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**Review of Information on the
Radiation Chemistry of Materials
Around Waste Canisters in Salt
and Assessment of the Need for
Additional Experimental Information**

G. H. Jenks

OPERATED BY
UNION CARBIDE CORPORATION
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CHEMICAL TECHNOLOGY DIVISION

NUCLEAR FUEL AND WASTE PROGRAMS

Study of Radiation Chemistry of Salt Mine Brines

(Activity No. AP 05 15 15; 189 No. ONW-02804)

**REVIEW OF INFORMATION ON THE RADIATION CHEMISTRY OF MATERIALS
AROUND WASTE CANISTERS IN SALT AND ASSESSMENT OF THE NEED
FOR ADDITIONAL EXPERIMENTAL INFORMATION**

G. H. Jenks

With an Appendix by C. F. Baes, Jr.

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DEPARTMENT OF ENERGY**

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REVIEW OF INFORMATION ON THE RADIATION CHEMISTRY
OF MATERIALS AROUND WASTE CANISTERS IN SALT
AND ASSESSMENT OF THE NEED FOR ADDITIONAL
EXPERIMENTAL INFORMATION*

G. H. Jenks

ABSTRACT

The brines, vapors, and salts precipitated from the brines will be exposed to gamma rays and to elevated temperatures in the regions close to a waste package in the salt. According¹, they will be subject to changes in composition brought about by reactions induced by the radiations and heat.

The objectives of the work discussed in this report were to review the status of information on the radiation chemistry of brines, gases, and solids which might be present around a waste package in salt and to assess the need for additional laboratory investigations on the radiation chemistry of these materials.

The basic aspects of the radiation chemistry of water and aqueous solutions, including concentrated salt solutions, were reviewed briefly and found to be substantially unchanged from those presented in Jenks's 1972 review of radiolysis and hydrolysis in salt-mine brines. Some additional information pertaining to the radiolytic yields and reactions in brine solutions has become available since the previous review, and this information will be useful in the eventual, complete elucidation of the radiation chemistry of the salt-mine brines.

1. INTRODUCTION

The types of salt deposits that are being considered for use in the disposal of spent Light-Water Reactor (LWR) fuel and/or of solidified high-level wastes may contain a small volume fraction of brine inclusions,

* SI units are used throughout the report. Pertinent conversion factors are listed in Appendix D.

which are located within crystals and/or on crystal boundaries. Some brine from these inclusions will enter the spaces around a waste package in the salt as a result of the migration of the inclusions under the influence of thermal gradients and elevated temperatures in the salt immediately adjacent to a waste package. Other possible sources of brine in the spaces close to a waste package include the condensation of H_2O from ventilation air onto hygroscopic minerals, if any are present, and H_2O release from unstable hydrated minerals, again if any are present.

Brines, vapors, and any salts precipitated from the brines will be exposed to gamma rays and to elevated temperatures in regions that are in close proximity to a waste package in the salt.* Accordingly, they will be subject to changes in composition brought about by reactions induced by the radiations and heat.

The objectives of the work presented in this report were to review the status of information on the radiation chemistry of brines, gases, and solids which might be present around a waste package in salt and to assess the need for further investigations of the radiation chemistry of these materials.

The radiation chemistry, as well as the effects of radiolysis, depends on both the compositions of liquids and solids around a waste package and on the design of the waste package, including dimensions, thermal power, age of waste, and backfill material. Accordingly, it was necessary to first delineate reference characteristics for spent fuel (SF) and high-level waste (HLW) packages in salt and to consider the compositions and amounts of brines, gases, and solids which might be present in the repository.

* Neutrons at a very low flux are included among the radiations emanating from a waste canister. Most of these neutrons will be absorbed by ^{35}Cl to form ^{36}Cl , which decays by β emission with a half-life of 3×10^5 yr.

2. CHARACTERISTICS OF THE REFERENCE PACKAGES OF HIGH-LEVEL WASTE AND SPENT FUEL IN SALT

Several pertinent characteristics of the reference SF and HLW packages in salt, which are assumed in this report, are listed and/or referenced in Tables 1 to 4 and Figs. 1 and 2.

Table 1. Characteristics of reference spent fuel package disposed in salt

Canister material ^{a,b}	Mild steel.
Canister dimensions ^{a,b}	343-mm ID, 368-mm OD. Contains pressurized water reactor (PWR) SF assembly of 3.7-m active length.
Canister contents ^{a-c}	One PWR assembly with burnup of 33 MWd/kg of uranium. Open spaces around assembly within canister are backfilled with helium. ^{a,d}
Emplacement hole in salt ^{a-c}	46 mm diam. Backfilled with air or with granular salt such as sand or salt or one of these mixed with a desiccant such as quick lime (CaO).
Gamma dose rates	Calculated values for locations around the midplane vs age of spent fuel are listed in Table 2. Sources of information and calculation methods are described in Appendix A.
Temperatures in salt at midplane	Plots are shown in Fig. 1 of temperatures calculated by Llewellyn ^e for the following system. The 450-mm-OD canister is in good thermal contact with salt; age of SF at emplacement is 10 yr; single row of canisters along center of 5.5-m room in salt; distance of 1.55 m between centers. Calculations by others ^f for a similar system but with the solid salt separated from the canister by ~50 mm indicated that the maximum temperature of ~120°C in the solid salt is reached ~50 yr after emplacement.

^aG. H. Jenks, *Effects of Gaseous Radioactive Nuclides on the Design and Operation of Repositories for Spent LWR Fuel in Rock Salt*, ORNL-5578 (December 1979).

^bA National Waste Terminal Storage Repository in Bedded Salt Formation for Spent Unreprocessed Fuel, *Conceptual Design Description*, KE Report No. 78-58-R, Kaiser Engineers (December 1978).

^cJ. P. Russell, *Areal Thermal Loading Recommendations for Nuclear Waste Repositories in Salt*, Y/OWI/TM-37 (June 1979).

^dThe helium is used for leak testing purposes. The final design might employ air or another gas mixed with helium at a low partial pressure. Some other means of leak testing, not requiring helium, might also be used.

^eG. H. Llewellyn, *Prediction of Temperature Increases in a Salt Repository Expected from the Storage of Spent Fuel of High-Level Waste*, ORNL/ENG/TM-7 (April 1978).

^fH. C. Claiborne and L. D. Rickertsen, *Expected Environments in Nuclear Waste/Spent Fuel Repositories in Salt* (in preparation).

Table 2. Calculated values for dose rates in H₂O at several locations around reference spent fuel package placed in salt^a

Location and backfill ^b	Dose rate in H ₂ O at indicated age of spent fuel (10 ²³ eV/kg·yr)				
	10 yr	20 yr	30 yr	40 yr	100 yr
I' _{14.5}	82 [150] ^c	66 [120]	50 [92]	22 [40]	7.1 [13]
I' _{18a}	66 [120]	53 [97]	41 [75]	17 [32]	6.0 [11]
I' _{18h}	39 [72]	32 [58]	25 [45]	10 [19]	3.4 [6.3]
I' _{20h}	26 [48]	21 [39]	16 [30]	7.1 [13]	2.3 [4.2]

^aPWR assembly exposed at 33 MWd/kg of uranium; canister-343-mm ID, 368-mm OD, 3.7-m active length; package placed in 460-mm-diam hole in salt. Air is used as backfill around the assembly within the canister unless otherwise noted.

^bI'_{14.5} - midplane surface of canister.

I'_{18a} - surface of solid salt at midplane with air backfill between canister and salt.

I'_{18h} - surface of solid salt at midplane, with backfill between canister and salt which has gamma-ray absorption coefficient, per unit thickness, equal to that of solid salt.

I'_{20h} - 25 mm radially into solid salt at midplane, with backfill between the canister and solid salt as described for I'_{18h}.

^cNumbers in brackets show dose rate in Gy/h.

Table 3. Characteristics of reference high-level waste package disposed in salt

Outer canister material	Mild steel.
Canister dimensions	305-mm ID, 330-mm OD, 2.4-m active length.
Canister contents ^a	Solid HLW obtained by processing 2.0 to 2.2 Mg of UO ₂ (fuel which was exposed to 33 MWd/kg of uranium in a PWR). The thermal powers of these wastes at age 10 yr after discharge are ~2.1 and 2.3 kW. ^b
Emplacement hole in salt ^c	430-mm diam. Backfilled with air or with granular solids such as sand or one of these mixed with a desiccant such as quick lime (CaO).
Gamma dose rates	Calculated values for locations around the midplane vs age, after discharge, are listed in Table 4. Sources of information and calculation methods are described in Appendix A.
Temperatures in salt at midplane	<p>Plots are shown in Fig. 2 of temperatures calculated by Llewellyn^d for the following system. The 450-mm-OD canister contains 2.1 kW of 10-yr-old HLW; salt and canister are in good thermal contact; single row of canisters along center of 5.5-m room; distance of 2.38 m between centers.</p> <p>Recent calculations by others^e for a similar system but with the solid salt separated from the canister by ~25 mm indicated that the maximum temperature of ~210°C in the solid salt is reached ~15 yr after emplacement.</p>

^aJ. E. Russell, *Areal Thermal Loading Recommendations for Nuclear Waste Repositories in Salt*, Y/OWI/TM-37 (June 1979).

^bCalculations using the recently updated ORIGEN code (refs. 4 and 5) indicated 1.9 and 2.1 kW rather than 2.1 and 2.3 kW for the wastes from 2.0 and 2.2 Mg of fuel.

^cG. H. Jenks, *Effects of Gaseous Radioactive Nuclides on the Design and Operation of Repositories for Spent Fuel in Rock Salt*, ORNL-5578 (December 1979).

^dG. H. Llewellyn, *Prediction of Temperature Increases in a Salt Repository Expected from the Storage of Spent Fuel of High-Level Waste*, ORNL/ENG/TM-7 (April 1978).

^eH. C. Claiborne and I. D. Rickertsen, *Expected Environments in Nuclear Waste/Spent Fuel Repositories in Salt* (in preparation).

Table 4. Calculated values for dose rates in H₂O at several locations around reference HLW package placed in salt^a

Location and backfill ^b	Dose rate in H ₂ O at indicated age of waste (10 ²³ eV/kg·yr) ^c				
	10 yr	20 yr	30 yr	60 yr	100 yr
I ₁₃	490 [900]	350 [640]	260 [470]	130 [230]	50 [92]
I _{17a}	380 [690]	270 [490]	200 [360]	98 [180]	38 [70]
I _{17h}	210 [390]	150 [280]	110 [200]	55 [100]	22 [40]
I _{19h}	140 [260]	100 [190]	77 [140]	37 [67]	15 [27]

^a 305-mm ID, 330-mm OD, 2.4-m active length; contains HLW from processing 2.2 Mg of UO₂ fuel exposed to 33 MWd/kg of uranium in a PWR; canister placed in a 450-mm-diam hole in salt.

^b I₁₃ - midplane surface of canister.

I_{17a} - surface of solid salt at midplane with air backfill between canister and salt.

I_{17h} - surface of solid salt at midplane, with backfill between canister and salt which has gamma-ray absorption coefficient, per unit thickness, equal to that of solid salt.

I_{19h} - 25 mm radially into solid salt at midplane, with backfill between canister and solid salt as described under I_{17h} (above).

^c Numbers in brackets show dose rate in Gy/h.

Fig. 1. Salt temperature vs distance from center of SF canister at several different times after burial (burial age of spent fuel is 10 yr; one row of canisters per room; a distance of 1.55 m between centers).

Fig. 2. Salt temperature vs distance from center of 2.1-kW high-level waste canister at several different times after burial (burial age of spent fuel is 10 yr; one row of canisters per room; a distance of 2.38 m between centers).

3. COMPOSITION OF SALT-MINE BRINES

3.1 Brine Inclusions within Bedded Salt

Information on the composition of brine encapsulated within bedded salt was discussed in Appendix A of ref. 1. Table 5 gives a summary of analytical and deduced values for the composition (at a temperature of 25°C) of brine within bedded salt from Lyons and Hutchinson, Kansas. Less direct information for brines from New Mexico bedded-salt (halite) indicated compositions similar to those of the Kansas brines. The increase in NaCl concentration within encapsulated Kansas brines (2.41 m $MgCl_2$) with an increase in temperature was discussed in Appendix B of ref. 1. The values for NaCl molality at 25, 50, 100, 150, and 200°C were, respectively, 2.16, 2.32, 2.76, 3.30, and 4.02 m .

Table 5. Summary of analytical and deduced values for concentrations in brine encapsulated in Kansas bedded salt

	Concentration in brine at 25°C	
	(moles/l)	(moles/kg H ₂ O)
Mg	2.12	2.41
Na	1.91	2.16
K	0.28	0.32
Ca	0.03	0.034
Cl	6.29	7.15
Br	0.04	0.045
SO ₄	0.078	0.089

As discussed in Sects. 5 and 6, the Br⁻ content of these brines is of particular importance in estimating the radiolytic effects within encapsulated brine, since the Br⁻ will inhibit back reaction between radiolytic H₂ and oxidants to reform H₂O.

