RADIATION-INDUCED SODIUM-METAL-COLLOID FORMATION IN NATURAL ROCK SALT FROM
DIFFERENT GEOLOGICAL LOCALITIES*

CONF-811122--14

J. M. LOMAN,** P. W. LEVY,[†] AND K. J. SWYLER^{††}
Brookhaven National Laboratory, Upton, New York 11973, U.S.A.

MASTER

ABSTRACT

Radiation damage has been studied in natural rock salt from various localities, including potential repository sites. In the 100 to 300 C range the damage consists of point defects, primarily F-centers, and colloidal metal sodium particles. With increasing dose the F-centers grow to a saturation level, reached at 10^7 - 10^8 rad, that decreases with increasing temperature to a negligible level at 300 C. Colloid concentration vs. irradiation-time curves follow nucleation and growth curves accurately described by Ct^n , or $C(\text{dose})^n$, relations at large irradiation times. For fourteen samples, $n=1.85 \pm 0.18$ but the values of C vary by a factor of more than 10^2 . The constant C is related to the sample strain, the impurity and void content, dose rate, and possibly other factors. The currently available data indicate that rock salt adjacent to radioactive waste canisters, at a temperature of 150 C, will contain between 0.01 and 10^{-10} mole percent of sodium metal when the total dose reaches 10^{10} rad.

INTRODUCTION

Gamma-ray induced radiation damage, particularly Na metal colloid formation, has been studied in natural rock salt from different geological localities, including some potential radioactive waste repository sites, and different horizons at certain locations. The basic radiation damage phenomenology in both synthetic melt grown NaCl crystals and natural evaporite rock salt has been described in numerous Office of Nuclear Waste Isolation (ONWI) reports, in previous publications [1]-[3] and in a summary article [4]. This article will emphasize measurements on radiation related parameters that are important for radioactive waste repository site selection, design, safety assessment, etc. in both bedded and dome salt. Also included are comments on unresolved radiation related problems, especially the possibility that chlorine gas will be generated from irradiated rock salt.

*Research supported by the Dept. of Energy Office of Nuclear Waste Isolation, operated by Battelle Inst.-Columbus, Ohio, and the Dept. of Energy Division of Basic Energy Sciences, under contract DE-AC02-76CH00016.

**Now with Ford Astronautics, Palo Alto, California.

[†]Physics Department.

^{††}Now with the Brookhaven National Laboratory Dept. of Nuclear Energy -
NRC Nuclear Waste Management Division.

EXPERIMENTAL DETAILS

All measurements described below were made with equipment at Brookhaven National Laboratory for making optical absorption and luminescence measurements on samples while they are being irradiated with monoenergetic electrons, of selected energy, between 0.5 and 3.0 MeV. Samples are irradiated in a temperature controlled chamber containing an exchange gas. Except for dose rate studies, the dose rate was 1.2×10^8 rad/hr; appreciably above that expected in repositories. Typically, absorption and luminescence spectra--the latter will not be discussed in this paper--are recorded as often as every 50 sec during the entire irradiation. Usually they cover the 350 to 750 nm range, i.e. 1.6 to 3.0 eV photon energy. At low doses the absorption spectra contain only F-center absorption bands but at high doses both F-center and colloid bands are present. Using previously described techniques [4], a sufficient number of spectra are resolved into individual F-center and colloid bands to construct precise F-center concentration and colloidal Na metal concentration vs. irradiation time, or total dose, curves.

Natural rock salt samples were obtained from the localities, and from different horizons at certain localities, listed in Table I. Measurements were made on single crystals, usually $8 \times 8 \times 0.75$ mm, or thinner, cleaved from cores or pieces. Single crystals of this size which are relatively free of voids, inclusions, etc. are infrequent and often 0.5 kg, or so, of rock has to be carefully separated before a suitable crystal is located. Roughly 1/3 of all samples received do not contain crystals large enough to measure. Because of this selection process the results are biased toward samples with large crystallites. Methods are being developed for studying samples containing only small crystallites.

