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Reactor Chemistry

Radiolysis and Hydrolysis in Salt-Mine-Brines

G. H. Jenks

MARCH 1972

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Summery

We made a detailed review and a salysis of literature information bearing on the radiation and thermal chemistries of the salt and brines within the vicinity of a buried waste can in a salt-mine, high-level, waste repository. The objectives were to identify the final radiolysisand thermal reaction-products and to estimate the amounts formed and released into the spaces around a can.

Important radiolysis products include Π_2 , O_2 and possibly ClO_3^- , and BrO_3^- . Nost of the ClO_3^- and ErO_3^- vill decompose to balides and O_2 at the high temperatures around a can; $Mg(BrO_3)_2$ if present may give rise to some Br_2 . Rearly all of the H_2 , and the accompanying oxidized species, are formed within the migrating brine inclusions by the radiations absorbed within the brine and by dissolution of the interstitial chlorine and trapped electrons from the irradiated solid salt. The brine is rich in N_6Cl_2 (2.3 to 3M), and hydrolysis of the M_6Cl_2 around a can will produce BC1.

No possibly-serious problems arising from radiolytic or thermal effects in the repository were recognized which couldn't be counteracted by some modification of the design or operation of the repository. However, the possible effects have not been completely evaluated. The repository project is planning or is presently conducting additional work in a number of additional areas including work in brine migration and radiolysis and radiation damage in the salt. The results of this work will help in evaluating the amounts and the effects of radiolysis, hydrolysis and corrosion products.

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Radiolysis and Hydrolysis in Salt-Mine-Brines

G. H. Jenks

1. Introduction

Salt deposits of the type to be used for radioactive vaste disposal contain a small volume-fraction of brine-inclusions (~ 0.5%). Some brine from these inclusions will be on the surfaces of the crushed salt around a can at the time of burial, Fig. 1. Additional brine will enter the open and unconfined spaces in the crushed salt region after burial due to the migration of the inclusions which takes place in the presence of thermal gradients in the salt, and due to the salt-fracture which takes place at high temperatures starting at about 250° C.

The brine, vapors and any salts precipitated from the brine till be exposed to high γ -ray intensities and to high temperatures, Table 1. Accordingly, they will be subject to radiation decomposition and to changes in composition brought about thru thermally-induced reactions.

I have reviewed and analyzed pertinent theoretical and experimental information with the objectives of identifying possibly bothersome decomposition products and of obtaining estimates of rates of formation of these within the spaces aroun: the can. Results of this work are summarized below and are presented in detail in Appendixes 1-7. The arrangement of the presentation is set forth in the Table of Contents.

- 2. Thermal and Radiation Chemistries of Exposure System
 - 2.1 Composition of Encapsulated Brine

Holser" reported experimental values (Table 1.1) for the ratios of Mg, Br, SO4 and Ca to Cl in the brine inclusions in salt from the

ABrine is released from the cavities by crushing the salt.

^DThe fracture of the salt at high temperature is thought to be a result of the high vapor pressure of water within the brine inclusion and of strain due to the thermal expansion of liquid within cavities. See Appendix 1.



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Fig. 1 - Waste Container in Backfilled Hole

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TABLE 1.1	
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Illustrative Values for Dose Rates, Doses and Temperatures for Waste Cans Containing 10-Year Aged Wastes; Midplane Values^A

2 kW	5 kW
2 X 10 ⁵	5 × 10 ⁵
10 ⁵	2.5 × 10 ⁵
4 X 10 ¹⁰	1011
8 X 10 ¹⁰	2 × 10 ^{1 1}
>250	>340
(25y)	(ly)
240	>280
	2 kW 2 X 10 ⁵ 10 ⁵ 4 X 10 ¹⁰ 8 X 10 ¹⁰ >250 (25y) 240

^BFrom information in Refs. 2 and 3.

•

Carey Mine at Hutchinson, Kansas, and from a core from the Naval Air Station at the same location.^B He did not report any ionic concentrations, but he stated that his results showed that the brine inclusions were formed by the evaporation of sea water and that the concentration factor was about 60.

Using Holser's data and interpretations together with data on the concentration of K in sea water after concentration⁵ by 60X and on the solubility of NaCl in MgCl₂ solutions, 6,7 I deduced that the composition of the brine is within the following range of compositions.

Ion	Holerity
Ng	2.3 to 3
κ	0.4
Na	2 to 1
Cl	7 to 7.5
Br	0.05
pH	Slightly basic

2.2 G-Value for H₂ in Brine

The only known reaction by which radiolytic H_2 is removed from vater or from chloride solution is,

$$OH + H_2 \rightarrow H + H_2O$$
 (2.17)

 $k = 4.5 \times 10^7 \text{ M}^{-1}$, sec⁻¹ at 25°C in vater.

The rate of buildup of dissolved H_2 in the brine as well as the steady state concentration will also depend importantly upon values of g'(OH) and g'(H₂)^I. They will also depend importantly upon the occurrence of

SAt room temperature, Ref. 8. The (H⁺) at elevated temperatures will be several hundred μ molar due to hydrolysis of MgCl₂ in solution.⁹ ^GThe number of a species which appear as a final product per 100 ev of

absorbed energy is symbolized in this paper by $G(H_2)$, $G(O_2)$, etc. See Appendix 2.