3.2 Brine Formed by Dissolution of Solid Bedded Salt with Fresh H₂O

Probably the most pertinent information on this subject is that of Beane and Popp² and of Molecke,³ who analyzed solutions formed by dissolving core samples from the halite horizons of AEC Cores 7 and 8 (New Mexico). The reported results were summarized in Appendix A of ref. 1. In general, the results showed that NaCl was the major constituent and anhydrite was a minor constituent of the cores. The results also indicated trace amounts of one or more of the following: polyhalite, iron oxide, K-feldspar, talc, chlorite, carnallite, bloedite, and quartz.

Pertinent inferences that were drawn from the analytical results are:¹

1. The salt samples contained very little potassium (0.032 wt % average).
2. The magnesium content of the salt samples was very low, averaging 0.006 wt % in the soluble portions. If the brine inclusions within the crystals and on the boundaries of the salt contained all of this MgCl₂ at a concentration of 2 M, the average amount of H₂O within the inclusions was 0.13 wt %.
3. All of the calcium (0.62 wt % average) was in the form of anhydrite. No calcium was present as CaCl₂.

3.3 Brine Formed by Dissolution of Solid Dome Salt with Fresh H₂O

Chemical analyses of dome salt from the mine at Avery Island, Louisiana, were reported by Kaufmann.⁶ The results showed that NaCl comprised >99 wt % of the dissolved solids; CaSO₄ comprised ~0.2 wt %; and MgCl₂ and CaCl₂ each comprised ~0.005 wt %.

I found no comparable analytical information from other dome salts in the United States.

3.4 Brine Inclusions within Dome Salt

Moisture in the salt samples referred to in Sect. 3.3 was reported to equal 0.023 wt %. This was probably determined by heating samples to a temperature of 105°C for 1 h.⁷ From this I have inferred that the

brine, if actually present within the undisturbed salt, was located on grain boundaries. The temperature and time of heating of the samples were insufficient to drive any brine inclusions out of a crystal.

It is notable that the ~ 0.005 wt % MgCl_2 in the dissolved solids of the Avery Island samples⁶ indicates about the same amount of moisture as that found by heating, if it is assumed that all of the MgCl_2 was located within brine, and that its concentration within this brine was ~ 2 M; 2.1 M was the concentration of magnesium in the brine inclusions within bedded salt (Sect. 3.1).

3.5 Changes in Composition of Brine Encapsulated in Bedded Salt upon Loss of H_2O in Open Spaces around Waste Package

As reported in Sect. 3.1, the brines that are encapsulated within bedded salt will probably be rich in MgCl_2 (~ 2 m). The brines are, of course, saturated in NaCl . When and if some of these inclusions enter the open spaces around a waste canister, they will lose H_2O by several processes, including reaction with the iron canister, radiolytic decomposition, and evaporation. Loss of H_2O from the MgCl_2 -rich, NaCl -saturated solutions results in the precipitation of NaCl and an increase in the concentration of MgCl_2 ^{8-11,*} (Figs. 3 to 5). With continued loss of H_2O , the solutions become saturated in MgCl_2 , and either $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ or $\text{MgCl}_2 \cdot 4\text{H}_2\text{O}$ precipitates, depending upon the temperature of the system (see Figs. 4 and 5). These hydrates exert sensible vapor pressures of H_2O , and they can be converted to still lower hydrates at suitably low partial pressures of H_2O vapor^{8,9,11} (Figs. 4 and 5).

* The values for NaCl concentration plotted in Fig. 3 and those for vapor pressures in lines 2 and 3 of Fig. 4 were calculated by Baes.¹¹ A summary of his method is presented in Appendix C. Tabulated results of the calculations are included in Appendix C. The dotted portion of the 200°C plot in Fig. 3 is an extrapolation of the calculated values.¹⁰

Experimental data for solubilities in NaCl - MgCl_2 solutions are given by Seidell.¹⁰ Those for temperatures of 25 , 100 , and 200°C are plotted in Fig. 3 for comparison with the values calculated by Baes (ref. 11 and Appendix C). Reasonable agreement between calculated and experimental values is indicated.

Fig. 3. Calculated concentration of NaCl vs concentration of MgCl_2 in NaCl-saturated solutions at 25 to 200°C. (Data obtained from A. Seidell, Solubilities of Inorganic and Metal Organic Compounds, Vol. 1, 3rd ed., D. Van Nostrand, 1940, pp. 966 and 1224.)

Fig. 4. Vapor pressure of H₂O over NaCl and MgCl₂ solutions and over MgCl₂ solid hydrates vs temperature.

Fig. 5. Vapor pressure of H₂O over NaCl and MgCl₂ solutions and over MgCl₂ solid hydrates vs temperature.

Information on the hydrolysis of these solutions was reviewed and discussed in Appendix C of ref. 1. It was estimated that the maximum H^+ which would result from the hydrolysis of saturated $MgCl_2$ solutions at 100 and 140°C would be $\sim 3 \text{ E-}05 \text{ m}$ and $\sim 3 \text{ E-}04 \text{ m}$, respectively. By extrapolating the hydrolysis quotient values at 100 and 140°C, reported by Russian scientists,^{12,13} I have estimated that

$$H^+ \cong 1.2 \text{ E-}03 \text{ m}$$

in 10 m $MgCl_2$ solutions at 200°C, as a result of hydrolysis in solution.

The hydrates can also undergo hydrolysis to form solid hydroxy chloride and HCl gas [Eq. (1)] at temperatures above $\sim 180^\circ\text{C}$:¹⁴

Equation (1) is reversible, and the reported values for the ratio of the partial pressure of HCl to that of H_2O vapor, at approximate equilibrium, are 0.0081 at 183°C and 0.017 at 200°C.^{14,15} The values for this ratio continue to increase with increasing temperatures above 200°C. Whether or not this hydrolysis occurs to a significant extent below 180°C is uncertain.

4. FACTORS THAT MIGHT AFFECT MIGRATION OF BRINE FROM SURROUNDING SALT TO WASTE PACKAGE AND SOME ESTIMATES OF AMOUNTS OF IN-MIGRATION

Information on the effects of temperature and temperature gradients on brine migration through single crystals of salt was reviewed and analyzed in ref. 1. The effects of stress, pressure, and irradiation of salt on brine migration through crystals in a repository were also considered. It was concluded that the following empirical equation for V/G_g (migration velocity of brine inclusion per unit temperature gradient in the salt) represents the maximum values for this parameter which would result from thermal gradients in the bedded-salt crystals in a repository:

$$\log V/G_g = 0.00656T - 0.6036 \quad (2)$$

where T is the temperature of the salt ($^{\circ}\text{C}$), and V/G_s is measured in $\text{cm}^2/\text{yr}\cdot^{\circ}\text{C}$.

The presence of stored radiation energy within a salt crystal could affect the rate of brine migration within the crystal if the stored energy causes an increase in the solubility of the salt. However, results obtained in Project Salt Vault suggested that stored radiation energy had little, if any, influence on the rate of brine flow into the emplacement cavities in the salt. No direct information regarding the effect of stored energy on the solubility of salt is available.

The greatest uncertainty relative to the prediction of rates of brine migration into a waste emplacement cavity in bedded salt is associated with questions concerning the effects of the grain boundaries (within the aggregates of single crystals which comprise a rock salt deposit) on brine migration through the deposit. It is likely that the grain boundary trapping will tend to retard brine migration under the conditions expected to prevail with probable repository designs (i.e., $G_s \leq 2^{\circ}\text{C}/\text{cm}$ maximum, impurities present on grain boundaries, and boundaries compressed by thermal expansion of the salt). It is also conceivable that the effects of grain boundaries will be opposite to those suggested above under some circumstances (e.g., when salt that has been heated is allowed to cool).

The results of certain estimates of the amounts of brine in-migration to a waste package were described in Sect. 6 of ref. 1. These estimates employed the results of temperature calculations of Llewellyn, which were illustrated in Figs. 1 and 2, and they assumed that the emplacement hole in the salt was 0.60 m in diameter. They also employed the assumptions that (1) the salt contained 0.5 vol % brine inclusions, (2) these inclusions migrated at the maximum rates shown by Eq. (2), and (3) grain boundaries had no effect on the migration. The step-by-step method of carrying out these estimates was described in ref. 14. The results of these estimates are illustrated here in Figs. 6 and 7.

Others¹⁶ have recently made brine in-migration calculations for the emplacement systems outlined in the preceding paragraphs using more sophisticated methods of calculation than those described in ref. 14.

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Fig. 6. Cumulative brine inflow to spent fuel canister vs time after emplacement at age 10 yr (one row of canisters per room, and a distance of 1.55 m between centers).

They also assumed canister dimensions and surroundings that closely resemble those assumed for the reference packages in this report (Tables 1 and 3). Their results indicated total inflows of 15 l per hole after 500 yr for HLW and 8 l per hole after 1500 yr for SF. There is no apparent conflict between these recent results and those shown in Figs. 6 and 7, which were calculated by the more approximate method of ref. 14, and for much shorter periods.

Fig. 7. Cumulative brine inflow to high-level waste canister vs time after emplacement at age 10 yr (one row of canisters per room, and a distance of 2.38 m between centers).

All of the brine migration calculations mentioned above assumed 0.5 vol % brine included within the salt. This brine content is typical of bedded salt. Dome salt may have relatively few brine inclusions and may thus exhibit very little brine migration of the type considered for the above calculations.* However, the possibilities have not been ruled out that other types of brine migration to a waste package may take place within a given dome-salt formation.¹⁷

* My examinations, with a low-power microscope, of a few samples of salt crystals from several different Gulf Coast domes (Avery Island, Jefferson Island, and Weeks Island) did not reveal any brine inclusions. Personnel at the Institute for Environmental Studies at Louisiana State University have recently observed some fluid inclusions in salt crystals from Vacherie Dome and Rayburn's Dome during their detailed examinations of the cores from these domes.^{22,23} However, these inclusions were considered sparse, and the sizes were mostly $<100\mu$.²³

5. BASIC ASPECTS OF RADIATION CHEMISTRY OF H₂O AND AQUEOUS SOLUTIONS

5.1 Pure H₂O and Dilute Aqueous Solutions at Room Temperature

The important initial products formed upon irradiation of H₂O are believed to be ionized water, H₂O⁺, and the dry electron, e⁻.^{18,19} The H₂O⁺ reacts rapidly with neighboring H₂O molecules to form the hydroxy radical, OH, and the unhydrated ion, H₃O⁺,^{18,20}

The H₃O⁺ also reacts rapidly with neighboring H₂O molecules,²⁰

The dry electron reacts rapidly with H₂O molecules to form the hydrated electron,²¹

The number of an initial species that is formed per 100 eV of absorbed radiation energy is symbolized by $g^0(e_{aq}^-)$, etc. The value for $g^0(e_{aq}^-)$, and thus for $g^0(\text{OH})$, in pure H₂O under β-γ irradiation, is 4.0.²⁰

With β-γ irradiations, most of these initial species are formed in heterogeneous distribution within small volume elements called spurs. These species interact as they diffuse into homogeneous distribution,* and the products which appear in homogeneous distribution are, primarily,

*Homogeneous distribution from the standpoint of reaction kinetics.

e_{aq}^- , H, OH, H_2O_2 , H_2 , and H_3O^+ . These are called "primary products." The number of a species that appears as a primary product per 100 eV of absorbed radiation energy is symbolized here by $g(H_2)$, $g(OH)$, etc.* The g -values for these products in pure H_2O under β - γ irradiation are listed below.^{20,24}

Number of given radiolytic product entering
homogeneous distribution per 100 eV
(β - γ radiation, pure H_2O
or dilute solutions)

$$g(H_2) = 0.45$$

$$g(e_{aq}^-) = 2.7$$

$$g(H) = 0.6$$

$$g(H_2O_2) = 0.75$$

$$g(OH) = 2.7$$

The primary products interact further to form products which include O_2 and H_2O .^{25,26} They may also react with other solutes present in solution. The overall results of the primary decomposition (expressed as G -values) depend strongly upon these additional reactions. This can be illustrated by noting that a very low net decomposition occurs in pure H_2O during exposure to β - γ when the radiolysis products remain in solution.

If the radicals are removed from solution by reaction with radical-scavenger solutes** (e.g., Cu^{2+} or Br^-) and the molecular products remain in solution, the molecular products will accumulate until concentrations are reached at which they can successfully compete with the scavenger ions. Depending upon the properties of the particular scavenger

* The symbols, $g'(H_2)$, $g'(OH)$, etc., were used for these quantities in ORNL/TM-3717, ref. 14.

** Radical scavenger ions are those which, in effect, catalyze the removal of the radiation-induced radicals by undergoing oxidation with the OH radical followed by reduction with the reducing radicals, or vice versa.

ions under consideration, the molecular product concentration may become several hundred times greater than that of the scavenger before reformation of H_2O becomes significant.^{25,26} Alternatively, if the molecular products escape from the solution, their concentrations in solution might not become great enough for them to take part to a significant extent in recombination reactions.