TABLE I

The constants, C and n, in the relation (Mole Fraction NaCl Converted to Colloidal Na) = Ct^n where t is irradiation time in seconds. These values were obtained from the data used for Fig. 2. The validity of this relation has not been experimentally verified beyond the doses shown in Fig. 2.

Sample	n	C
AEC-8, NM, USA	1.87	4.50×10^{-13}
ALT AUSEE, Austria	1.98	3.60×10^{-13}
ASSE 1, FRG	1.84	2.71×10^{-12}
ASSE 4, FRG	1.77	1.34×10^{-12}
ASSE 6, FRG	2.08	1.60×10^{-13}
ASSE 8, FRG	2.17	1.86×10^{-14}
ASSE 9, FRG	2.05	6.47×10^{-14}
Avery Island, LA, USA	1.66	8.80×10^{-12}
ERDA-9, NM, USA	1.73	2.82×10^{-12}
Lyons, KS, USA	1.87	7.43×10^{-13}
Retsof, NY, USA	1.56	4.14×10^{-11}
Rocanville, SK (above ore)	1.57	2.72×10^{-11}
Rocanville, SK (with ore)	1.83	6.78×10^{-13}
Rocanville, SK (recrystallized)	2.41	6.14×10^{-15}

BASIC RADIATION DAMAGE PHENOMENOLOGY IN ROCK SALT

As described previously [1]-[4], both natural and synthetic rock salt develop radiation damage in a qualitatively similar fashion. At temperatures where both negative-ion vacancies (F-centers) and colloids are observed, between approximately 115 and 250 C, the F-center concentration vs. dose curves increase monotonically to well defined plateaus, which are reached in the 10^7 to 10^8 rad range. Colloidal metal Na formation follows classical nucleation and growth curves with the transition from the induction period to the rapid growth region occurring at about the dose where the F-center concentration reaches saturation. Both F-center and colloid growth is strongly temperature dependent. In both natural and synthetic salt the F-center formation rate and saturation level is largest at 100-115 C and decreases monotonically until it reaches a negligible level at 250-300 C.

The temperature dependence of the colloid formation is qualitatively similar for both natural and synthetic salt. Radiation induced colloid formation for samples from the 810 m level of the WIPP site (Waste Isolation Pilot Project, Los Medanos, NM) is shown in Fig. 1. In this plot the solid line contours show that the colloid formation rate is low or zero at 115 C, increases rapidly with increasing temperature to a maximum in the 150-170 C range and as the temperature increases further decreases to a negligible level at 250 C. The dashed contour lines show that the colloid formation induction period is more than 10^4 sec at 100 C, decreases with increasing temperature to a minimum of 3000 sec around 150 C, and increases to more than 10^4 sec at 250 C. The induction period dependence in synthetic NaCl is similar. Two important aspects of the induction period at room temperature should be mentioned. First, samples exposed to 10^8 rad at room temperature do not contain colloids at the end of the irradiation. However, they exhibit pronounced colloid content after being stored for 3 to 6 months in darkness at room temperature. Second, similarly irradiated

NATURAL ROCK SALT - DRILL HOLE AEC-8,810m LEVEL
RADIATION INDUCED COLLOID FORMATION
AT VARIOUS TEMPERATURES
DOSE RATE: 1.2×10^8 rad/hr

Fig. 1. Radiation induced colloid growth curves for natural rock salt from the WIPP site measured at the indicated temperature. At the high dose end these curves are well described by Ct^n relations. The contour lines show how the colloid formation rate and induction period depend on irradiation temperature.

4

samples develop appreciable concentrations of colloids when heated for 1 to 2 hrs in the 150 to 250 C range [5].