¹The number of a species which appears in homogeneous distribution in the initial radiation-decomposition per 100 ev of absorbed energy is symbolized in this paper by $g'(H_2)$, $g'(H_2)$, etc.

These deposits are thought to be substantially the same as those at Lyons, Kanses.

^bHolser further stated that the brine inclusions are probably uncharged samples of bitterns left behind in Permian time.

scavenger-type reactions in which CH is removed from solution before it can react with H_2 , and upon whether H_2 escapes from the irradiated solution and thus escapes the radiation-induced back reaction within the solution.

2.1.1 Value of $g'(H_2)$

Reported information on $G(H_2)$ in chloride solutions indicates that $g'(H_2)$ will be about 2.1 in the brine at 25°C. On the basis of certain theoretical considerations and on the basis of experimental information relating to the effects of changing temperature on g'-values in water, I believe that $g'(H_2)$ in the brine will not change substantially with temperatures to 250°C.

Some additional generation of H_2 within the encapsulated brine may result from the dissolution of irradiated salt which takes place during migration of the brine. It is possible that at certain temperatures the amount of H_2 from this source will exceed that generated by direct absorption of radiation at $G(H_2)$ equal to 2.1 (Section 4).

2.2.2 Value for g'(OH)

The radiation chemistries of vater and aqueous solutions are usually described in terms of the spur diffusion model. Several pairs of radicals or ions (primarily e_{aq}^{-} , OH and H_3O^4 in pure vater) are formed in small, isolated volume elements (spurs) in the initial radiation process. Species vithin the spurs interact as they diffuse into homogeneous distribution, and these interactions result in the reformation of vater and in the formation of other molecular products. In pure vater under γ -irradiation, the decomposition products which appear in homogeneous distribution are principally,

 e_{a0} , OH, H₂, and H₂O₂.

The H_2O_2 and H_2 are formed, primarily, by the following reactions,

$$c_{aq}^{-} + c_{aq}^{-} + 2H_2 0 \rightarrow H_2 + 20H^{-},$$
 (2.4)

 $OH + OH \rightarrow H_2O_2$. (2.5)

Important water-reformation reactions are,

$$e^{-}_{-} + H_2O_2 \rightarrow OH + OH^{-}$$
(2.6)

$$e^{-}$$
 + OH \rightarrow OH⁻ (2.7)

$$OH^{-} + H_3 O^{+} - 2H_2 O.$$
 (2.8)

Reactive solutes at high concentrations can react with radicals within the spurs and thus cause changes in g'-values from those in pure water and, at the same time, cause the formation of additional g'-species.

It is known that Cl_2 is formed during γ -irradiation of concentrated, neutral, chloride solutions. According to the spur diffusion model, most of the Cl_2 is formed from Cl^0 which is formed within spurs by reaction 2.13,

> $OH + C1^{-} + H_{3}O^{+} - C1^{0} + 2H_{2}O$ (2.13) k = 1.7 x 10¹⁰ H⁻², sec⁻¹ at 25^oC

The removal of OH from the spur by reaction 2.13 would presumably cause reductions in g'(OH) and $g'(H_2O_2)$ from those in pure water. It would also promote increases in $g'(e_{aq})$ and $g'(H_2)$ providing that the new products of the spur reactions (i.e., Cl_2^- and possibly Cl_2) do not react as readily with e_{aq}^- as do OH and H_2O_2 in the pure water system. Increases in $g'(H_2)$ in chloride solutions have been indicated by experimental data as discussed under, a, above.^A Decreases in $g'(H_2O_2)$ have also been observed, Fig. 2.2. It is likely that g'(OH) in chloride solution: is substantially below that in pure water.

2.2.3 Scavenger Reactions

It is well known^{10,11} that Br⁻ is a scavenger for OH radicals. The scavenger reactions are comprised of reaction 2.18 followed by a reaction between some form of Br⁰ and a reducing radical to reform Br⁻.

$$GH + Br^{-} \rightarrow Br^{0} + OH^{-}$$
 (2.18)
 $x = 1 \times 10^{9} H^{-1}, \ sec^{-1} \ at \ 25^{\circ}C$

^BHowever, the extent of the increase in $g'(H_2)$ is not readily explained on the basis of the spur diffusion model (Section 2-2). Chloride ion is also an effective scavenger in acid solutions. Thus at 10^{-3} M H⁺, for example, reaction 2.13 has an equivalent bimolecular rate constant for reaction between Cl⁻ and OH of 1.7 x 10^7 y⁻¹, sec⁻¹.

On the sole basis of the expected scavenger action of .05 M Br, it can be confidently assumed that little recombination of H_2 within the brine will take place until (H_2) exceeds about .05 M.

