO_2	He, N_2O, H_2	O_2, N_2	HC: C_1-C_4, CO, CO_2

* FPD: flame photometric detector
  TCD: thermal conductivity detector
  FID: flame ionisation detector
** HC   hydrocarbons (C_1 - C_4 with one to four carbon atoms)

Usually, the analyses were performed within two weeks after the ampoules were taken out of the irradiation facility at Petten. The influence of the time lag between the removal of the ampoules from the irradiation facility and the analysis was studied experimentally. Some ampoules were stored for four weeks in the laboratory and then analyzed. No significant differences were observed between samples analyzed four weeks after irradiation and those samples that were analyzed within two weeks.

3.   ENERGY STORAGE IN SULFATE-CONTAINING MINERALS

One of the open questions is as to which extent radiation-induced energy storage occurs in the sulfate-containing minerals. The salt samples used in the DSC-measurements were chemically analyzed afterwards and their individual polyhalite and anhydrite content was calculated based on elemental analyses. From these data no correlation between the amount of stored energy and the content of sulfate-containing minerals could be derived (see Mönig et al. 1995 [article 16 in this volume]).

Table 2: *Mineral composition calculated from chemical analyses of natural salt samples*

name of salt and location	halite [weight-%]	anhydrite [weight-%]	polyhalite [weight-%]
Asse-halite (Asse - Na2S)	98,10	0,20	1,40
anhydrite 1 (Asse - A3/ 750-m)	1,33	98,70	0,00
anhydrite 2 (Asse - Na2ß/ dam constr. test field)	0,24	99,20	0,00
polyhalite (Hattorf - Potash Mine)	33,20	12,30	64,50

Table 3: *Composition of samples with especially prepared mineral mixtures of natural salt used for studying the effect of sulfate-containing minerals on stored energy in γ-irradiated salt.*

number of irradiation ampoules	Asse-halite [g]	anhydrite 1 [g]	polyhalite [g]
5	300	0	0
5	225	75	0
5	150	150	0
5	75	225	0
5	0	300	0
3	200	0	0
3	150	0	50
3	100	0	100
3	50	0	150
3	0	0	200
5	0	200 (anhydrite 2)	0
5	300 NaCl suprapure	0	0

In order to shed more light onto this question, a series of about 45 especially defined mixtures of natural halite, anhydrite and polyhalite in various relations were prepared (see Tables 2 and 3). Also some anhydrite samples from different locations as well as samples using suprapure NaCl have been prepared for comparison. These samples have been irradiated at a temperature of 140 °C over 28 days. The resulting dose will only be calculated, as there were no dosimeters available any more. The irradiations were performed between November 1994 and May 1995. Every 28 days the irradiation facility is charged with new samples. The irradiated samples are analyzed for the amount of colloidal sodium and molecular chlorine as described above. Then, subsamples (~ 0.3 g) will be taken for the calorimetric determination of the stored energy, which are afterwards analyzed for their mineralogical composition. As this investigation is still going on, the final results cannot be included in this volume and will be reported independently.

ACKNOWLEDGEMENT

REFERENCES

A.J. NOLTEN, 1994: "*Irradiation of Salt Samples in a Gamma Field. GIRAF/GSF exp. no. 284. Design and Safety Report*", ECN-C--94-033, 22 p.