5.2 Concentrated Aqueous Salt Solutions at Room Temperature

The basic concepts described in Sect. 5.1 also apply to concentrated solutions of salt such as NaCl . However, it is possible that certain solutes at high concentration will take part in the formation of initial radiolytic products and/or in the spur reactions.

For example, Reaction (5) followed by Reaction (6) might account for some of the large primary yield of Cl_2^- in neutral NaCl solutions^{14,27} [$g(\text{Cl}_2^-) = 1.6$ in 2 M NaCl solutions at $\text{pH} = 7$]:¹⁸

The Cl_2^- might also be formed as an initial product by Reaction (7) followed by Reaction (6), as suggested by Hamill and co-workers.¹⁸

Formation of Cl_2^- within spurs by means of Reaction (8) would require that an appreciable concentration of H_{aq}^+ be present within the spur, since Reaction (8) does not take place in neutral solutions.

The rate constant for Reaction (8) is $1.66 \text{ E}+10/\text{M}^2 \cdot \text{s}$ at 25°C . H_{aq}^+ is an initial product of radiolysis [Reactions (3) and (4)], and the concentration of H_{aq}^+ within a spur might be appreciable. However, available experimental evidence appears to discount spur reactions as the source of Cl_2^- as a primary product in neutral solutions,^{18,20} although they might account for some of the yield of Cl_2^- in acid solutions; in 2 M NaCl solutions at $\text{pH} = 2$, $g(\text{Cl}_2^-) = 3.4$.¹⁸

Ions of sodium and magnesium in solution do not affect radiolysis of aqueous solutions.

6. STATUS OF EXPERIMENTAL AND THEORETICAL INFORMATION ON RADIOLYSIS IN SALT-MINE BRINES IN A WASTE REPOSITORY

Experimental and theoretical information relevant to the prediction of radiolysis in salt-mine brines in a waste repository was reviewed and discussed in detail in ORNL/TM-3717.¹⁴

The theoretical information presently available is essentially the same as that reviewed in the 1972 report.¹⁴ Some important basic aspects were summarized in Sect. 5; the 1972 report should be consulted for information on other theoretical aspects.

Some additional experimental information pertaining to values for $g^0(e_{\text{aq}}^-)$,^{*} $g(e_{\text{aq}}^-)$,^{*} $g(\text{Cl}_2^-)$,^{*} and $G(\text{H}_2)$ ^{*} in NaCl solutions and for $(\text{H}_2)_{\text{ss}}$ ^{**} in encapsulated brines has become available, and this information is summarized below. The 1972 report should be consulted for other experimental information of radiolysis of chloride solutions. The value of $g^0(e_{\text{aq}}^-)$ at 25°C is 4.0 in pure H_2O , and it remains substantially the same in NaCl solutions at concentrations of up to 5 M,^{20,21} although Cl^- very likely is taking part in the initial radiolytic reactions in the solutions (Sect. 5.2). The value of $g(e_{\text{aq}}^-)$ at 25°C is 2.7 in pure H_2O , and it apparently remains relatively unchanged in NaCl solutions up to the maximum concentration tested (2 M).²⁸

* See Sect. 5.1 for definitions of these symbols.

** $(\text{H}_2)_{\text{ss}}$ represents the concentration of H_2 at the steady state.

Fisher and Hamill¹⁸ reported that their experimental values for $g(\text{Cl}_2^-)$ for neutral NaCl solutions of 0.1, 0.5, 1.0, and 2.0 M were well represented by Eq. (9). Experimental values for NaCl solutions of the same concentrations but with 10 mM H_2SO_4 in each solution were well represented by Eq. (10).

$$\text{pH} = 7, \quad g(\text{Cl}_2^-) = 3.8\{0.38[\text{Cl}^-]/(1 + 0.38[\text{Cl}^-])\} . \quad (9)$$

$$\text{pH} = 2, \quad g(\text{Cl}_2^-) = 2.8 + 1.0\{0.67[\text{Cl}^-]/(1 + 0.67[\text{Cl}^-])\} . \quad (10)$$

A summary of experimental work and results bearing on the value of $(\text{H}_2)_{\text{ss}}$ is as follows. A sample of salt from the Carey Mine at Lyons, Kansas, was irradiated at 160°C with γ rays, at ORNL, to a dose of $1.3 \text{ E}+08 \text{ Gy}$ and then analyzed for H_2O and permanent gases, H_2 , O_2 , and N_2 .²⁹ The results indicated 0.22 m H_2 , 0.048 m O_2 , and 0.005 m N_2 , assuming that all of these gases were contained within the solutions.²⁹ However, it can be estimated that an overpressure on the solutions of $>69 \text{ MPa}$ would have been required to keep all of the gases within the encapsulated brine solutions (Appendix B). Accordingly, it is likely that the salt surrounding the inclusions either expanded to accommodate some of the radiolytic gases within the gas phase or the salt developed transient cracks through which some vapors and gases escaped to the surrounding atmosphere, thus creating a gas phase over the brine inclusions.

Assuming the first of these possibilities, and that the expansion of the salt was initiated and continued at an internal pressure of 5.2 to 6.9 MPa, it can be estimated (Appendix B) that ~8 to 10% of the gases remained dissolved in the encapsulated brines. The remainder was in the gas-vapor spaces which were created by the expansion of the salt.

As discussed in ref. 14 (and alluded to in Sect. 5), the Br^- in the Kansas brines (0.045 m Br^-) would prevent the recombination of H_2 and O_2 to form H_2O until the concentration of H_2 exceeded that of the Br^- by some factor, the value of which was uncertain for elevated temperatures. The result of the experiment and the discussion presented in the preceding paragraphs in this section show that the value of this factor at a temperature of 160°C could be >0.4 .

A sample of salt that was irradiated in Project Salt Vatic at a maximum temperature of 150 to 155°C and to a gamma dose of 5 E+06 Gy was also analyzed for H₂O and permanent gases.²⁹ The results and interpretations were similar to those discussed above for the sample irradiated at ORNL.

As discussed in ref. 14, a value of ~2.1 for $G(H_2)^+$ in concentrated (5 M) neutral chloride solutions could be deduced from experimental results reported by Russian workers.^{30,31} However, Sawai and Hamill³² had reported that $g(H_2)$ in 2 M NaCl is not appreciably different from that in pure H₂O. More recent work reported by other workers²⁸ supports the findings of Sawai and Hamill. However, both groups of investigators added alcohol to their test solutions of NaCl, and it is possible that the alcohol caused a reduction in the value of $g(H_2)$ from that which would have otherwise prevailed.¹⁴ In general, the radiolytic reactions and mechanisms that occur in concentrated chloride solutions are poorly understood, and I continue to believe¹⁴ that the value of $G(H_2)$ in highly concentrated chloride solutions may be ~2.1, or greater.

It is worth restating here that knowledge of the value of $G(H_2)$ is of prime importance when making estimates of the rate of radiolysis in a given chloride system, since H₂ is the only nonradical reduced species which is formed in these solutions. Several different oxidized species are conceivable, but the total yield of these must be related to $G(H_2)$, as shown by Eq. (11).^{*,**}

$$2G(H_2) = 2G(Cl_2) + 5G(ClO_2) + 2G(Cl_2O) + 4G(O_2) + \\ 2G(H_2O_2) + 6G(ClO_3^-) + 8G(ClO_4^-) + 4G(ClO_2^-) . \quad (11)$$

It is also worth restating here that any neutral chlorine species which are formed radiolytically in brine solutions will be accompanied by a loss of H⁺ from the solution as shown by Eq. (12), derived from charge-balance considerations.^{*}

$$2G(Cl_2) + 5G(ClO_2) + 2G(Cl_2O) = G(-H^+) . \quad (12)$$

* See Appendix A for definition of $G(X)$.

** The relationship in Eq. (11) results from the fact that an oxidation-reduction balance must prevail among the radiolytic species.

7. STATUS OF EXPERIMENTAL AND THEORETICAL INFORMATION ON RADIOLYSIS IN VAPORS AND GASES AROUND WASTE PACKAGES IN SALT

The principal radiolytic reaction will be the reformation of H_2O from H_2 and O_2 within the gas space.^{33,34} The value of $G(H_2O)$ will probably be between 3 and 6, based on energy absorption in all of the species present within the gas-vapor phase.*

Some HNO_3 and/or other nitrogen oxides may also form³⁵ if N_2 is present. The details of the reactions are uncertain. The available evidence indicates that HNO_3 is formed initially at a G -value in the range of 1 to 3,* and that the formation continues until the H_2O vapor is exhausted. Nitrogen dioxide (NO_2) is then formed, and no further HNO_3 is produced in the presence of NO_2 .³⁵

If Cl_2 enters the gas space, it will probably react radiolytically with H_2 to form HCl . A chain reaction occurs in gas mixtures that contain only H_2 and Cl_2 ,³⁶ and the effective value for $G(HCl)$ is >3000 ,³⁶ based on the rate of energy absorption in the H_2 and Cl_2 . The values for $G(HCl)$ in gas mixtures containing other molecules (e.g., H_2O vapor and O_2 in addition to H_2 and Cl_2) have not been studied. However, it seems reasonable to assume that $G(HCl) > 1$ in the gas mixtures which might prevail around a waste canister in salt, based on radiation energy absorption in all of the species present within the gas-vapor space.

Ozone is formed during irradiation of air, and the value of $G(O_3)$ at temperatures <400 K may be in the range of 3 to 6.³⁷ The O_3 that might be formed around a SF or HLW package in salt would presumably undergo rapid reaction with H_2 to form H_2O . It is possible that O_3 is an intermediate in the radiolytic formation of H_2O vapor referred to in the first paragraph of this section.

*Number of product species per 100 eV of radiation energy absorbed in the gas-vapor phase.

8. STATUS OF EXPERIMENTAL AND THEORETICAL INFORMATION ON THE RADIOLYSIS OF SOLIDS AROUND WASTE PACKAGES IN SALT

8.1 Solid NaCl

Information on the radiolysis of this material was presented and discussed in detail by Jenks et al.^{29,38} It was also recently summarized by Jenks.³⁹

8.2 Anhydrous Chlorates

As discussed in ref. 14, it is likely that chlorates will be formed radiolytically within brines which are encapsulated within the salt surrounding a waste package in a salt repository (some bromates might be formed also).¹⁴ These soluble chlorates and bromates would be carried into the spaces around a waste package along with the irradiated brines which might migrate from the salt into the open spaces.

These salts will be decomposed thermally above certain temperatures if they become dry.¹⁴ The anhydrous salt will probably also be decomposed radiolytically. Reported information on the radiolysis of NaClO_3 , KClO_3 , KClO_2 ⁴⁰⁻⁴³ and of perchlorates of Li, Na, K, Rb, Cs, Mg, Ca, Sr, and Ba indicates that the final products of radiolysis will be O_2 and Cl^- , and that intermediate products will probably include ClO_4^- , ClO_2^- , ClO^- , and ClO_2 . The value for $G(\text{Cl}^-)^*$ will probably be ~ 1.5 to 2 at the temperatures around reference waste packages in salt.⁴⁰⁻⁴⁵

8.3 Hydrates of MgCl_2

As discussed in Sect. 3.5, hydrates of MgCl_2 could be precipitated from bedded salt brines upon loss of H_2O after the brines migrate into the spaces around a waste package. Apparently, the radiation chemistry of these hydrates has not been investigated experimentally. It seems likely, however, that the hydrates will undergo radiolysis with decomposition products similar to those in concentrated chloride solutions, as discussed in Sect. 6.

* See footnote, p. 24.

9. STATUS OF INFORMATION ON RADIATION CHEMISTRY OF PRODUCTS OF DESICCANT-BRINE INTERACTIONS

A mixture of sand and quick lime (CaO) used as a backfill around a waste package in salt has been suggested⁴⁶ as a means of protecting the metal wall of the package from rapid localized corrosive attack by brines. Presumably, the CaO would react with H₂O in the brines to form thermally stable Ca(OH)₂. I have found no definitive information on the identities, physical properties, phase behavior, and radiation chemistry of the products of reaction between the CaO and MgCl₂-rich brines.

Other types of desiccants for use around waste packages in salt are being considered, including chemical additions which would promote the formation of tachyhydrite (2MgCl₂·CaCl₂·12H₂O).^{46,47} I have found no information on either the radiation chemistry of this mineral or on the effects of gamma radiations on the formation of this material.