2.2.4 Escape of Radiolytic Gases from Encapsulated Brine

Radiolytic gases will escape from the brine into a gas-vapor phase when the pressure of dissolved gases plus water vapor exceeds the over-pressure. Most of the brine cavities are completely filled with liquid so that no gas-vapor phase can form unless cavity-expansion takes place. In this contained environment, the pressure from dissolved radiolytic gases could be substantial. For example, with 1M H2 the vater vapor-dissolved gas pressures could exceed 19,000, 13,000 and 9,000 psi at 150, 200 and 250°C, respectively.^D The bedded salt will undergo plastic deformation (creep) under stress, and the case of deformation increases with temperature. 13,14 Also, the salt at the edge of the hole will be unsupported until consolidation takes place. After consolidation is complete (including that of the salt in the room above the hole) the pressure on the salt will be about 1000 psi. Considerations of these several factors led me to postulate that cavity-expansion will take place before the concentration of dissolved H₂ reaches 1M. Recently-reported information¹⁴ on cavity expansion in NaCl and KCl lends support to this postulate.

It can be shown that radiation induced recombination of H_2 and O_2 in the gas-vapor phase would be slow compared with the rate at which the gases are formed in solution at $G(H_2)$ equal to 2.1. Accordingly, the escape of gases into a gas phase would effectively remove them from any recombination-action.

^aThe (H⁺) within encapsulated brine at elevated temperatures will be several hundred μ molar² and scavenging of OH by Cl⁻ will be of significance.

^bI assumed that gas solubility in the brine is the same as that in water.¹² Also, I assumed that the radiolytic H_2 is balanced by radiolytic O_2 .

Since this report was drafted, I learned of reported¹⁵ experimental and theoretical evidence that bubbles which contain both gas and liquid phases will migrate in a reverse direction, i.e., down a temperature gradient. The possible significance of this effect in the waste repository will be investigated and reported in a later paper.

2.2.5 Conclusions

I concluded that $g'(H_2)$ may be as high as 2.1 in the brine at all temperatures up to 250°C. The value of $G(H_2)$ will, of course, be equal to that of $g'(H_2)$ unless recombination of the H_2 takes place.

On the sole basis of the expected scavenger action of .05M Br⁻, it can be confidently assumed that little recombination of H₂ within the brine will take place until (H₂) exceeds 0.05M. In addition to this Br⁻effect, it is possible that a low value of g'(OE) would contribute to an inhibition of recombination. Also, it is conceivable that Cl⁻ is an effective scavenger for OH in neutral solutions at high temperatures. Escape of radiolytic gases from encapsulated brine (and from any significant recombination action) probably will take place at (H₂) less than about IN. Taking all possible effects into account, I concluded that $G(H_2)$ could equal g'(H₂) at all exposure times and temperatures both in the unconfined brines and in the encapsulated brine. The concentration of H₂ within the encapsulated droplets reaching the open spaces around a can would be limited to < IN if formation of two-phase droplets takes place at (H₂) <IN; droplets containing the gas phase would migrate away from the can.

2.3 Identities and G-Values of the Oxidized Species formed Radiolytically Within the Brine

2.3.1 Theory

Formation of reduced species in the radiolysis process must be balanced by formation of a stoichiometrically equivalent number of oxidized species. Hydrogen, H₂, is the only reduced species which would appear as a final product in the brine solutions. The possible oxidized species include O_2 , H₂O₂, and chlorine species with oxidation

-See Appendix 4.

numbers > -1. These statements are expressed by the following relationship between G-values when it is assumed that Cl_2 and ClO_3^- are the only final chlorine species,

$$G(H_2) = 2G(O_2) + G(H_2O_2) + G(Cl_2) + 3G(ClO_3).$$
(4.1)

The g'-products would include radicals and Cl₂ as set forth in the following oxidation-reduction balance relationship,

$$2g'(H_2) + g'(e_{aq}) + g'(H) = g'(OH) +$$

$$2g'(H_2O_2) + g'(Cl_2) + 2g'(Cl_2)$$
(4.2)

2.3.2 Experimental Information Regarding Identities

a. Neutral Chloride Solutions; < 35°C; < 5H Cl⁻

Oxygen was the only oxidized species which appeared as a final product (See Fig. 2.3).

Considerations of the known g'-values for Cl_2 , H_2 and H_2O_2 led me to conclude that the absence of Cl_2 and the presence of O_2 among the final products must be accounted for by assuming the occurrence of reactions between Cl_2 or HClO and H_2O in which H_2O is oxidized to O_2 and the chlorine species are reduced to Cl^- . The probable reactions are of the types which have been proposed by others to explain photolytic behavior of chlorine solutions,

> $Cl_2 + H_2O \implies Cl^- + H^+ + HClo$ (4.6) $Cl_2^- + HClO \implies H^+ + Cl^- + ClO^0$ (4.7)

$$(12 + H010 - H + 201 + 010^{\circ}$$
 (4.7)

$$C10^{\circ} + HC10 - H^{+} + C12^{-} + O2$$
 (4.8)

b. pH 11 Chloride Solutions; < 35°C; < 5N C1⁻

Values of $G(Cl_2)$ in solutions of KCl, MaCl and BaCl₂, Fig. 2.11, were only slightly less than the expected values on the basis of the values of $G(H_2)$ in Fig. 2.3.