In both natural and synthetic rock salt, at large irradiation times the colloid concentration vs. irradiation time, or dose, curves are well described by Ct^n , or $C(\text{dose})^n$, relations, where C and n are constants and t is irradiation time. Data demonstrating the applicability of this relation to WIPP samples and synthetic NaCl is given in reference 4; the 150 C data in Fig. 1 is curve "a" in Fig. 2. However, it is important to point out that the behavior of the exponent, n, for WIPP salt is markedly different from that for synthetic NaCl. For WIPP salt n is between 1.5 and 2.2 and any temperature dependence is much less than that in synthetic NaCl. In the latter n is 3.8 at 130 C, increases irregularly to 6.2 at 190 C and decreases to 1.5 at 230 C.

SURVEY OF RADIATION INDUCED COLLOID FORMATION IN NATURAL ROCK SALT

To determine if radiation damage--especially colloid formation--depends on sample origin, studies are being made on bedded and dome salt samples from widely separated localities. For this survey, all measurements were made at 150 C and at a dose rate of 1.2×10^8 rad/hr. In every case samples were selected which were as free as possible from voids and obvious macroscopic defects. The resulting colloid absorption band area vs. irradiation time curves are shown in Fig. 2 for the first 14 samples studied. The constants in the Ct^n relation, obtained by fitting this expression to the high irradiation time end of the data, are contained in Table I. As discussed below, this information can be used to estimate the colloid content of the rock salt in the vicinity of emplaced canisters. For the 14 samples listed in Table I, the n values are between 1.6 and 2.4 and the average n is 1.85 ± 0.18 . However, the C values vary by factors of 10^3 or more. This difference in colloid formation rate can be expressed alternatively. After an irradiation of 10^4 sec (3.3×10^8 rad) the colloid content of the 14 samples described in Table I varies by a factor of roughly 80. These results indicate that radiation damage effects in an actual repository can be greatly reduced by a careful choice of sites and/or horizons.

FACTORS INFLUENCING RADIATION INDUCED COLLOID FORMATION

At least three factors have been shown to influence colloid formation. First, as shown previously, straining both synthetic and natural rock salt by uniaxial compression prior to irradiation reduces the colloid growth induction period [1],[2],[4]. For strains below roughly 10 percent it decreases with increasing strain. At roughly 10 percent strain the induction period is zero. Strains above this value do not introduce any large additional effects. Second, the colloid formation rate depends strongly on dose rate. Colloid formation in WIPP site salt is shown in Fig. 3 for three dose rates. The colloid formation increases as the dose rate decreases; i.e. on a unit dose basis, low dose rates produce more colloids than high dose rates. Third, as expected from well known color center studies, colloid growth depends on the impurities present. One indication of impurity effects is contained in the data for samples from Rocanville, Sask., Canada, shown in Fig. 2. Colloid formation in samples from a layer of bedded salt above the ore horizon is appreciably greater than that observed in samples from a lower horizon of intermixed rock salt and potash ore. Almost certainly salt from the upper horizon is purer than the salt from the lower horizon. Additional information on impurity effects is obtained from studies on crystals that are not colored uniformly. Figure 4 shows a region in natural rock salt after irradiation. The dark areas are blue-black showing

Fig. 2. Colloid formation in natural rock salt, measured at 150 C and during irradiation at a dose rate of 1.2×10^8 rad/hr. At the high irradiation time end, these curves are well described by Ct^n relations.

the presence of both F-centers and colloid particles. The light area is golden-yellow, the color occurring when only F-centers are present. The center of the light area contains a line of voids containing brine. In this case, colloid formation is suppressed in the region surrounding the voids. Similar light and dark areas, which may or may not contain voids, have been examined with a proton microprobe [6]. Typical impurity content of the two types of areas is shown in Table II.