10. RADIOLYTIC GASES WITHIN BRINES ENCAPSULATED WITHIN BEDDED SALT AROUND REFERENCE WASTE PACKAGES

Calculated values for $N(\text{H}_2)/W$ (total number of moles radiolytic H₂ formed per unit mass of H₂O within brine, during exposure to a given radiation dose) and related quantities in brine encapsulated within salt around reference waste packages are listed in Tables 6 and 7, for certain locations around a package and for exposure times of 1 yr and 20 yr after emplacement of the package. Methods and information for determining the values of parameters entering into, and/or affecting, the estimates are described and discussed in Appendixes A and B. The value of V_g in the tables is the volume (l) of the gas-vapor space which is formed over the encapsulated brine in order to accommodate the radiolytic H₂ and O₂ at a pressure P_g . P_g is the assumed value of the pressure of dissolved gases at which the salt surrounding the inclusion will expand to form a gas-vapor phase within the inclusion and will continue to expand at P_g as additional radiolytic gases are formed. The assumed value of P_g at 100°C is 31 MPa. The values for V_g/W were calculated using Eqs. (B.7) and (B.8) of Appendix B. A full discussion of derivations and assumptions for these equations is given in Appendix B. The

Table 6. Calculated values for $N(H_2)/W$ and related quantities in brine encapsulated within salt around reference spent fuel package at 1 yr and 20 yr after emplacement of 10-yr-old waste^a

Location and backfill ^b	I'_{18a}	I'_{18h}	I'_{20h}
Dose rate at emplacement at $t = 10$ yr (10^{23} eV/kg-yr)			
water ^c	66	39	26
brine ^d	89	53	35
Dose in brine (10^{23} eV/kg H ₂ O) ^e			
11 yr	89	53	35
30 yr	1420	850	560
$N(H_2)/W$ (mole/kg H ₂ O) ^a			
11 yr	0.31	0.18	0.12
30 yr	4.9	2.9	1.9
$N(H_2 + O_2)/W$ (mole/kg H ₂ O) ^f			
11 yr	0.47	0.27	0.18
30 yr	7.4	4.4	2.9
V_2/W at 100°C (l/kg H ₂ O)			
11 yr	0.040	0.024	0.016
30 yr	0.74	0.44	0.29
V_g/W at 150°C (l/kg H ₂ O) ^g			
11 yr	0.042	0.025	0.017
30 yr	0.81	0.48	0.32

^a $N(H_2)/W$ = total number of moles of radiolytic species, H₂, formed per unit mass of H₂O, W , within the brine during exposure to radiation dose, D . These values were calculated using Eq. (A.2) of Appendix A with $G(H_2) = 2.1$. It is assumed that no recombination of radiolytic H₂ and oxidants takes place within the irradiated brine (Sect. 6).

^bSee Table 2. 18a and 18h refer to the surface of the emplacement hole at midplane, with air and solid backfill around the canister, respectively. 20h is located 25 mm into the solid salt from the 18h location.

^cSee Table 2.

^dAssuming an average value of 1.35 for I_g/I_w in the encapsulated brine (Appendix A).

^eThese values, for the assumed locations, were calculated using Eqs. (A.1) and (A.11) of Appendix A.

^fThese values are based on the assumption that O₂ comprises all of the oxidant which accompanies the formation of radiolytic H₂ within the encapsulated brine.

^gThe assumed value for P_g at 150°C is 30.7 MPa.

Table 7. Calculated values for $N(H_2)/W$ and related quantities in brine encapsulated within salt around reference high-level waste package at 1 yr and 20 yr after emplacement of 10-yr-old waste

Location and backfill ^a	I_{17a}	I_{17h}	I_{19h}
Dose rate at emplacement at $t = 10$ yr (10^{23} eV/kg·yr)			
water ^b	380	210	140
brine ^c	510	280	190
Dose in brine (10^{23} eV/kg H ₂ O) ^d			
11 yr	500	275	185
30 yr	7450	4000	2700
$N(H_2)/W$ (mole/kg H ₂ O)			
11 yr	1.75	0.96	0.65
30 yr	26.0	14.0	9.4
$N(H_2 + O_2)/W$ (mole/kg H ₂ O) ^e			
11 yr	2.6	1.4	0.98
30 yr	39.0	21.0	14.0
V_g/W at 150°C (l/kg H ₂ O)			
11 yr	0.28	0.14	0.097
30 yr	4.3	2.3	1.5
V_g/W at 200°C (l/kg H ₂ O) ^f			
11 yr	0.32	0.16	0.11
30 yr	5.1	2.7	1.8

^aSee Table 4. 17a and 17h refer to the surface of the emplacement hole at midplane with air and solid backfill around the canister, respectively. 19h is located 25 mm into the solid salt from the 17h location.

^bSee Table 4.

^cAssuming an average value of 1.35 for I_g/I in the encapsulated brine (Appendix A)

^dThese values, for the assumed locations, were calculated using Eqs. (A.1) and (A.9) of Appendix A.

^eThese values are based on the assumption that O₂ comprises all of the oxidant which accompanies the formation of radiolytic H₂ within the encapsulated brine.

^fThe assumed value for P_g at 200°C is 29.9 MPa. The value of N/W at which $V_g > 0$ at 200°C is >0.14 for the assumed values for P_g and for the solubility coefficient, α' , of the gases within the brine.

value of V_g is assumed to equal zero until the pressure exerted by the dissolved radiolytic gases exceeds the value of P_g . This occurs at $N/W > 0.067$ and >0.096 at 100°C and 150°C, respectively, for the assumed values of P_g and for the solubility coefficient, α' , of the gases within the brine.

Footnotes to Tables 6 and 7 provide additional information regarding the meanings of the symbols and the assumptions made in arriving at the tabulated quantities.

An important assumption employed in the estimates shown in Tables 6 and 7 was that $G(\text{H}_2) = 2.1$. As discussed in Sect. 6 and elsewhere,¹⁴ the actual value for this parameter in concentrated chloride solutions is uncertain. It is conceivable that it is as low as 0.45 (the value for pure H_2O); however, there are reasons to believe that it may be 2.1 or more.¹⁴ The range of possible values for $G(\text{H}_2)$ should probably be covered in estimates of the effects of radiolysis in brines.

Another important assumption was that at some pressure of dissolved radiolytic gas, P_g , the salt surrounding a brine inclusion will expand to form a gas-vapor phase within the inclusion and will continue to expand at P_g as additional radiolytic gases are formed. The assumed value of P_g at 100°C was 31 MPa. At 150 and 200°C, this value was reduced from 31 MPa by amounts equal to the vapor pressure of the brines at these temperatures. A somewhat similar assumption could have been made that cracking of the surrounding crystal takes place at pressure P_g so that the gases can escape to and collect on an adjacent crystal boundary.

A third important assumption was that no significant recombination of dissolved radiolytic gases would take place until the concentration of H_2 exceeded that of the Br^- (0.045 *m*) by a factor greater than ~ 50 . The theoretical basis for this assumption was discussed in ref. 14 and reviewed briefly in Sects. 5 and 6. Experimental results with irradiated salt from Lyons, Kansas, discussed in Sect. 6, support the validity of this assumption.

The values for $N(\text{H}_2 + \text{O}_2)/W$ for SF listed in Table 6 indicate that, at the midplane edge of the salt, the assumed value of P_g (31 MPa) would be exceeded during a period of ~ 3 months after emplacement of the reference SF package, if $G(\text{H}_2)$ is equal to 2.1. A longer period of ~ 15 months would be required if the lowest conceivable value for $G(\text{H}_2)$, 0.45, prevails. The period of irradiation at a given dose rate that is required to reach P_g will probably be directly proportional to the assumed value of P_g , and accordingly, the actual times required to reach P_g in a

repository might be either greater or less than the 3- and 15-month periods mentioned above. Similarly, the values of $N(\text{H}_2 + \text{O}_2)/W$ for HLW in Table 7 indicate that, at the midplane edge of the salt, the assumed value of P_g is reached during the first month after emplacement of the HLW reference package if $G(\text{H}_2)$ is equal to 2.1. If the lowest value of $G(\text{H}_2)$, 0.45, prevails, the period of time is increased to ~5 months. In practice, the latter time period could be appreciably more than 5 months since the brine might be migrating through the salt toward the edge at the prevailing temperature and temperature gradients. The highest migration rates at the highest temperatures and temperature gradients, ~200°C and ~2°C/cm, will probably be ~100 mm/yr.¹ At this high migration rate, and if $G(\text{H}_2)$ is equal to 0.45, the pressure P_g of dissolved radiolytic gases would barely be reached in the migrating brine at the time that it reaches the edge of the hole (i.e., reaches the location identified as I_{17h}).

Another factor of possible importance, which has been neglected in the calculations to this point, is the generation of radiolytic gases within a brine inclusion by the dissolution, as an inclusion migrates, of aggregates of trapped electrons and trapped holes in the irradiated salt.^{14,38} The maximum rate of H_2 generation (and the accompanying oxidants) by this process will depend upon several parameters, as shown by the approximate relationship in Eq. (13):¹⁴

$$F \cong 1000 \cdot V \cdot C / L, \quad (13)$$

where

F = rate of production of H_2 within inclusion by dissolution of salt during migration of inclusion, mole/l·yr;

V = rate of migration of droplet, mm/yr;

C = concentration of trapped electrons in salt, mole/g; and

L = dimension of droplet parallel to the direction of migration, mm.

The approximate maximum value of C for salt irradiated at temperatures in the range of ~80 to ~150°C and at gamma doses of up to ~1 E+08 Gy is given by Eq. (14),^{14,29}

$$C = 1.4 \text{ E-12 } D_h, \quad (14)$$

where

D_h = gamma dose in salt, Gy.

At temperatures $>150^\circ\text{C}$, thermal annealing will probably preclude the accumulation of significant concentrations of radiation defects in salt.²⁹ Below ~ 60 to 80°C , the radiation-induced back reaction of defects (radiation annealing) will probably preclude the accumulation of appreciable amounts of radiation damage.²⁹ Radiation annealing in the temperature range 80 to 150°C will become important at gamma doses above $\sim 1 \text{ E+08 Gy}$.²⁹

The actual value of F may be less than that given by Eq. (13) as a result of some interaction between defects and solutes during dissolution.^{29,38}

The possible contribution to the value of $N(\text{H}_2)/W$ within encapsulated brine of the dissolution of defects within irradiated salt is illustrated as follows.

Assuming that

1. $V = 25 \text{ mm/yr}$ (This is the approximate maximum value expected for completely filled brine inclusions in salt at $\sim 150^\circ\text{C}$ and with ∇T equal to 0.1°C/mm ; see Sect. 4.),
2. $L = 1.0 \text{ mm}$, and
3. $D_h = 5.0 \text{ E+07 Gy}$ (This is the average value of D_h within a 25-mm-thick layer of solid salt at the midplane around a reference HLW package after 20 yr of emplacement of the package; see Table 7.),

then,

$$C = 7.0 \text{ E-05 mole/g [found using Eq. (14)] .}$$

Introducing the above values for V , X , and C into Eq. (13), we find that F is equal to $1.8 \text{ moles H}_2/\ell\cdot\text{yr}$. Converting this value for F into molal units, we find that $N(\text{H}_2)/W$ is equal to $2.0 \text{ mole H}_2/\text{kg}\cdot\text{yr}$.

This value of $N(\text{H}_2)/W$ in salt around a reference HLW package exceeds by a factor of ~ 2.5 the maximum value for this quantity (at $t = 20$ yr) which would result from direct absorption of the gamma rays within the brine migrating within the 25-mm-thick layer (Table 7). This result indicates the possibility that after a few years following emplacement of HLW or SF, much of the radiolysis within migrating brine might result from the dissolution of the irradiated salt, when the salt temperatures are in the range of ~ 30 to 150°C while the salt is being irradiated.

Still another factor of possible importance is the radiation-induced reaction between H_2 and O_2 in the gas phase to form H_2O , which will probably occur within any irradiated gas-vapor phase which contains both these elements (Sect. 7). The effects of the gas-vapor phase reactions on the net decomposition of the brine within an inclusion will depend upon several factors, including (1) whether O_2 comprises the oxidant which is formed along with radiolytic H_2 within the brine, (2) the relative values of $G(\text{H}_2)$ in the liquid and of $G(\text{H}_2\text{O})$ in the gas-vapor phase, and (3) the relative masses of H_2O and gases and the relative values for gamma dose rates within the two different phases. I have made no detailed estimates of the effects of gas-phase radiolytic reactions on net radiolysis of a brine inclusion within any of the many systems which can be postulated. My rough estimates indicate that the net effects will be minor for the migrating brine systems which will, in practice, prevail.