The occurrence of appreciable values of $G(H_2)$, at this high pH might be explained by assuming that Cl_2 is quickly hydrolyzed to ClO^{-1} and that this negatively charged species does not react with Cl_1^{-1} in the chain-step reaction comparable to reaction 4.7.

c. Acid Chloride Solution; < 35°C; up to 11M Cl⁻

The occurrence of some Cl_2 as a final product has been reported. Also, it can be inferred from reported data that ClO_3^- is formed in 10M LiCl, zero to 0.4M HCl, under *a*-irradiation.

The occurrence of Cl_2 in acid solution might be explained by assuming that chain reactions analogous to reactions 4.7 and 4.8 are required to effect reduction of Cl_2 by H_2O in acid solutions, and that these reactions are increasingly inhibited with increasing concentrations of acid and of chlorides,

$$Cl_2 + Cl_2 + H_2 0 \rightarrow 2H^+ + 3Cl^- + Cl0^0$$
 (4.13)

$$C10^{0} + C1_{2} + H_{2}0 \rightarrow 2H^{+} + 2C1^{-} + C1^{0} + O_{2}$$
 (4.14)

Chlorate can be formed from Cl₂ thru reactions involving radicals;¹⁶ it can also be formed from Cl₂ by hydrolysis, e.g.,

$$2C10^{-} \rightarrow C10_2^{-} + C1^{-}$$
 (4.21a)

$$C10_2^{-} + C10^{-} \rightarrow C10_3^{-} + C1^{-}$$
 (4.21b)

Chlorate formation by hydrolysis in chlorine solutions occurs at appreciable rates at temperatures above 50°C.

2.3.3 Predicted Identities of Oxidized Species in Encapsulated Brine

I concluded that it is very likely that the only oxidized species vill be O_2 and/or ClO_3^- and BrO_3^- . The reactions between Cl_2 (and Br_2) with water would limit the concentration of Cl_2 and Br_2 to low values. Reaction 4.21 would be of some importance in the conversion of Br_2 to BrO_3^- ,

 $Br_2 + 2ClO_3 \rightarrow 2BrO_3 + Cl_2$ (4.21)

2.3.4 Predicted Identities and Amounts of Oxidized Species in Brine Around Can at Start of Exposure

The products of radiolysis of unconfined brine around the can may differ from those of the encapsulated brine because any gaseous radiolytic products will readily escape from solution. I concluded that the possible radiolytic products under these conditions include Cl_2 , Br_2 , ClO_3^- , BrO_3^- , ClO_2 , ClO_4^- and ClO_2^- alorg with H_2 and O_2 . The Cl_2 would react radiolytically to form HCl within the vapor phase. The ClO_2 would decompose thermally or by reaction with reducing agents including the metal can.

It can be shown that the amounts of these products which will be generated before brine-boiling-temperatures are reached will be negligibly small with a 5 Kw can. With a 2 Kw can, it is possible that the rate of H₂ generation would be .8 mole per year for a period of about 0.1 year after burial and then .3 mole per year or less for a period of 0.5 years or less. These production rates are much less than the maximum rate at which H₂ may appear around a can as a result of migration of brine to the can (Table 4). The maximum amounts of O_2 , ClO_3^- , BrO_3^- and $Cl_2(HC1)$ would also be well below those associated with the migrating brine.

2.4 Hydrolysis of MgCl₂ to Form HCl²

Magnesium chloride reacts with water (including water of hydration) or steam at high temperature to form HCl. The probable reactions are,

$M_{\rm gCl_2} + H_20 \rightleftharpoons M_{\rm gOHCl} + HCl$	(5.1)
$2M_{gOHC1} \Leftrightarrow M_{gC1_2} + M_{gO} + H_2O$	(5.2)

From the available fragmentary data on equilibria in these reactions, I concluded that 50 to 65% of the MgCl₂ around the waste can will react sooner or later to form HCl providing that the location of the MgCl₂ is such that the HCl moves away from the MgCl₂.

3. Rates of Introduction of Migrating Brine Into Open Spaces Around Can

I made estimates of the brine inflow to three different waste can systems which are presently under consideration and for which temperature-time-position information was available. The reference dimensions for these cans are shown in Fig. 1. Other characteristics of these systems are summarized below.

^ASee Appendix 5. ^bSee Appendix 6.

	Case C-1	Case B-2	Case C-2
Heat output at burial Age of waste at burial Layout in mine	2 Kw 10 years Cans on 22 ft centers. Two rows of cans per room.	5 Kw 10 years Cans on 27 ft centers.	5 Kw 10 years Cans in one row in middle of 30 ft room; 42 ft between cans.

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Temperatures for Cases C-1 and C-2 were available for times out to 50 years-three dimensional calculations.²

Temperatures for Case B-2 were available for times out to 5 years and for the horizontal midplane only-two dimensional line source calculations.¹⁷

The method which I employed in making the estimates of brine inflow was basically the same as that of Bradshaw <u>et al.</u>^{18,19,19} However, my method differed in two important respects; (1) I used the more conservative estimates of $f(T)^{\circ}$ which are shown in Fig. 6.1, and (2) I assumed that the salt fractured and released brine at high temperatures starting at 250°C,²⁰ and that the edge of the open spaces around the can followed the 250°C front within the salt. In the event that the salt did not reach 250°C as in Case C-1, I assumed that the edge of the open spaces remained at the original distance of 5 inches from the center of the can.

