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STORED ENERGY OF GAMMA-IRRADIATED WIPP SALT

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Prepared by Sandia Laboratories, Albuquerque, New Mexico 87185
and Livermore, California 94550 for the United States Department of
Energy under Contract AT(29-1)-789

March, 1980

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SAND 80-0416

STORED ENERGY OF GAMMA-IRRADIATED WIPP SALT*

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Abstract

Samples of WIPP salt exposed at 363 K to gamma radiation from a Co^{60} source were annealed at constant rates of heating in a differential scanning calorimeter in order to release the energy stored. Radiation doses were 2.2, 5.4, 8.2, 11 and 13×10^9 rad, and temperature scans were conducted from room temperature to 800 K. The specific stored energy-dose relationship deduced from 80 K/min scans could be only approximately established due to the extreme variability of the specific energy in samples of a given dose. This variability probably results from unequal amounts of impurities in the 10-25 mg samples required for the calorimeter. The energy-dose relationship is best described empirically by $\ln Q_0 (\text{cal/g}) = (-40.6 \pm 2.6) + (1.84 \pm 0.12) \ln D (\text{rad})$. Temperature scans of 10, 20, 40 and 80 K/min were performed to determine the activation energy E of the annealing process. For the four more highly dosed samples, $E = 31.1 \pm 5.6$ kcal/mole. Based upon criteria established elsewhere, there appears to be no danger of the stored energy being released quickly in a nuclear waste repository of bedded salt, nor could serious consequences result from such a release by some unforeseen mechanism.

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Nomenclature

- D - dose of gamma radiation (rad)
- E - activation energy (kcal/mole)
- I - dose rate (rad/s)
- K_0 - pre-exponential constant in rate equation
- K_1 - defect formation constant (cal/rad-g)
- K_2 - defect annealing constant (1/rad)
- m - mass of sample (g)
- n_0 - fractional concentration of defects before annealing
- n - fractional concentration of defects
- P - power released by sample (cal/min)
- Q_0 - specific stored energy before annealing (cal/g)
- Q - specific stored energy (cal/g)
- R - gas constant = 1.9863 cal/mole-K
- T - temperature (K)
- T_f - temperature at end of exotherm (K)
- T_p - temperature at peak of exotherm (K)
- t - time (s)
- α - temperature scan rate (K/min)
- γ - kinetic order of annealing process

Introduction

The gamma irradiation of salt in a proposed bedded-salt nuclear waste repository could produce various kinds of damage to the salt, such as the displacement of atoms and the formation of other point defects.¹⁻³ This results in energy being accumulated and the plasticity of the crystal being reduced.

It is important to assess the effects of the release of this stored energy on the integrity of the repository. Given the expected temperatures in the vicinity of waste canisters, one would like to predict how rapidly the defects in the irradiated salt will release their energy. Should there be an abrupt and large exothermic reaction, damage to the canisters and the salt might occur. Cracks in an embrittled material might permit brine and, hence, radionuclide movement.

Measurements of stored energy in alkali halides have been made by various calorimetric methods.¹⁻⁷ Differences are noted between pure NaCl and the salts mined from various deposits which generally contain several percent of assorted impurities. This study is of material from the Carlsbad, New Mexico area associated with the proposed Waste Isolation Pilot Plant (WIPP).⁸ The salt samples were obtained from a core taken from the 741.3 and 796.0 m levels of the ERDA-9 drill hole, both within the same geological formation. The materials from these levels probably do not differ any more in composition than cores taken from adjacent locations at the same level. This, however, is a presumption and is not based on chemical analysis.

The mechanical properties and thermoluminescence of irradiated salt are also being measured at Sandia National Laboratories by G. W. Arnold.

Experiment

The WIPP salt used in this experiment was approximately 97% NaCl, the balance being clay, anhydrite (CaSO_4), and lesser quantities of minerals containing potassium, strontium and magnesium. The irradiation of the salt was conducted by G. W. Arnold of Sandia National Laboratories in its Co^{60} gamma-irradiation facility. Source intensity of the 1.3 MeV radiation was

approximately 10 Mrad/h, and samples were exposed to 2.2, 5.4, 8.2, 11 and 13 $\times 10^9$ rad. The last dose represents 7.7 weeks of irradiation. All doses are considered accurate to within 15%. Temperature of the salt during irradiation was approximately 363 K. The 2.2×10^9 and 13×10^9 rad samples were from the 796.0 m level of the ERDA-9 drill hole, the others coming from the 741.3 m level.