TABLE II

Impurity content of colloid-rich and colloid-free areas in irradiated natural rock salt

Colloid Level	Impurity Content					
	S	Ca	Fe	Co	Cu	Br
Low or zero	1.0%	1.2%	4 ppm	4 ppm	6 ppm	40 ppm
High	ND	ND	ND	ND	5 ppm	36 ppm

ND = Not Detected

The data in Table II clearly shows that colloid formation is suppressed in impure regions. Thus the presence of voids and impurities inhibit colloid formation. It has not been demonstrated that the clear regions around voids contain high impurity levels.

Fig. 3. Colloid formation in natural rock salt irradiated at different dose rates. This data indicates that, on a unit dose basis, low dose rates produce more colloids than high dose rates.

Fig. 4. Micrograph of irradiated natural rock salt. The dark area contains both F-centers and colloid particles. The light area surrounding a line of voids contains only F-centers. Similar light areas, which may or may not contain voids, are comparatively impure.

APPLICATIONS TO WASTE REPOSITORIES IN ROCK SALT

The information sketched above is applicable to repository site selection, design, etc. To begin, the total amount of radiation induced colloidal Na metal expected in a repository can be estimated from the data in Table I. More explicitly, this data can be used to extrapolate the curves in Fig. 2 to any irradiation time, subject to the assumptions: 1) the dose rate is 1.2×10^8 rad/hr, 2) the canisters have heated the surrounding rock to 150 C, and 3) the gamma-ray dose imparted to material at the canister surface will reach 10^{10} to 10^{11} rad in 10 to 1000 years. Under these conditions rock salt at the canister surface can be expected to contain between 0.01 and 10 mole percent sodium when the dose reaches 10^{10} rad. Dose rate and strain related effects can be expected to increase this fraction while impurity related effects may decrease it. Also, 150 C is roughly the temperature at which the colloid formation induction period is a minimum. If the effective temperature of the salt is between room temperature and 100 C it is quite possible that the total amount of colloid formed will not be diminished. The lower temperature may simply extend the induction period. As mentioned above, colloids are formed at room temperature, particularly in strained samples, but the induction period is in the 3 to 6 month range. Data on colloid formation between room temperature and 100 C is not yet available.

There are numerous consequences of rock salt adjacent to canisters reaching the 0.01 and 10 percent level. For example, rock salt with this much radiation damage is hard, brittle, and is so susceptible to cleaving it is close to friable, i.e. almost completely lacking in sheer strength. Such salt is quite reactive chemically; when in contact with water hydrogen gas is formed readily. Most importantly, with 0.01 to 10 percent of the salt converted to Na metal it is essential to determine what has happened to the chlorine released when the metal is formed. It may remain trapped in the lattice, collect into voids, diffuse out of the crystal, some combination of these, or enter into some not-so-obvious process. Now under way are studies, utilizing a mass spectrometer gas analyzer, to determine the conditions whereby chlorine gas is--or is not--released by rock salt during or after gamma-ray irradiation under repository conditions.

REFERENCES

1. K. J. Swyler, R. W. Klaffky, and P. W. Levy in: Scientific Basis for Nuclear Waste Management 1, G. J. McCarthy, ed. (Plenum, New York 1979) pp. 349-354).
2. K. J. Swyler, R. W. Klaffky, and P. W. Levy in: Scientific Basis for Nuclear Waste Management 2, Clyde J. M. Northrup, Jr., ed. (Plenum, New York 1980) pp. 553-560.
3. P. W. Levy, K. J. Swyler, and R. W. Klaffky, J. de Physique 41, Supplement-Colloque C6, pp. 344-347 (1980).
4. P. W. Levy, J. M. Loman, K. J. Swyler, and R. W. Klaffky, to be published in: Advances in the Science and Technology of the Management of High Level Nuclear Waste, Peter L. Hofmann, ed.
5. K. J. Swyler, J. M. Loman, L. J. Teutonico, G. E. Elgort, and P. W. Levy, Report-ONWI/SUB/78/E511-1000-17 (1980).
6. C. P. Swann, J. M. Loman, and P. W. Levy, to be published.