As implied by the discussions in the preceding paragraphs, there are several uncertainties regarding the rates of buildup and the effects of radiolytic gases within brine inclusions in salt. It seems very likely, however, that high pressures will develop within brine inclusions, and that these pressures will result in the formation of a gas-vapor phase over the liquid within an inclusion. One result of the formation of a gas-vapor phase would be migration, by reflux action, of this phase away from the waste package, down the temperature gradient, if the vapor pressure-temperature relationships for the brine are the same as those for the saturated brine solution which would be formed by dissolving the surrounding salt in pure H_2O . This would be the case if the surrounding

salt is essentially pure NaCl and the brine within the inclusion is formed by the dissolution of this salt. However, as discussed in Sect. 3 and elsewhere,⁴⁸ MgCl₂-rich brines occur within bedded salt, and these brines have vapor pressures which are substantially below those of a saturated NaCl solution, at a given temperature.⁴⁶ For example, the temperature at which a 2.41 *m* MgCl₂ solution, saturated with NaCl, has a vapor pressure equal to that of a saturated NaCl solution, free of MgCl₂, is 2 to 3°C greater than the given temperature of the NaCl solution. Accordingly, it is very unlikely that migration of gas-vapor inclusions in bedded salt will take place when the inclusions are in contact with the original liquid inclusions.* Of course, the liquid phase could continue to migrate and possibly leave the gas-vapor inclusion at the site where it was formed. It seems possible that a string of isolated inclusions could be formed and left behind the migrating liquid inclusion. Radiation-induced formation of H₂O would take place within these gas-vapor inclusions if radiolytic O₂ is a major constituent of the gases. This H₂O might effect down-temperature-gradient migration of the inclusion if MgCl₂ and similar salts are not retained within the gas-vapor inclusion when it is separated from the migrating liquid inclusion.

11. AMOUNTS OF RADIOLYTIC H₂ AND OXIDANTS ACCOMPANYING MIGRATING BRINE INTO SPACES AROUND A CANISTER IN SALT

As discussed in Sect. 10, it seems likely that any brine which migrates through the salt into the space around a waste canister will be saturated with H₂ at some pressure P_g . The estimated values for the saturation concentrations of H₂ within brine inclusion in a 670-m-deep salt repository at temperatures of 100, 150, 200°C were 0.067, 0.096, and 0.14 *m*. The estimated molality of radiolytic H₂ in in-migrating brine at other salt temperatures and/or at other depths can be obtained similarly (Sect. 10 and Appendix A).

* In previous reports,^{49,50} I stated or assumed that a gas-vapor inclusion in salt would migrate down a temperature gradient in the salt. These previous statements and assumptions require qualification, as discussed in this paragraph.

The radiolytic H_2 within the in-migrating brine might not be accompanied by a stoichiometric amount of radiolytic oxidant, depending upon whether O_2 comprises all of the radiolytic oxidant within a brine inclusion. Oxidants such as ClO_3^- would not accompany a gas phase which is separating and moving away from the liquid phase and, accordingly, would be concentrated within the liquid phase. The fraction of oxidant that will occur as O_2 in a given repository is unknown.

12. RADIOLYSIS OF BRINES AROUND WASTE PACKAGES IN SALT

12.1 Unconfined $MgCl_2$ -rich Brines

A useful relationship between the rate of generation of radiolytic H_2 , time after emplacement of the wastes, and other parameters, is shown as Eq. (15).

$$dN(H_2)dt' = G(H_2) \cdot I \cdot (1 + E_g/E_w) (W/W_z) C \cdot t' / 6.02 \text{ E}+25, \quad (15)$$

where

$N(H_2)$ = total number of moles of radiolytic H_2 formed within the brine located in the spaces around a waste package at a given time after emplacement of the wastes;

t' = time after emplacement of the waste, yr;

$G(H_2)$ = number of H_2 formed within the irradiated brine solution, per 100 eV of radiation energy absorbed in the solution;

I = rate of deposition of gamma-ray energy in H_2O at location of brine, eV/kg·yr;

E_g/E_w = ratio of the number of orbital electrons associated with the solutes dissolved in a given mass of H_2O to the number of orbital electrons associated with the given mass of H_2O solvent. Values for this ratio are listed in Table A.3 for solutions saturated in NaCl and containing $MgCl_2$ at several concentrations to saturation, at temperatures ranging from 25 to 200°C.

W = total mass of H_2O (as brine) exposed to gamma radiations around package at any time, kg; and

W_i = total mass of H_2O which migrated (as brine) into the spaces around a waste package up to time t' , kg ($W_i = C \cdot t'$);

C = assumed constant rate of brine in-migration, kg H_2O /yr.

Also given in Table A.3 are values for the ratio W/W_i and for the quantity $(1 + E_s/E_w)(W/W_i)$. As can be noted, the value of E_s/E_w increases as that of W/W_i decreases. Consequently, the value of $(1 + E_s/E_w)(W/W_i)$ does not change as rapidly as the value of W/W_i with variations in the composition of the brine which accompany loss of H_2O from the brine.

Equation (15) can be derived using both the information and methods presented in Appendix A and the symbol definitions presented above. The formation of radiolytic H_2 will be accompanied by one or more of the oxidized species shown in Eq. (11). Oxygen and/or ClO_3^- are the most likely oxidized species in brines of the compositions expected around waste packages (see Sect. 3).¹⁴ The presence of chlorine (Cl_2) is very unlikely at the relatively low acidities which will probably prevail in the brine solutions.¹⁴ Radiation-induced back reaction between H_2 and the oxidized species within the brine to reform H_2O is very unlikely (see Sect. 9 and ref. 14) and was assumed to be negligible in deriving Eq. (15).

Equation (15) can be integrated to form Eq. (16), an expression for the total number of moles of H_2 which is generated subsequent to some initial period t'_1 , if it is assumed that the coefficient of t' remains constant following the initial period.

$$N(H_2) - N(H_2)_{t'_1} = G(H_2) \cdot I \cdot (1 + E_s/E_w)(W/W_i)C \cdot [(t')^2 - (t'_1)^2] / 12.04 \text{ E+25} . \quad (16)$$

In order to illustrate the rates at which radiolytic H_2 might be formed in $MgCl_2$ -rich brines around a waste package, I will assume certain

values for $G(H_2)$, I , C , and $(1 + E_g/E_w)(W/W_i)$ as listed and discussed below:

1. $G(H_2)$ — The bases for assuming that $G(H_2)$ is equal to 2.1 were discussed in Sects. 6 and 9 and in ref. 14.
2. C — Conservative values of C for the first several years after emplacement of the waste can be estimated from information in Sect. 4 and Figs. 6 and 7 and are 0.1 kg/yr and 1.0 kg/yr for SF and HLW, respectively.
3. I — The value of I for a reference waste package will depend upon the age of the waste, the specific location around the package, and the shielding between the canister and the location of the brine. For illustrative purposes, I selected the average of the values for t equal to 10 yr and 20 yr, listed in Tables 2 and 4, for locations at the midplane surface of the solid salt with air backfill around the canister, as follows:

$$I = 60 \text{ E+23 eV/kg}\cdot\text{yr}$$

and

$$I = 325 \text{ E+23 eV/kg}\cdot\text{yr}$$

for SF and HLW, respectively.

4. $(1 + E_g/E_w)(W/W_i)$ — A reasonably typical value for this quantity is 0.50 (Table A.3), even assuming that a desiccant is used which removes most of the H_2O but leaves a hydrate of $MgCl_2$. The values of this quantity for the 6 and 4 hydrates of $MgCl_2$ are 0.46 and 0.37, respectively, if it is further assumed that the given hydrate can be treated as a $MgCl_2$ solution which has the same $MgCl_2$ -to- H_2O ratio as that in the hydrate.

Introducing the above values into Eqs. (15) and (16), we obtain the estimated values listed in Table 8 for $dN(H_2)/dt'$ and $N(H_2)$ at t' equal to 1 yr and 10 yr. Table 8 also contains estimates of the contribution to the value for $N(H_2)$ around the canister which would be made by the H_2

Table 8. Values for $dN(H_2)/dt'$ and $N(H_2)$ found using Eqs. (15) and (16) and parameter values listed in Sect. 12.1. Values also listed for the contribution to $N(H_2)$ from H_2 within in-migrating brine

Parameter	SF	HLW
$dN(H_2)/dt'$ (mole H_2 /yr)		
$t' = 1$ yr	0.010 (0.002) ^a	0.57 (0.12)
$t' = 10$ yr	0.10 (0.02)	5.7 (1.2)
$N(H_2)$ from Eq. (16) ^b (mole H_2)		
$t' = 1$ yr	0.005 (0.001)	0.28 (0.06)
$t' = 10$ yr	0.50 (0.11)	28.3 (6.1)
$N(H_2)$, with in-migrating brine (mole H_2) ^c		
$t' = 1$ yr	0.01	0.1
$t' = 10$ yr	0.1	1.0

^aValues within parentheses were calculated by assuming that $G(H_2)$ is equal to 0.45. Other adjacent values were calculated by assuming that $G(H_2)$ is equal to 2.1.

^b t'_1 in Eq. (16) was assumed equal to zero.

^cSaturation concentration of H_2 within in-migrating brine was assumed to equal 0.1 m (Sects. 10 and 11).

dissolved within the in-migrating brine. I assumed that the saturation concentration of H_2 in the migrating brine is 0.1 m for these estimates (Sects. 10 and 11).

Comparisons between the different values in Table 8 indicate that the contribution from the H_2 dissolved within the in-migrating brine will be relatively small, unless the brines go to complete dryness around the waste canister, or unless the value for $G(H_2)$ is substantially <2.1.

12.2 Unconfined NaCl Brines^{*}

The radiolytic behavior of these brines can be discussed with reference to Eq. (15) and to the parameter values discussed in Sect. 12.1. The principal differences, in the present context, between the NaCl and the MgCl₂-rich brines are as follows:

1. The value of the quantity $1 + E_g/E_w$ does not change as H₂O is lost from the NaCl brines since the composition of a saturated brine solution is constant at a given temperature, to a close approximation. As shown in Table A.2, the values for E_g/E_w increase moderately with increasing temperature, ranging from 0.31 at 25°C to 0.40 at 200°C.
2. The vapor pressures of the NaCl brines are relatively high, and these brines are more likely to lose H₂O and go to dryness than the MgCl₂-rich brines. Accordingly, the H₂ dissolved in the in-migrating NaCl brines is more likely to be the principal source of radiolytic H₂ around a waste canister. Also, reflux action with vapor condensing on solid salt is more likely to occur with NaCl brines (Sect. 10).
3. The NaCl brines might not contain significant amounts of Br⁻ or other strong radical scavengers; in which case, recombination of H₂ and oxidant could take place within the brine, and this recombination could greatly reduce the maximum pressure of H₂ and O₂ mixtures which could exist in contact with the brine.

12.3 Confined NaCl and MgCl₂-rich Brines

Several different cases of confined NaCl and MgCl₂-rich brines can be visualized.

In one case, the brine is confined in salt around the waste canister. The system is analogous to that of a brine inclusion within solid salt (Sect. 10). With NaCl brines which contain appreciable concentrations of a radical scavenger, the gas phase will probably migrate down the

^{*}The brines identified as NaCl brines are assumed to be nearly free of MgCl₂ or CaCl₂.

temperature gradient, away from the canister. The liquid phase will migrate toward the canister, stopping only when it touches the canister at the hottest elevation. The brine will continue to be decomposed by the gamma radiations at the canister surface. It will also be decomposed by corrosive reactions with the metal canister in which H_2 is generated. These processes of decomposition, with gas generation and migration away from the gases, will probably continue until the brine solutions have gone to dryness.

If the NaCl brine does not contain appreciable concentrations of Br^- or another strong radical scavenger, neither high gas pressures nor a gas-vapor phase will probably develop in the confined brine which is surrounded by salt.

With $MgCl_2$ -rich brines, the gas-vapor phase will not migrate unless the ∇T across the gas-vapor space exceeds $\sim 0.2^\circ C/mm$. However, the liquid phase could migrate and separate from the gas-vapor phase. Gas pressure buildup at the surface of the canister may cause expansion of the confining material to provide space for the gas. The gas pressure buildup could also cause cracking of the confining material and escape of the gas into the overlying room.

In a second case, the brine is confined within a porous, insoluble backfill such as sand, and the liquid brine will have no tendency to migrate. With either brine, there may be some condensation of H_2O vapor on solid salt surfaces of the emplacement hole, leading to reflux action and possibly to migration of the gas-vapor phase into the salt. With both brines, gas-pressure buildup could occur when radical scavengers are present, which could lead to expansion of the confining material and/or to fracture of the material and escape of the gas into the overlying room. The radiation-induced recombination of H_2 and O_2 in the gas-vapor phase over a brine might preclude the net formation of any radiolytic gases within the gas-vapor phase under certain conditions.³⁹

13. POSSIBLE EFFECTS OF RADIATION AROUND WASTE CANISTERS ON FACTORS AFFECTING THE DESIGN AND OPERATION OF A REPOSITORY IN SALT

A discussion and an analysis were recently reported of the possible effects of irradiation around a SF package in salt on the corrosion of the carbon steel canister and on the other local interactions of possible importance in evaluating the optimum design and operation of a repository in salt.^{39,46} It was concluded that O_2 which was formed radiolytically in $MgCl_2$ -rich brines around the canister could contribute to localized corrosion of the canister if most of the O_2 could diffuse to a small wetted portion of the canister surface at which the localized corrosion was taking place. Diffusion of the O_2 to the local wetted area could probably be prevented through the use of appropriate backfill materials; a mixture of quick lime and sand was suggested as a possible suitable mixture.^{39,46} No other radiation effects were apparent which would have significant impact on the design and operation of a repository in salt.