I also assumed that the inflow at midplane conditions is representative of that at all elevations of the can. This assumption made the estimated values of total brine inflow too high because of the lower temperatures and migration rates at the ends of the cans. However, for Case C-1, I could show that the error introduced in this amounted to only 5 to 10%.

ⁿThe results of temperature calculations for this case became available after this report was drafted.

DBradshaw et al., also used the can dimensions shown in Fig. 1.

 $[\]mathcal{L}_{f}(T)$ represents the migration rate per unit temperature gradient at the site of the cavity.

Plots of estimated total brine inflow vs time after burial are shown in Figs. 6.13, 6.14, and 6.17 for Cases C-1, B-2 and C-2, respectively. Inflow rates vs time are shown in Figs. 6.15 and 6.15. Total brine inflows at some representative times were: 0.6, 8, 16, 22 and 30 liters at 1, 10, 20, 30 and 50 years after burial for Case C-1, and 7, 16, 24, 39 and < 53 liters at 1, 6, 10, 20 and 50 years, respectively, for Case C-2. The differences between results for Cases C-1 and C-2 stemmed from the differences between temperature and temperature gradients and salt fracturing in the two systems.

The results of my estimates of brine inflow differ from the commonly-quoted estimates of Bradshav et al., (3 to 30 liters over a period of 20 to 30 years with zero inflow thereafter). The difference between the present and previous results can be ascribed, in part, to my more conservative estimates of f(T) and to my accounting for brine release by salt fracture. Also, it is probable that part of the differences is due to differences between the precision and appropriateness of the calculated temperatures which were employed. Thus, the previous estimates were based on considerations of a system of cans loaded with 3.66 Kw of 3 1/3 year aged wastes and spaced on 10 ft centers. The peak temperature between cans with this system was 380°C. The results of these considerations were extrapolated to the systems of interest which were those in which the distance between cans was increased so that the peak temperatures was only 200°C. No accounting for brine released by salt fracture was made in the previous estimates. 4. Effects of Migration of Brine Filled Cavities on Radiolysis of

Brine and on Amounts of Radiation Damage in Salt

4.1 Introduction

Radiation damage produced by γ -rays in MaCl (and in other alkali halides) is comprised of displaced atoms and of trapped electrons and boles. Chemically, the trapped electrons and holes are reducing and oxidizing agents, respectively, and dissolution of radiation-damaged NaCl results in the injection of oxidizing and reduction agents into the aqueous solution. ²¹⁻²³ The oxidizing agent entering solution corresponds to Cl₂ and/or Cl₃ while the reducing agent can be treated as a hydrated electron, e_{aq}^{A} . The thermal-gradient-induced migration of brine-filled cavities thru salt takes place by dissolution of salt at the higher temperature face of a cavity and precipitation of salt at the lower temperature face.^{6.1} Accordingly, the migration of these cavities thru radiation-damaged salt will result in the injection of Cl_2^{-} and/or Cl_3^{-} and e_{aq}^{-} into the brine, and the radiochemical results of the dissolution is qualitatively the same as the results of absorption of radiation by chloride ions in solution (Appendix 2). Also, the migration will accomplish some annealing of the radiation damage since the precipitated salt should be more or less free of damage.

The rate, ζ , of introduction of trapped electrons and holes into a migrating brine droplet will depend upon several parameters as shown approximately by the relationship, Eqn. 1,

$$\zeta = 2000 \frac{mC}{\chi} (mole, l^{-1}, yr^{-1})$$
 (1)

where

- m = velocity of migration of droplet (cm, yr⁻¹),
- X = dimension of droplet | to thermal gradient (cm),
- C = concentration of pairs of trapped electrons and holes in that salt lying in front of the migrating droplet (mole, g^{-1}).

A radiation annealing constant, k, can be written as in Eqn. 2 if it is assumed that the cavities are uniformly dispersed as cubes of dimension, X, and that the amounts and uniformity of this heterogeneous annealing suffice to approximate a homogeneous process,

$$k = \frac{mb}{X} (yr^{-1}), \qquad (2)$$

where b is the fraction of the salt which is occupied by brine.

The reducing agent might be thought of as Na^0 . However, reaction of Na^0 with H₂O would probably produce e_{aq}^{24} as an intermediate which could then react to form H₂ and OH⁻ or undergo other reactions depending upon the solution composition.

$$Na^{0} + H_{2}O \longrightarrow Na^{+} + e^{-}aq \qquad (8.1)$$

$$e^{-}aq + e^{-}e^{-}q \longrightarrow H_{2} + 2OH^{-} \qquad (2.4)$$

Discussions are presented below of information bearing on these parameters and of estimates of the rates of injection of trapped electrons and holes into migrating brine.