All post-irradiation samples were of a dense violet color. Upon heating to 800 K, the color disappeared leaving the crystals transparent and light gray. Annealing was done in a Perkin-Elmer differential scanning calorimeter, Model DSC-2. For stored energy measurements, samples weighing 10-25 mg were hermetically sealed in gold capsules, and heated at 80 K/min from room temperature to 800 K, well above the temperature required to release all stored energy.

Temperature scans of 10, 20, 40 and 80 K/min were performed on unsealed samples for the purpose of determining the temperature T_f which marked the end of an energy release. The fact that the gold capsules were unsealed did not affect the value of T_f . All runs were performed with the samples in flowing dry argon and in total darkness since light enhances the annealing process.²

Results

Figure 1 is the trace of a temperature scan of 80 K/min for WIPP salt with $D = 11 \times 10^9$ rad. P is the power released by the sample as a function of temperature T . This scan rate typically produced one well-defined exotherm peaking at a temperature T_p around 600 K for the 2.2×10^9 rad samples, the peak increasing to 660 K for 13×10^9 rad. Slower scans gave broader and lower exotherms which were more difficult to interpret and, therefore, not used in determinations of stored energy.

Others have noted more than one event, each associated with the annealing of a particular defect.^{4,6} It was not the purpose of this study to elucidate

Figure 1. Differential scanning calorimeter trace of energy release from WIPP salt. $D = 11 \times 10^9$ rad, $\alpha = 80$ K/min. T_p is the temperature at the peak of the exotherm, and T_f is the temperature at its end.

the various mechanisms of the annealing process, but rather to determine the total energy release. Energy releases peak and end at temperatures which depend upon heating rate (Table I). The heating rates here are generally higher than those used by others because the exotherms could be more clearly identified.

Table I. Temperatures at Peaks (T_p) and Ends (T_f) of Exothermic Reactions in WIPP Salt.

T_p (K) is on top, T_f (K) is below it.

Dose, D (10^9 rad)	Temperature Scan Rate, α (K/min)			
	10	20	40	80
2.2	---	---	560	598
	---	---	---	---
5.4	578	590	605	625
	623	640	655	678
8.2	593	601	625	646
	638	656	677	698
11	601	618	632	656
	650	663	685	712
13	617	629	642	660
	668	678	695	714

The specific stored energy Q_o found from a trace like Fig. 1 is

$$Q_o = \int \frac{PdT}{m\alpha} \quad , \quad (1)$$

the integration being taken over the entire area of the exotherm; m is the mass of the sample and α is the heating rate. Jenks and Bopp³ propose a semi-theoretical relation for the time rate of change of Q_o .

$$\frac{dQ_o}{dt} = K_1 I - K_2 I Q_o \quad , \quad (2)$$

in which I is the dose rate, and K_1 and K_2 are the defect formation and annealing constants, respectively. Equation (2) expresses the rate of increase of stored energy as a balance between the production and annihilation rates of defects, the former being proportional to the dose rate, and the latter to the dose rate and stored energy.

The integral of Eq. (2),

$$Q_o(t) = \frac{K_1}{K_2} \left(1 - e^{-K_2 D(t)} \right) \quad , \quad (3)$$

describes the specific stored energy where the dose $D(t) = \int_0^t I(\tau) d\tau$. In this experiment I is a constant and, consequently, $D(t) = It$.

Figure 2 shows the data; the levels of Q_o agree generally with Jenks and Bopp's.³ Q_o as a function of D (solid lines) for three choices of the parameters K_1 and K_2 is also shown. The curves A, B and C, represent $K_2 = 10 \times 10^{-11}$, 15×10^{-11} , and $20 \times 10^{-11} \text{ rad}^{-1}$, respectively, with $K_1 = 1.4 \times 10^{-9} \text{ cal/rad-g}$ for all three. None of these curves appears to represent the data adequately.