I have nothing to add to the previous discussions and conclusions. No comparable detailed analyses have been made for HLW in salt. However, the results of my cursory considerations indicate that the concepts discussed and the conclusions reached for SF in the previous report are generally applicable to HLW also.

14. SUMMARY, CONCLUSIONS, AND RECOMMENDATIONS

The brines, vapors, and any salts precipitated from the brines will be exposed to gamma rays and to elevated temperatures in the regions close to a waste package in the salt. Accordingly, they will be subject to changes in composition brought about by reactions induced by the radiations and heat.

The objectives of the work presented in this report were to review the status of information on the radiation chemistry of brines, gases, and solids which might occur around a waste package in salt and to assess the need for additional laboratory investigations of the radiation chemistry of these materials.

It was recognized at the start of this work that the radiation chemistry, as well as the effects of irradiation in a repository, would depend upon the compositions and amounts of liquids and solids around a waste package and also upon the design of the waste package, including dimensions, thermal power and age of waste, and backfill material. Accordingly, an appreciable part of this report was devoted to the following considerations: (1) the probable characteristics of packages of HLW and SF in a salt repository, (2) the probable compositions of the salt-mine brines, both within the solid salt and in the spaces around a waste canister, and (3) factors which might affect migration of brine from surrounding salt to waste packages, and some estimates of probable amounts of brine migrating to waste packages.

The basic aspects of the radiation chemistry of H_2O and aqueous solutions including concentrated salt solutions were reviewed briefly and found to be substantially unchanged from those presented in my 1972 review of radiolysis and hydrolysis in salt-mine brines. Some additional information on the radiolytic yields and reactions in brine solutions has become available since the early review, and this information will be useful in the eventual complete elucidation of the radiation chemistry of the salt-mine brines.

Presently available values for $G(H_2)$ in brines are in the range of 0.45 to 2.1. The radiolytic oxidant that accompanies the radiolytic H_2 will probably be either O_2 or ClO_3^- or some of each. The relative yields of these oxidant species is unknown.

Analyses were made of the possible rates of buildup and the effects of radiolytic gases within brine inclusions in salt. It seems very likely that high pressures will develop within brine inclusions and that these pressures will result in the formation of a gas-vapor phase over the liquid within an inclusion. One result of the formation of a gas-vapor phase would be migration, by reflux action, of this phase away from the waste package, down the temperature gradient, if the vapor pressure-temperature relationships for the brine are the same as those for the saturated brine solution which would be formed by dissolving the surrounding salt in pure H_2O . This would be the case if the surrounding salt is essentially pure $NaCl$ and the brine within the inclusion was formed by dissolution of this salt.

However, MgCl_2 -rich brines occur within bedded salt, and these brines have vapor pressures which are substantially below those of a saturated NaCl solution, at a given temperature. For example, the temperature at which a 2.41 *m* MgCl_2 solution, saturated with NaCl , has a vapor pressure equal to that of a saturated NaCl solution, free of MgCl_2 , is 2 to 3°C greater than the given temperature of the NaCl solution. Accordingly, it is very unlikely that migration of gas-vapor inclusion in bedded salt will take place when the inclusions are in contact with the original liquid inclusions. Of course, the liquid phase could continue to migrate and possibly leave the gas-vapor inclusion at the site where it was formed. It seems possible that a string of isolated inclusions could be formed and left behind the migrating liquid inclusion. Radiation-induced formation of H_2O would take place within these gas-vapor inclusions if radiolytic O_2 is a major constituent of the gases, and this H_2O might effect down-temperature gradient migration of the resulting two-phase inclusion.

The results of this work, together with those presented in previous review reports, indicate that significant effects of the gamma radiations on the design and operation of a repository in rock salt are most likely to result from the radiolytic formation of oxidants (O_2 or ClO_3^- or both) which, under certain conditions, could react with the canister in the corrosion process. The basic aspects of the radiation chemistries that may be involved are adequately understood. However, the possibilities of encountering significant effects in the repository will depend upon several factors, including the compositions and amounts of liquids, solids, and gases around a waste canister; the design of the waste package, including dimensions, thermal power, and age of waste; the material that is used to backfill the space between the canister and the solid salt of the emplacement hole; and the actual values for certain radiation-chemistry parameters. These latter parameters include:

1. The values for $G(\text{H}_2)$ in the concentrated NaCl and MgCl_2 solutions which might occur around a canister. The available information indicates that values for this parameter are in the range of 0.45 to 2.1.

2. The values for $G(O_2)$ and $G(ClO_3^-)$ which accompany the values for $G(H_2)$ in the concentrated NaCl and $MgCl_2$ solutions. Present information indicates that one or both of these species will comprise the radiolytically formed oxidant which will accompany the formation of radiolytic H_2 in the brines.
3. The values for $G(H_2)$, $G(O_2)$, $G(ClO_3^-)$, and G values for other unspecified oxidants in the gamma irradiation of hydrates of $MgCl_2$.
4. The radiation stability of the product of reaction between brines and any desiccant which might be used as backfill around a waste canister would also be a factor.

Because of the simultaneous occurrence of the many factors described above which could influence the effects of radiation on canister corrosion or influence other unrecognized effects of possible significance to the design and operation of a repository, any experiments which are aimed at establishing the effects of irradiation would most appropriately, be conducted in situ, in the salt in which the repository would be established. Alternatively, most of the factors and combinations of factors could be mocked up and studied in a hot cell experiment using ^{60}Co and electrical heaters to simulate the radiation and heat emanating from a waste canister. (Brine migration through the solid salt would not be studied in these mock-up experiments.) It seems likely that experiments of one or both types will be needed to provide information for use in detailing the design and operation of a repository.

In addition, information on the actual G -values for the species listed above (H_2 , O_2 , ClO_3^- , and other unspecified oxidants) would be helpful in the prediction and interpretation either of the behavior with actual waste emplacements in salt or of results with mock-up or in situ experiments with waste package in salt. Such information could be obtained from laboratory experiments using a ^{60}Co source. The radiation stability of desiccants and their reaction products could also be studied in similar laboratory experiments, and helpful information could be obtained from such experiments.

APPENDIX A. METHODS AND INFORMATION FOR ESTIMATING GAMMA-RAY DOSES
TO AND NUMBER OF RADIOLYTIC SPECIES FORMED WITHIN AQUEOUS
BRINE SOLUTIONS AROUND A WASTE PACKAGE IN SALT

A.1 Relationships Between Gamma Dose Rate, Gamma Dose,
G-Values, and Amounts of Radiolytic Species

Let:

t = age of waste (time after discharge from reactor), yr;

t_e = age of waste at time of emplacement in salt, yr;

I = rate of deposition of gamma-ray energy in H_2O at location of
brine, eV/kg·yr;

I_s = rate of deposition of gamma-ray energy in H_2O in brine solution,
eV/kg·yr;

D_s = integrated amount of gamma-ray energy deposited in brine
solution, eV/kg H_2O ;

$G(X)$ = number of species, X , formed within an irradiated solution per
100 eV of radiation energy absorbed in the solution; and

$N(X)/W$ = total number moles of radiolytic species, X , formed per unit
mass of H_2O , W , within the brine during exposure to radiation
dose, D_s .

From these definitions, we can write the following equations:

$$D_s = \int_{t_e}^t I_s(t) dt , \quad (A.1)$$

$$N(X)/W = G(X) \cdot D_s / 6.02 \text{ E}+25 . \quad (A.2)$$

From other considerations,

$$I_s \cong I(1 + E_s/E_w) , \quad (A.3)$$

where

E_s/E_w = the ratio of the number of orbital electrons associated with the solutes dissolved in a given mass of H_2O to the number of orbital electrons associated with the given mass of H_2O solvent.

A.2 Values for E_s/E_w in Confined Brine Solutions at Temperatures Ranging from 25 to 200°C

The approximate composition of the brine encapsulated in bedded salt at Lyons and Hutchinson, Kansas,⁴⁸ and the corresponding values for E_s/E_w are listed in Table A.1.

Table A.1. Approximate composition of brine encapsulated in bedded salt at temperatures up to 200°C and corresponding values for E_s/E_w

Solution temperature (°C)	Concentration of NaCl in 2.41 m MgCl ₂ solution (mole/kg H ₂ O)	E_s/E_w
25	2.16	0.30
50	2.32	0.31
100	2.76	0.33
150	3.30	0.36
200	4.02	0.39

As discussed in ref. 48, it is likely that the composition of the brine in the halite located in or near the WIPP* site in New Mexico is about the same as that of Kansas brines.

* Waste Isolation Pilot Plant.

The compositions of solutions that are saturated in NaCl, but contain no other solutes, are listed in Table A.2 together with corresponding values for E_s/E_w .

The values of E_s/E_w range from ~0.30 at 25°C to 0.40 at 200°C for both the pure NaCl solutions and for the 2.41 *m* MgCl₂ solutions.

Table A.2. Concentration of NaCl in saturated NaCl solutions at temperatures up to 200°C and corresponding values for E_s/E_w

Solution temperature (°C)	Concentration of NaCl (mole/kg H ₂ O)	E_s/E_w
25	6.15	0.31
40	6.22	0.31
80	6.50	0.33
100	6.68	0.34
120	6.88	0.35
140	7.10	0.36
180	7.65	0.39
200	7.98	0.40

A.3 Values for E_s/E_w in Unconfined Brine Solutions at Temperatures from 25 to 200°C

Any brine that enters the open spaces around a canister will lose H₂O by several processes, including reaction with the iron canister, radiolytic decomposition, and evaporation. The loss of H₂O from the MgCl₂-rich, NaCl-saturated solutions results in the precipitation of NaCl and an increase in the concentration of MgCl₂. With the continued loss of H₂O, the solutions become saturated in MgCl₂, and a solid hydrate — either MgCl₂·6H₂O and/or MgCl₂·4H₂O, depending upon the temperature of the system — precipitates (Sect. 3.5).

Table A.3 shows values for the saturation concentration of NaCl solutions containing MgCl₂ at several concentrations from 3.0 *m* to

Table A.3 Saturation concentration of NaCl in solutions containing MgCl_2 at several concentrations to saturation and values for E_s/E_u , w/w_i , and $(1 + E_s/E_u)(w/w_i)$

Temperature (°C)	Concentration (mole/kg H_2O)		E_s/E_u	w/w_i	$(1 + E_s/E_u)(w/w_i)$
	MgCl_2	NaCl			
25	3.00	1.25	0.31	0.80	1.05
	4.00	0.49	0.36	0.60	0.82
	5.00	0.15	0.42	0.48	0.68
	5.82	0.05	0.49	0.41	0.62
60	3.00	1.56	0.33	0.80	1.06
	4.00	0.71	0.37	0.60	0.82
	5.00	0.28	0.42	0.48	0.69
	6.00	0.09	0.50	0.40	0.60
	6.42	0.06	0.54	0.38	0.58
100	3.00	1.96	0.35	0.80	1.08
	4.00	1.02	0.38	0.60	0.83
	5.00	0.474	0.44	0.48	0.69
	6.00	0.207	0.51	0.40	0.60
	7.00	0.089	0.60	0.34	0.55
	7.67	0.051	0.64	0.31	0.51
140	3.00	2.40	0.37	0.80	1.10
	4.00	1.39	0.40	0.60	0.84
	5.00	0.74	0.45	0.48	0.70
	6.00	0.379	0.52	0.40	0.61
	7.00	0.194	0.59	0.34	0.54
	8.00	0.102	0.67	0.31	0.50
	9.00	0.056	0.75	0.27	0.47
	9.64	0.039	0.80	0.25	0.45
160	3.00	2.65	0.38	0.80	1.11
	4.00	1.6	0.41	0.60	0.85
	5.00	0.98	0.46	0.48	0.70
	6.00	0.495	0.52	0.40	0.61
	7.00	0.270	0.59	0.34	0.54
	8.00	0.152	0.67	0.31	0.50
	9.00	0.090	0.75	0.27	0.47
	10.00	0.055	0.83	0.24	0.44
	10.51	0.044	0.87	0.23	0.43
180	3.00	2.92	0.40	0.80	1.12
	4.00	1.84	0.42	0.60	0.85
	5.00	1.095	0.47	0.48	0.71
	6.00	0.632	0.53	0.40	0.61
	7.00	0.367	0.60	0.34	0.54
	8.00	0.222	0.67	0.31	0.50
	9.00	0.137	0.75	0.27	0.47
	10.00	0.090	0.83	0.24	0.44
	11.00	0.063	0.91	0.22	0.42
	12.00	0.046	1.00	0.20	0.40
	12.71	0.038	1.05	0.19	0.39
200	3.00	3.22	0.41	0.80	1.13
	4.00	2.10	0.44	0.60	0.86
	5.00	1.31	0.48	0.48	0.71
	6.00	0.795	0.54	0.40	0.61
	7.00	0.486	0.60	0.34	0.54
	8.00	0.307	0.68	0.31	0.51
	9.00	0.202	0.76	0.27	0.47
	10.00	0.140	0.84	0.24	0.44
	11.00	0.103	0.92	0.22	0.42
	12.00	0.080	1.00	0.20	0.40
	12.71	-	1.15	0.17	0.38
$\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$	9.26	0	0.77	0.26	0.46
$\text{MgCl}_2 \cdot 4\text{H}_2\text{O}$	13.89	0	1.15	0.17	0.37

saturation at several different temperatures ranging from 25 to 200°C (Sect. 3.5). Also shown are corresponding values for E_s/E_w and for the ratio (W/W_i) of the mass of H_2O for a given number of moles of $MgCl_2$ in the given solution to the mass of H_2O for the same number of moles of $MgCl_2$ in a 2.41 m $MgCl_2$ solution. The value of this ratio corresponds to the fractional amount of H_2O remaining from an original 2.41 m $MgCl_2$ solution after the original solution loses H_2O to form the more concentrated $MgCl_2$ solution. The product, $(1 + E_s/E_w)(W/W_i)$, also listed in Table A.3, is proportional to the ratio of the rates of deposition of gamma-ray energy in the concentrated brine to that in the initial brine with the same amount of $MgCl_2$.