4.2 Concentration of Trapped Electrons and Holes in Salt

The radiation behavior, with respect to accumulation of trapped electrons and holes, of NaCl at the high temperatures and doses which will prevail in the waste repository has not been completely established. It has been suggested that the concentrations of defects which can be accumulated at certain high temperatures exceed those which can be accumulated at normal temperatures.²² Also, it is believed that colloids, rather than F-centers, are the predominant trappedelectron-defects which are present in NaCl after irradiation at certain high temperatures.²³

Some of the available quantitive data relating stored energy (or concentration of defects) and γ -ray or electron dose at high temperatures are plotted in Fig. 2.^{a,b} Other high temperature data obtained with samples of salt which were irradiated in the Project Salt Vault experiment are listed in Table 2. Some of the available data from lower temperature studies (< 100°C) are included in Fig. 2. Ordinate scales show values both for stored energy and for concentration of pairs of trapped electrons and holes. The values for defect concentrations were obtained from those for stored energy, or vice versa, using a conversion factor of 5.5 ev per defect.^C Information

Refs. 3, 21, 23, 25.

^bThe rock salt sample which gave 14 cal/g (Fig. 2) by solution calorimetry gave 21 ± 6 cal/g by scanning differential calorimetry. ^CRecent theoretical considerations by Schweinler²⁶ indicated that the stored energy per defect (displaced atom and vacancy pair) in NaCl is unlikely to exceed 5.5 to 6 ev. Experimental values of 9.2 and 12.4 ev per F center have been reported, respectively, by Phelps and Pearlstein²⁷ and by Bunch and Pearlstein.²⁸ The former workers employed solution calorimetry, and they added 3.6 ev to the measured value of 5.6 ev on the unverified assumption that I_2 and OC1 were formed upon dissolution of the defects. The latter workers heated the irradiated samples to 400°C and measured the heat released by calorimetry. They employed a plot of stored energy vs N_F + 2M_M in evaluations of their data, and they fitted the data with a straight line. However, they mentioned that the data could have been fitted also with a curve concave upward. In the latter case, their energy per F center could be substantially less than the reported 12.4 ev.





Sample Source	Exposure Tump. Final 60 Days ^e (°C)	Average Dose Rate (N red/hr)	Total Dose (M red)	Stored Barry (Cal/g)	Defect Conc ^a (s mola/g)	Nethod	Juference
Bole 2 Core	1.00	0.080	600	.67 and .62 ⁴	5.0	Sola, Cal.	Mastroisesi et al.4
Bole 2 Core	145	0.065	450	.62 and .56	4.5	Sola, Cal.	Matroiani et al.
Role 6 Jore	180	0.080	600	1.2 and 1.6	10.5	Sola, Cal.	Martroiami et al.
Nole & Core	ບາ	0.01	83	1.1	4.5	Sola. Cal.	Mastroianni et al.d
Nele 4 Teraping-11 ft	360	0.095	700	6	4	DEA	Zeller et al.
Nole 4 Arraping-9.5 to 11 ft	145-200	0.08	600	0 + 0.2	•=•	Sola, Cal.	Somer et al."
Nelo 4 Seroping-11 ft	700 [°]	0.095	700	0 • 0.2	•••	Sola. Cal.	Senter et al.

Table 2. Stored Emergy in Salt Irradiated in Project Salt Yault

"Calvulated from stored emergy using 5.5 ev per defect.

"Movard Zeller, Gisela Dresshaoff and Marold Yarger, "Emergy Storage and Radiation Damage Rifects in Rocksalt," in final report, Geology and Rydrology of the Proposed Large, Kaness, Waste Repository Site, Compiled by E. E. Angino and V. V. Rashleton, University of Kaness, Center for Research, Inc., March 1971, Campter 3, p. 103.

J. O. Blancke, E. Sonder, et al., OPEL-DE-3403, June 1971. Average sample.

41. J. Mastrolanni and C. D. Ropp, Private communication, Oct. 22 and Nov. 8, 1971. The listed stored energy values were evaluated from the difference between the beats of solution of the irrediated samples and of pure unirrediated MaCl. Average sample.

The following regarding temperatures can be informed from information in Ref. 19, 1) Total time at temperature was about 570 days; 2) Temperatures at the edge of a hole at 200 to 400 days were 40 to 50°C below those at 570 days. Between 400 and 490 days the temperatures were intermediate between these at 400 and 570 days. Still lower temperature provalled prior to 100 days; 3) Balt temperatures away from the edge of the hole also changed during the 570 days exposures but the changes probably were consult loss than those at the edge of the hole.

f Sonder et al., 11sted this exposure temperature as 163-200°C. However, from information in Ref. 19, it can be inferred that the maximum temperature at the edge of the hole was 160°C.

Deplicate membes.

on the sample form, radiation exposure conditions, and methods of measurements are set forth in the legend in Fig. 2 and are listed in Table 2.