Figure 2. Specific stored energy vs. dose in WIPP salt. Where datum points overlap, the number of such points is indicated by the dots to the right of the cross. In Eq. (3), $K_1 = 1.4 \times 10^{-9}$ cal/rad-g and (A) $K_2 = 10 \times 10^{-11}$ rad $^{-1}$, (B) $K_2 = 15 \times 10^{-11}$ rad $^{-1}$, and (C) $K_2 = 20 \times 10^{-11}$ rad $^{-1}$ (solid curves). For the dashed curve (D), $\ln Q_0$ (cal/g) = $-40.6 + 1.84 \ln D$ (rad). Curves (D') and (D'') represent the standard deviation (see text).

K_1 is the same as Jenks and Bopp's value.³ For pure Harshaw salt irradiated at 368 K, they found $K_2 = 4.4 \times 10^{-11} \text{ rad}^{-1}$.

My data were empirically fitted by least squares to the equation $\ln Q_0 (\text{cal/g}) = a + b \ln D (\text{rad})$, in which $a = -40.6 \pm 2.6$ and $b = 1.84 \pm 0.12$, the second number in each case being the standard deviation. The dashed line D in Fig. 2 represents this relation and has no theoretical basis. The dashed lines D' and D'' represent the probable limits of uncertainty given by $dQ_0 = Q_0 (da + db \ln D)$, where da and db are the standard deviations quoted above. The trend of rapidly increasing Q_0 with D is not consistent with the saturation of Q_0 with D observed in other experiments which, however, spanned a range of D three to four times larger than in this study.^{1-3,5}

Figure 3 shows the average values of Q_0 at each D with the standard deviations for Q_0 shown vertically, and the 15% experimental uncertainty in D, horizontally. The curves D, D' and D'' from Fig. 2 are also given. A straight line (which must pass through $Q_0 = 0, D = 0$) can also be drawn for a reasonable fit to the data of Fig. 3 (solid line E). It may be seen that in Eq. (3), for $K_2 D \ll 1$, the term in parenthesis may be approximated by $K_2 D$. Therefore, $Q_0(t) \approx K_1 D$ in which K_1 defines the maximum slope of Eq. (3), that is, where D is very small. The slope of the straight line in Fig. 3 is $0.73 \times 10^{-9} \text{ cal/rad-g}$ compared with Jenks and Bopp's value of $K_1 = 1.4 \times 10^{-9} \text{ cal/rad-g}$.

The method used to determine the activation energy E of the annealing process is described by Damask and Dienes.⁹ Temperature is increased at a constant rate α until a certain defect concentration is reached at T. The procedure is repeated for other values of α , the final state always being the same. In this experiment, the final state was zero stored energy ($Q = 0$) at which point $T = T_f$, the temperature at the end of the exotherm.

Figure 3. Specific stored energy vs. dose in WIPP salt. Average values of Q_0 are given with the standard deviations shown vertically, and the 15% uncertainty in D horizontally. Curves D, D' and D'' are repeated from Fig. 2.

The rate of change of the defect concentration for a single activated process of constant activation energy E is given by⁹

$$\frac{dn}{dT} = - \frac{F(n)K_0 e^{-E/RT}}{\alpha} \quad (4)$$

in which R is the gas constant, K_0 the pre-exponential constant, and $F(n)$ is any continuous function of n , the fractional concentration of defects. For $E/RT \gg 1$, which is supported by Jenks and Bopp's value of $E = 38.9$ kcal/mole,³ one gets

$$\int_{n_0}^n \frac{dn}{F(n)} = - \frac{K_0 RT_f^2 e^{-E/RT_f}}{\alpha E} \quad (5)$$

At identical values of n , the integral is a constant. Hence, running experiments for several values of α permits E to be determined from the slope of a plot of $\ln \frac{T_f^2}{\alpha}$ vs. $\frac{1}{T_f}$. This has been done for $\alpha = 10, 20, 40$ and 80 K/min, and for all doses except $D = 2.2 \times 10^9$ rad for which T_f data were inadequate, the DSC-2 signal being too small at this low level of Q_0 .

The results are plotted in Fig. 4. Lines A, B, C and D represent the highest through the lowest value of D in that order. Slopes (E/R) for B, C and D are approximately equal, yielding an activation energy in the range 27.7-29.1 kcal/mole; line A gives 39.4 kcal/mole. It is not known why the most highly dosed sample yields the highest E value. The average of the four values is represented by line E (31.1 kcal/mole), and the 5.6 kcal/mole standard deviation by E' and E'' . Jenks and Bopp's value of 38.9 kcal/mole is their best "eyeball" fit for three different salt specimens, both pure and impure.³ Taken individually, their two Lyons salt specimens gave 39.8 and

Figure 4.