The final two entries in Table A.3 show values for hydrates of $MgCl_2$ derived by treating the hydrate as a $MgCl_2$ solution which has the same $MgCl_2$ -to- H_2O ratio as that of the hydrate.

A.4 Dose Rates around Canisters of High-Level Waste and of Spent Fuel Emplaced in Salt

A.4.1 HLW canisters, 330-mm-OD, 2.4-m active length, 10-yr-old waste at emplacement

Information relating to the gamma-ray dose rates in salt surrounding and contacting a 305-mm-OD, 2.4-m active length HLW canister was discussed in ORNL-5058.²⁹ This information showed that with 10-yr-old HLW from UO_2 -fueled PWRs, the calculated dose rate at the midplane varied with the radial distance from the surface of the canister according to Eq. (A.4) out to at least 150 mm from the surface.^{29,51}

$$I/I_{305} = \exp [-0.0162 X] , \quad (A.4)$$

where

X = radial distance from canister surface, mm.

This equation also expressed the values of I/I_{305} , to a close approximation, out to waste ages of more than 200 yr.⁵¹

The reference HLW canisters considered in this present report have outside diameters of 330 mm rather than 305 mm. The canisters are emplaced in 430-mm-diam holes in salt, and the 50-mm annular space between a canister and solid salt is backfilled with air or with some other material such as sand. For the case in which the gamma-ray absorption coefficient of the backfill per unit thickness is equal to that of the solid salt, the variation of dose rate with radial distance should be analogous to that shown in the above equation,

$$I/I_{330} = \exp [-0.0162 X] , \quad (A.5)$$

where

X = radial distance from the surface of the 330-mm canister, mm.

For the case in which air fills the 50-mm annular space around the reference HLW canister, the dose rate at the surface of the solid salt relative to that at the canister can be estimated using geometrical considerations,

$$I_{430a}/I_{330} = 13/17 = 0.76 , \quad (A.6)$$

where a designates air-backfilled waste package.

The dose rate within the solid salt relative to that at the edge of the 430-mm hole is, in this case,

$$(I_{HXa}/I_{430a})_s = \exp [-0.0162 HX] , \quad (A.7)$$

$$(I_{HXa}/I_{430a})_s = \exp [-0.0162 (X - 50.8)] , \quad (A.8)$$

where

HX = radial distance into salt starting at the surface of the 430-mm hole, and

s indicates solid salt.

The calculated⁵¹ value for I_{305s} in salt at the midplane corresponded to

$$I_{305s} = 810 \text{ Gy/h}$$

in salt when t was equal to 10 yr and the HLW was obtained by processing 2.25 Mg of UO_2 fuel exposed to 33 MWd/kg in a PWR. Equations that relate the initial midplane dose rates to those at other values of t were obtained from information discussed and/or referenced in ORNL-5058.²⁹ These are

$$I_t/I_{t10} = \exp [-0.0333 (t - 10)], \quad 10 \leq t \leq 30 ; \quad (A.9)$$

$$I_t/I_{t30} = \exp [-0.0232 (t - 30)], \quad 30 \leq t \leq 200 . \quad (A.10)$$

The dose rate in H_2O at a given location around an HLW canister will probably be 10% to 12% greater than that in salt at the same location. Values are listed in Table 4 for dose rates in H_2O at several locations around a reference HLW package in salt which were estimated by using the information discussed in this section.

A.4.2 Canisters containing PWR spent fuel assembly

Calculated values for gamma-ray dose rates in air-filled regions surrounding a PWR SF assembly (33 MWd/kg) were recently reported by Croff et al.⁵² The model employed by these workers was 240 mm in diameter, 3.60 m high, and the end pieces, top and bottom, were 120 mm thick. There was no canister. Their plotted decay factors can be expressed by Eq. (A.11) for t between 10 and 30 yr and by Eq. (A.12) for t between 30 and 100 yr.

$$I'_t/I'_{t10} = \exp [-0.0239 (t - 10)], \quad 10 \leq t \leq 30 ; \quad (A.11)$$

$$I'_t/I'_{t30} = \exp [-0.0277 (t - 30)], \quad 30 \leq t \leq 100. \quad (\text{A.12})$$

The dose rate at the midplane surface of the model assembly was 230 Gy/h when t was equal to 10 yr.

The reference SF canisters considered in this report have outside diameters of 368 mm and inside diameters of 343 mm. They are emplaced in 460-mm-diam holes in salt, and, as with HLW, the 44.5-mm annular region between the canister and the solid salt will be backfilled with air or with some other material such as sand. Also, the spaces within a canister that are not occupied by the assembly may be backfilled with helium or with some other material such as sand.⁴⁶

Apparently no calculations are available of the variation of dose rate with radial distance into salt around a canister of SF. Assuming that the variation is substantially the same as that for HLW, we can write Eq. (A.13) for the case in which the gamma-ray absorption coefficient of the backfill, per unit thickness, is equal to that of solid salt.

$$I'/I'_{368} = \exp [-0.0162 X'] , \quad (\text{A.13})$$

where the primes are used to identify parameters that pertain to the SF package. Also, by analogy with Eqs. (A.6) and (A.8), we can write Eqs. (A.14) and (A.15) for the air backfill case.

$$I'_{460}/I'_{368} = 14.5/18 = 0.81 , \quad (\text{A.14})$$

$$(I'_{HX}/I'_{460})_g = \exp [-0.0162 (X' - 44.5)] . \quad (\text{A.15})$$

Values are listed in Table 2 for dose rates in H₂O at several locations around a reference PWR SF assembly in salt which were estimated by using the information discussed in this section.

APPENDIX B. DERIVATION OF RELATIONSHIP EXPRESSING DISTRIBUTION OF GASES BETWEEN AQUEOUS AND GAS PHASES WITHIN A GIVEN SYSTEM

Let:

α' = solubility coefficient of gas in liquid aqueous phase,

Pa·kg (H₂O)/mole gas ;

W = mass of H₂O within liquid aqueous phase, kg;

V_g = volume of gas-vapor space, l;

T = temperature of system, K;

R = gas constant, Pa·l/K·mole;

P = pressure exerted by dissolved gas, Pa;

N = number of moles of gas within system;

N_l = number of moles of gas dissolved within liquid phase;

N_g = number of moles of gas within gas phase.

Assuming that the ideal gas law is adequate,

$$N_g = P \cdot V_g / R \cdot T , \quad (B.1)$$

and by definition,

$$N_l = P \cdot W / \alpha' . \quad (B.2)$$

Also,

$$N_l + N_g = N . \quad (B.3)$$

Substituting Eqs. (B.1) and (B.2) into Eq. (B.3), and solving for V_g/W ,

$$V_g/W = (N \cdot R \cdot T / P \cdot W) - (R \cdot T / \alpha') . \quad (B.4)$$

For the system comprising brine encapsulated within irradiated salt, V_g is equal to zero until the pressure of dissolved radiolytic gases reaches some value, P_g , at which the salt surrounding the inclusion

will presumably expand to form a gas-vapor phase within the inclusion and continue to expand as additional radiolytic gases are formed.

For this brine-inclusion system,

$$V_g/W = (N \cdot R \cdot T / P_g \cdot W) - (R \cdot T / \alpha') . \quad (B.5)$$

Also, just prior to the initial expansion of the surrounding salt to form the gas-vapor phase within the inclusion,

$$N/W = P_g / \alpha' . \quad (B.6)$$

In order to simplify Eq. (B.5) and to illustrate conceivable values for V_g/W within brine encapsulated within irradiated salt, let us first introduce the following values for R , T , and α' at 100°C:

$$R = 8.314 \text{ E+03 Pa}\cdot\text{l/K}\cdot\text{mole};$$

$$T = 373 \text{ K}; \text{ and}$$

$$\alpha'_{100} = 4.6\text{E+08}; \text{ this value is 3.5 times greater than that for H}_2 \text{ or O}_2 \text{ in pure H}_2\text{O at 100}^\circ\text{C. The factor of 3.5 was introduced to account for the probable effects of large concentrations of dissolved salts on the solubility of H}_2 \text{ and O}_2 \text{ in salt-mine brines.}^{39,53}$$

Introducing these quantities into Eq. (B.5),

$$V_g/W = (3.10 \text{ E+06} \cdot N / P_g \cdot W) - 6.7 \text{ E-03} . \quad (B.7)$$

To continue the illustration for brine inclusions in salt, some estimate must be made of the value of P_g . Let us assume that this pressure is about two times greater than an overburden pressure of ~15 MPa on the repository salt, or P_g is equal to ~30 MPa.

Substituting this value for P_g into Eq. (B.7),

$$V_g/W = (0.10 N/W) - 6.7 \text{ E-03} . \quad (B.8)$$

Also,

$$N/W \geq 0.067 .$$

Similarly, at 200°C, where

$$\alpha_{200} \cong 2.1 \text{ E}+09$$

(estimated again to be 3.5 times greater than the solubility of H₂ or O₂ in pure H₂O), we have the relationship shown by Eq. (B.9) if the assumed value of

$$P_g = 3.0 \text{ E}+07 - 1.1 \text{ E}+06 = 2.9 \text{ E}+07 \text{ Pa}$$

(1.1 E+06 Pa is the calculated vapor pressure at 200°C of a 2.41 m MgCl₂ solution saturated with NaCl at 200°C).

$$V_g/W = (0.14 \text{ N/W}) - 1.35 \text{ E}-02 \text{ (for } P_g = 29 \text{ MPa) .} \quad (\text{B.9})$$

Also,

$$N/W \geq 0.097.$$

In addition, at 150°C, where $\alpha_{150} \cong 3.2 \text{ E}+08$ and $P_g \cong 31 \text{ MPa}$, we have

$$V_g/W = (0.11 \text{ N/W}) - 1.1 \text{ E}-02 \text{ (for } P_g = 31 \text{ MPa) .}$$

Also,

$$N/W \geq 0.096.$$

APPENDIX C. VAPOR PRESSURE OF NaCl-SATURATED MgCl_2 SOLUTIONS*

C. F. Baes, Jr.**

Values are presented in the accompanying tables for the vapor pressure of NaCl-saturated solutions containing MgCl_2 at concentrations up to saturation and temperatures in the range 0 to 200°C. The vapor pressures were calculated using Pitzer's treatment for electrolyte mixtures (ref. 1), in which the activity coefficient of each salt present was calculated from three parameters (B_0 , B_1 , and CP in the tables) characteristic of that salt, parameters which in turn were evaluated from the measured data for pure solutions of each salt in water. Pitzer's treatment also includes parameters that are characteristic of salt mixtures (PCC and $PCCA$ in the tables), but these have a minor effect on the activities of the salts and on the vapor pressure of the water and were neglected in the present calculations. The values of B_0 , B_1 , and CP for NaCl were obtained as a function of temperature from the expressions given by Sylvester and Pitzer (ref. 2). Values for MgCl_2 were obtained by fitting similar smoothing functions to the values given by Holmes et al. (ref. 3) for pure MgCl_2 solutions. Solubility data from Seidell (ref. 4) were used to obtain smoothed values for the solubility of NaCl in water, and these in turn were used to calculate the activity of NaCl in saturated aqueous solutions. The limiting solubility of NaCl calculated for MgCl_2 -saturated solutions, the last entry at each temperature in the tables, differs appreciably in some cases from data in the literature, possibly because of errors of extrapolation in the present treatment; however, the effect on the vapor pressure should be negligible. The MgCl_2 concentrations at saturation were taken from ICT (ref. 5).

The computation of vapor pressures was carried out as follows. At a specified temperature and concentration of MgCl_2 , a trial value of the NaCl concentration was chosen, the activity of NaCl in the mixture was

* References for this appendix are given on p. 64.