Consideration of these various data and of other information including that mentioned above led to the following conclusions regarding possible maximum concentrations of pairs of trapped electrons and holes in the waste repository salt.

a. The amounts of stored energy in the Project Salt Vault samples exceeded, by large factors, those expected for NaCl irradiated at comparable dose rates and doses but at lower temperatures (less than about 60° C). There are unexplained differences between the results of DTA and solution calorimeter measurements. There are also unexplained differences between the results of solution calorimeter measuremeasurements. There are also unexplained differences between the results of solution calorimeter measurements on samples exposed to presumably comparable conditions. The maximum experimental values for the Salt Vault samples are adequately represented by Eqn. 3,

$$C = 10^{-13} D,$$
 (3)

where D is the radiation dose, rad, and C was defined above.

b. There are some theoretical reasons for expecting that at saturation the number of defects will not exceed a few percent of the number of atoms in the salt crystal.^{3,A} The assumptions that saturation occurs at 1% defects (22 cal/g) and that Eqn. 3 is valid in the dose range below about 10^9 rads leads to Eqn. 4,

$$C = 1.7 \times 10^{-4} (1-c)$$
 (4)

"However, additional experimental information is needed to establish the actual defect concentration at saturation at the dose rates and temperatures which will obtain in the waste repository.

- c. The radiation and/or thermal annealing required to bring about the saturation indicated by Eqn. 4 would be greater than the migration annealing constant (Eqn. 2) unless the value of X is appreciably less than 1 mm. To be conservative, and for simplicity, I assumed that the droplets are about 1 mm in dimension and that migration annealing will be negligible.
- d. The data in Table 2 and the one 250°C datum point of Kubota's in Fig. 2 indicate that thermal annealing will limit the amount of energy storage in the salt mine to a few cal/g or less when the exposure temperature exceeds some value in the range 200 to 250°C.^A
- c. My earlier estimates of amounts of migration annealing and of the radiolysis caused by dissolution of trapped electrons and holes were based on the following assumed relationship between defect concentration and dose in the absence of migration annealing,

$$C = 3.2 \times 10^{-10} D^{\frac{1}{2}}$$
. (5)

The recent data and the interpretations discussed above indicate that this was not a conservative assumption for salt exposed within certain temperature ranges (say 130 to 160° C).

4.3 Values of Brine Migration Velocity

Brine inflow considerations (Section 3) for the 2 Kw can, Case C-1, indicated that the brine-migration-velocity, m, remains approximately constant over long periods of exposure; the velocity is about 6 cm per year after 1.7 year exposure, and 7.5 to 10 cm per year between exposure intervals of 3 and 30 years. Also, the volume of brine at the edge of the burial hole remains approximately constant at the initial value, 0.5 Vol \leq over long periods of exposure (50 years).

^AHowever, additional experimental information is needed to establish this for salt mine salt irradiated under waste repository conditions including conditions of light and moisture.

The similarly estimated values of m for the 5 Kv cans, Case C-2, are 15 cm/y during the first 20 years after burial and 6 cm/y between 20 and 30 years after burial.

4.4 Estimates of Rates of Injection of Defects into Higrating Brine

The steady state value of C from Eqn. 4 is 170 μ mole/g. Substituting this value in Eqn. 1,

$$\zeta = 2 \times 10^3 \frac{mC}{X} \tag{1}$$

with m and X equal to 6 cm/y and 0.1 cm, respectively, we have,

$$\zeta = \frac{(6)(1.7 \times 10^{-4})}{.1} 2 \times 10^{3}, \qquad (6)$$

or

$$\zeta = 20 \pmod{1^{-1}, yr^{-1}}.$$

For comparison with the rates at which chlorine is formed by direct absorption of radiation in the brine, I calculate that with $2g'(H_2) = g'(Cl_2^-) + 2g'(Cl_3^-) = 4.2$, and with dose rate = 8.8 x 10⁸ rad/yr (2 Kv can), the rate of formation of chlorine is 4.6 mole/ $\frac{1}{yr}$ (measured as Cl^0). Accordingly, the contribution from the salt could be several times that from direct absorption of radiation if it is assumed that all of the trapped electrons (or Ha⁰) react to form H₂ upon dissolution.

5. Amounts of MgCl₂ and Radiolytic H₂ Entering Open Spaces Around Can With Migrating Brine

Estimated rates at which MgCl₂ is introduced into the open spaces around a can with migrating brine in Cases C-1 and C-2 are plotted in Figs. 3 and 4. As indicated in the figures, the concentration of MgCl₂ in the brine was assumed to be 3 molar. Additional amounts of MgCl₂, about 1 mole in each system, would be associated with the crushed salt at the start and would be in the open spaces shortly after burial.

^BSee Appendix 7.









As discussed above, it is probable that the concentration of radiolytic H₂ within the brine will not exceed 1 molar. Assuming that this is the case, the rate of inflow of H₂ would not exceed one-third of that for MgCl₂. The plot for H₂ in Fig. 3 was made before this probable 1 molar limit for H₂ was recognized. The high initial rate of inflow of MgCl₂ shown in Fig. 4 resulted from the assumption that brine was released by high-temperature fracture of the salt (Section 3). The estimated rates of inflow of radiolytic H₂ in this case were less than 200 μ mole/hr during the first five years after burial. After this time, the estimated rates for H₂ would be about one-third of those for the MgCl₂.