Activation energy from slope of $\ln \frac{T_f^2}{\alpha}$ vs. $\frac{1}{T_f}$. The scan rate for each horizontal set of four datum points is given at the left. The values of E in kcal/mole and D in rad are, respectively: (A) 39.4; 13×10^9 , (B) 27.7; 11×10^9 , (C) 27.9; 8.2×10^9 , (D) 29.1; 5.4×10^9 . The average activation energy is $(E) 31.1 \pm 5.6$, (E') and (E'') representing the standard deviation. The positions of E , E' and E'' are arbitrary; only the slopes are meant to be represented.

40.5 kcal/mole, while their pure Harshaw salt gave 33.4 kcal/mole. These average to 37.9 ± 3.9 kcal/mole, somewhat different from their "eyeball" value. These values, while not stated by Jenks and Bopp, may be deduced from p. 83 of their report. It should be noted that the samples they used for determination of activation energy fell in the higher range of stored energy (7.5-13.1 cal/g) and, therefore, their average E value is consistent with the 39.4 kcal/mole found for my most highly dosed sample.

Jenks and Bopp³ and Lidiard¹⁰ agree that the kinetics of the annealing process is zero order, an unusual circumstance. This could not be confirmed in the present experiment. Isothermal annealing experiments are planned which will determine the order and will be reported later. Zero order means $\gamma = 0$ in the rate equation

$$\frac{dn}{dt} = -K_0 n^\gamma e^{-E/RT} ; \quad (6)$$

n^γ is, of course, $F(n)$ of Eqs. (4) and (5). Hence, Eq. (5) becomes

$$n_0 = \frac{K_0 RT_f^2 e^{-E/RT_f}}{\alpha E} , \quad (7)$$

since $n = 0$ (zero defect concentration at the final temperature T_f). From Eq. (7), one can determine the errors in $1/T_f$ and T_f^2/α of Fig. 3 due to the variation in n_0 as indicated by the standard deviation of Q_0 (Fig. 3):

$$\frac{d(1/T_f)}{1/T_f} = - \frac{dQ_0}{Q_0} \frac{1}{(2 + E/RT_f)} , \quad (8)$$

and

$$\frac{d(T_f^2/\alpha)}{T_f^2/\alpha} = \frac{dQ_0}{Q_0} \frac{1}{(1 + E/2RT_f)} , \quad (9)$$

where dQ_0/Q_0 has been substituted for dn_0/n_0 . These errors are shown in Fig. 4 as horizontal and vertical bars, respectively, unless the error in T_f^2/α is too small to be shown except by the datum point itself.

Conclusions

WIPP salt from the ERDA-9 drill hole (depths 741.3 and 796.0 m) in the Carlsbad, New Mexico area has been irradiated at 363 K by 1.3 MeV gamma radiation from a 10 Mrad/h ^{60}Co source. The specific stored energy Q_0 of samples dosed to 2.2, 5.4, 8.2, 11 and 13×10^9 rad has been measured on a Perkin-Elmer differential scanning calorimeter by constant-rate temperature scans (80 K/min) to 800 K. The levels of Q_0 agree generally with those found by Jenks and Bopp for other irradiated salts.³ Q_0 may be represented by the empirical relation, $\ln Q_0 (\text{cal/g}) = (-40.6 \pm 2.6) + (1.84 \pm 0.12) \ln D (\text{rad})$. This functional dependence does not agree with the results of Jenks and Bopp, particularly since it does not predict the expected saturation of stored energy with dose, but the dose range of this experiment was more restricted than theirs. Activation energy of the annealing process, measured by temperature scans of 10, 20, 40 and 80 K/min, was 31.1 ± 5.6 kcal/mole. For samples of comparable stored energy, Jenks and Bopp's value of E agrees quite well with mine. In view of the general agreement on stored energy levels and activation energy, the criteria for safe storage of nuclear waste, as described by Jenks and Bopp, are satisfied, i.e., there appears to be no danger of the stored energy being released quickly in a nuclear waste repository of bedded salt, nor could serious consequences result from such a release by some unforeseen mechanism. Future work is planned to determine the kinetic order of the annealing process.

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