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calculated, and this was compared with the activity corresponding to NaCl saturation. The concentration of NaCl in the mixture was then adjusted by an iterative procedure until the calculated activity of NaCl in the mixture equalled that for NaCl saturation.

The osmotic coefficient for this mixture of NaCl and MgCl_2 was calculated from the equation given by Pitzer (ref. 1), and this in turn gave the activity of water in the solution. The vapor pressure was approximated as the product of the water activity and the vapor pressure of pure water at the temperature involved, the effects of nonideal behavior in the vapor phase being neglected.

The tables are based on a computer output. The symbols in the tables are defined as follows:

B0, B1, CP = parameters in Pitzer's equations characteristic of each electrolyte.

CMG, CHA = concentrations of MgCl_2 and NaCl, molal (moles per kg of water).

NC = number of iterations used to obtain NaCl concentration.

PHI = osmotic coefficient of solution.

PCC, PCCA = parameters in Pitzer's equations characteristic of cation-cation pairwise interactions and cation-cation-anion triple ion interactions in mixture of electrolytes. These values were set equal to zero and are omitted here.

P0 = vapor pressure of pure water, bars (0.1 MPa).

PW = vapor pressure of solution, bars.

TC = temperature, °C.

The number of significant figures in the tables exceeds the accuracy of these calculations. The values of PW are probably reliable to a few percent at MgCl_2 concentrations below 4 molal. Uncertainties may be as large as 10% at higher concentrations.

TC	NaCl			MgCl ₂		
	BO	B1	CP	BO	B1	Cp
20.0	0.072730	0.262924	0.001815	0.355545	1.661631	0.005699
CNA	CMG	NC	PHI	PO	PW	
6.13249	0.00000	1	1.28387	0.023384	0.017608	
4.18100	1.00000	32	1.49836	0.023384	0.017208	
2.48578	2.00000	19	1.77603	0.023384	0.016461	
1.21214	3.00000	12	2.14112	0.023384	0.015050	
0.46439	4.00000	8	2.59787	0.023384	0.012768	
0.14487	5.00000	6	3.12515	0.023384	0.009887	
0.05745	5.72500	5	3.53668	0.023384	0.007771	

TC	NaCl			MgCl ₂		
	BO	B1	CP	BO	B1	Cp
25.0	0.076500	0.266400	0.001270	0.352524	1.681390	0.005157
CNA	CMG	NC	PHI	PO	PW	
6.15052	0.00000	1	1.28616	0.031689	0.023830	
4.21642	1.00000	32	1.49519	0.031689	0.023290	
2.53072	2.00000	19	1.76499	0.031689	0.022293	
1.25407	3.00000	12	2.11929	0.031689	0.020422	
0.49211	4.00000	8	2.56301	0.031689	0.017400	
0.15822	5.00000	6	3.07590	0.031689	0.013562	
0.05676	5.82330	5	3.53176	0.031689	0.010352	

TC	NaCl			MgCl ₂		
	BO	BI	CP	BO	BI	Cp
40.0	0.085680	0.277149	-0.000157	0.343666	1.749008	0.003688
CNA	CMG	NC	PHI	PO	PW	
6.22063	0.00000	1	1.28776	0.073833	0.055322	
4.33090	1.00000	30	1.48171	0.073833	0.054083	
2.66887	2.00000	19	1.73005	0.073833	0.051854	
1.38325	3.00000	12	2.05489	0.073833	0.047761	
0.58097	4.00000	8	2.46256	0.073833	0.041177	
0.20362	5.00000	6	2.93531	0.073833	0.032690	
0.06073	6.04900	5	3.47375	0.073833	0.023536	

TC	NaCl			MgCl ₂		
	BO	BI	CP	BO	BI	Cp
60.0	0.093925	0.292232	-0.001642	0.332332	1.858625	0.002042
CNA	CMG	NC	PHI	PO	PW	
6.34502	0.00000	1	1.27982	0.199395	0.148815	
4.50058	1.00000	26	1.45623	0.199395	0.145539	
2.86127	2.00000	18	1.68002	0.199395	0.139839	
1.56373	3.00000	12	1.97121	0.199395	0.129622	
0.71255	4.00000	8	2.33693	0.199395	0.113305	
0.27738	5.00000	6	2.76241	0.199395	0.091945	
0.09892	6.00000	5	3.22349	0.199395	0.069304	
0.06363	6.41700	4	3.42205	0.199395	0.060379	

TC	NaCl			MgCl ₂		
	BO	BI	CP	BO	BI	Cp
80.0	0.098786	0.308171	-0.002744	0.321541	1.990482	0.000693
CNA	CMG	NC	PHI	PO	PW	
6.49819	0.00000	1	1.26317	0.473871	0.352547	
4.68793	1.00000	22	1.42437	0.473871	0.344938	
3.06404	2.00000	17	1.62718	0.473871	0.332091	
1.75434	3.00000	12	1.88964	0.473871	0.309547	
0.85902	4.00000	8	2.21911	0.473871	0.273832	
0.36722	5.00000	6	2.60331	0.473871	0.226558	
0.14578	6.00000	5	3.01963	0.473871	0.175192	
0.06054	6.93100	4	3.42141	0.473871	0.130561	

TC	NaCl			MgCl ₂		
	BO	BI	CP	BO	BI	Cp
100.0	0.101196	0.324968	-0.003542	0.311302	2.144578	-0.000413
CNA	CMG	NC	PHI	PO	PW	
5.67653	0.00000	1	1.24004	1.013432	0.752043	
4.89263	1.00000	19	1.38786	1.013432	0.752043	
3.27865	2.00000	15	1.57237	1.013432	0.710089	
1.95632	3.00000	11	1.80986	1.013432	0.665194	
1.02062	4.00000	8	2.10761	1.013232	0.594644	
0.47405	5.00000	6	2.45549	1.013432	0.500502	
0.20689	6.00000	5	2.83265	1.013432	0.396003	
0.08928	7.00000	4	3.22250	1.013432	0.296365	
0.05143	7.66600	4	3.48486	1.013432	0.237652	

TC	NaCl			MgCl ₂		
	BO	BI	CP	BO	BI	Cp
120.0	0.101817	0.342622	-0.004096	0.301605	2.320913	-0.001319
CNA	CMG	NC	PHI	PO	PW	
6.87911	0.00000	1	1.21195	1.985201	1.470096	
5.11575	1.00000	16	1.34781	1.985201	1.439711	
3.50725	2.00000	14	1.51610	1.985201	1.391323	
2.17142	3.00000	11	1.73154	1.985201	1.309312	
1.19814	4.00000	8	2.00122	1.985201	1.181397	
0.59887	5.00000	6	2.31687	1.985201	1.009687	
0.28415	6.00000	5	2.65954	1.985201	0.815518	
0.13414	7.00000	4	3.01281	1.985201	0.625846	
0.06480	8.00000	4	3.36785	1.985201	0.459191	
0.03086	9.07400	3	3.74689	1.985201	0.314753	

TC	NaCl			MgCl ₂		
	BO	Bl	CP	BO	Bl	Cp
140.0	0.101113	0.361133	-0.004455	0.292454	2.519489	-0.002057
CNA	CMG	NC	PHI	PO	PW	
7.10697	0.00000	1	1.17983	3.612707	2.670699	
5.35963	1.00000	13	1.30489	3.612707	2.616782	
3.75264	2.00000	12	1.45860	3.612707	2.533438	
2.40195	3.00000	10	1.65431	3.612707	2.394230	
1.39293	4.00000	8	1.89890	3.612707	2.178518	
0.74287	5.00000	6	2.18573	3.612707	1.887598	
0.37941	6.00000	5	2.49776	3.612707	1.553248	
0.19370	7.00000	4	2.81900	3.612707	1.219322	
0.10161	8.00000	4	3.14012	3.612707	0.918765	
0.05550	9.00000	3	3.45690	3.612707	0.667686	
0.03857	9.64100	3	3.65681	3.612707	0.534709	

TC	NaCl			MgCl ₂		
	BO	Bl	CP	BO	Bl	Cp
160.0	0.099410	0.380501	-0.004656	0.283849	2.740303	-0.002656
CNA	CMG	NC	PHI	PO	PW	
7.36272	0.00000	1	1.14412	6.177969	4.560694	
5.62746	1.00000	11	1.25933	6.177969	4.470882	
4.01818	2.00000	10	1.39983	6.177969	4.336270	
2.65082	3.00000	9	1.57772	6.177969	4.114403	
1.60694	4.00000	7	1.79968	6.177969	3.772468	
0.90763	5.00000	6	2.06055	6.177969	3.309456	
0.49469	6.00000	5	2.34517	6.177969	2.769613	
0.27041	7.00000	4	2.63816	6.177969	2.219347	
0.15224	8.00000	3	2.92982	6.177969	1.712855	
0.08950	9.00000	3	3.21543	6.177969	1.279659	
0.05528	10.00000	3	3.49294	6.177969	0.928894	
0.04405	10.51300	3	3.63186	6.177969	0.780094	

TC	NaCl			MgCl ₂		
	BO	Bl	CP	BO	Bl	Cp
180.0	0.096930	0.400727	-0.004729	0.275790	2.983357	-0.002135
CNA	CMG	NC	PHI	PO	PW	
7.65033	0.00000	1	1.10482	10.020895	7.390049	
5.92344	1.00000	9	1.21101	10.020895	7.248264	
4.30789	2.00000	9	1.33949	10.020895	7.042587	
2.92132	3.00000	8	1.50115	10.020895	6.707807	
1.84261	4.00000	7	1.70257	10.020895	6.193929	
1.09516	5.00000	6	1.93990	10.020895	5.495378	
0.63223	6.00000	5	2.19982	10.020895	4.670257	
0.36691	7.00000	4	2.46772	10.020895	3.813160	
0.21953	8.00000	3	2.73364	10.020895	3.007512	
0.13733	9.00000	4	2.99239	10.202895	2.303271	
0.09043	10.00000	4	3.24156	10.020895	1.719754	
0.06287	11.00000	4	3.48010	10.020895	1.255903	
0.04620	12.00000	4	3.70751	10.020895	0.899417	
0.03843	12.70800	4	3.86166	10.020895	0.702633	

TC	NaCl			MgCl ₂		
	BO	Bl	CP	BO	Bl	Cp
200.0	0.093821	0.421810	-0.004699	0.268276	3.248651	-0.003513
CNA	CMG	NC	PHI	PO	PW	
7.97501	0.00000	1	1.06150	15.537251	11.452687	
6.25258	1.00000	8	1.15942	15.537251	11.238879	
4.62627	2.00000	8	1.27690	15.537251	10.939445	
3.21744	3.00000	7	1.42376	15.537251	10.457770	
2.10305	4.00000	6	1.60643	15.537251	9.720448	
1.30802	5.00000	5	1.82228	15.537251	8.713937	
0.79467	6.00000	4	2.05979	15.537251	7.510679	
0.48614	7.00000	3	2.30523	15.537251	6.238519	
0.30660	8.00000	4	2.54854	15.537251	5.018749	
0.20217	9.00000	4	2.78405	15.537251	3.930486	
0.14039	10.00000	4	3.00898	15.537251	3.009547	
0.10302	11.00000	4	3.22204	15.537251	2.260895	
0.08001	12.00000	4	3.42262	15.537251	1.671350	

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APPENDIX D. PERTINENT SI UNITS AND CONVERSION FACTORS^{*}

Table D.1. Units

Quantity	SI unit	SI symbol	Formula
Length	Meter	m	
Mass	Kilogram	kg	
Thermodynamic temperature	Kelvin	K	
Amount of substance	Mole (g-mole)	mol	
Time	Second	s	
Absorbed radiation dose	Gray	Gy	J/kg
Activity of a radio-nuclide	Becquerel	Bq	
Area	Square meter		m ²
Energy	Joule	J	N·m
Force	Newton	N	kg·m/s ²
Power	Watt	W	J/s
Pressure	Pascal	Pa	N/m ²
Volume	Cubic meter		m ³

^{*} Information taken from the American Society for Testing and Materials, *Standard for Metric Practice*, ASTM E 380-76, Philadelphia, PA, 1976.

Table D.2. Conversion of units

To convert from	to SI unit	multiply by
Length		
foot	m	3.048 E-01
inch		2.540 E-02
Area		
acre	m ²	4.047 E+03
foot ²		9.290 E-02
inch ²		6.452 E-04
Volume		
foot ³	m ³	2.832 E-02
Mass		
pound-mass (lbm avoirdupois)	kg	4.536 E-01
tonne (metric ton)		1.000 E+03
Energy		
British thermal unit	J	1.055 E+03
calorie		4.187 E+00
watt-second		1.000 E+00
Force		
dyne	N	1.000 E-05
Pressure and stress		
atmosphere (normal)	Pa	1.013 E+05
bar		1.000 E+05
psi		6.895 E+03
Radiation		
absorbed dose		
energy (rad)	Gy	1.000 E-02
activity (curie)	Bq	3.700 E+10

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