6. Fates of Chlorates and Bromates in Spaces Around Can

Sodium and magnesium chlorates and sodium bromate decompose into perchlorates, halides, and oxygen at elevated temperatures. The perchlorates in turn, decompose into chlorides and oxygen. The temperatures around a can may be a little below those at which some of the pure compounds would decompose. However, the mixtures of salt which would be present around a waste can probably would decompose at the temperatures which prevail around a can. No chlorine would be expected from the decomposition.

Magnesium bromate decomposes into the oxide, oxygen and bromine. Accordingly, some bromine might be formed in the spaces around a can if bromates are, in fact, formed within the migrating brine. The maximum amount of Br_2 which could form at an assumed high brine inflow rate of 5l/y would be about 0.1 mole/y.

7. Radiolysis of Vapors Around Can

Formation of O_3 takes place in dry or moist air at normal temperatures. However, at low partial pressures of air, its rate of formation would be very low.²⁹ At high temperatures, any O_3 which might be formed radiolytically would be quickly lost by thermal decomposition and/or by reactions with other species which might be present. Accordingly, I believe that O_3 -formation will not be a problem in these systems.

^aSee Appendix 5.

Nitric acid is formed by irradiation of moist air, and its formation might continue in gas mixtures containing low partial pressures of O_2 and N_2 at elevated temperatures.³⁰⁻³² The presence of HCl vapor might affect the radiolysis of the moist air, but there is no information on this.

Assumed values of $G(O_3)$ and $G(HNO_3)$ are listed in Table 3 together with calculated values for the corresponding rates of formation of these species. The G-values refer to energy absorption in the gas-water vapor mixture. Temperatures > 100°C will be reached within a few hours after burial of the 5 Kv cans.

> Table 3. Rates of Formation of HNO₃ and O₃ in Crushod Salt at 5 x 10⁵ Rad per Hour

	Initial Co	onditions	At Temp with P _{(ai}	. >100°C <u>a</u> c) < .1 atm		
	G-value	Rate of Formation (u mole/hr)	G-value	Rate of Formation (u mole/hr)		
03	7	100	< 0.2	ع و >		
HNO3	1 to 3	15 to 40	l	15		

^AMixtures of water vapor and air. ^bOzone is thermally unstable as well as reactive at high temperatures. It is unlikely that O₃ will accumulate. ^cInitial void volume about 30 liters.

8. Significance of the Results of the Work Reported in this Paper to the Design and Operation of the High-Level Waste Repository

8.1 Introduction

Presented in Table 4 is a summary of my conclusions regarding the identities of the species which will enter the open spaces around a waste can and also regarding the maximum rates of introduction of these species. Active and/or noxious chemicals are included among the species, and their presence may influence the final design and operating procedures for the waste repository. Avenues of possible influence which should be or have been considered are discussed below.

<u>Bpecies</u>	Radiolysis product vithin encapsulated brine	Max. rate of appearance and max. period after burial		Balancing oxidized	Remarks	
H2		(mole/yr) Z	<u>(yr)</u> < 1	O ₂ , chlorates, bromates	Comparable rates for 2 and 5 Kw cans.	
H2	Radiolysis of solu- tion around can	.8 folloved by .3	.1 .5	O ₂ , Cl ₂ , Br ₂ , ClO ₂ , ClO ₃ ⁻ , BrC ₃	For 2 Kv cans. Insignificant period of time with 5 Kv cans because of rapid heat up.	
H2	Corrosion of can (50 mils/yr)	400	< 1		Assumed brine inflow rate of 7 for with all H_2O reacting with can.	
HCl	Hydrolysis of MgCl ₂	20	< 1		Assume brine inflow rate of 7 Ayr, 3M MgCl ₂ within brine, and 50% hydrolysis of MgCl ₂ .	
HNO3	Radiolysis of moist mixtures of M_2 and O_2	•50	<.1		Likely that all N ₂ will inve been expelled at < .lyr after burial	
O ₂ and other oxidized species	Radiolysis				To balance radiolytic H ₂ .	

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Table 4. Summary of Conclusions Regarding Identities of Species Appearing Around a Waste Can and Regarding Maximum Rate of Appearance

It can be noted here that the effects of the species in Table 4 on the design and operation of the waste repository have not been completely evaluated. However, we haven't yet recognized any possibly serious detrimental effect which couldn't be counteracted by some modification of the design or operation of the repository. Also, the repository project is planning or is presently conducting additional work in a number of different areas including work in brine migration, radiolysis and stored energy. The results of this work will help in evaluating the amount and the effects of the radiolysis, hydrolysis and corrosion products.

It should be emphasized that the rate values in the table are maximum values. The analyses in this report were aimed at providing conservative estimates. The actual rates of formation of a species are expected to be equal to or less than the value indicated in Table 4 and elsewhere in this report.

8.2 Reference Information

The following reference material is presented here for convenience in the following discussion.

Each room will be backfilled with crushed salt after completion of burial operations (backfilling of a section of a room after completion of burial operations in that section could also be done if desired).¹⁷

With 5 Kw cans, a total of 10 cans will be buried below a single room. The room volume per 5 Kw hole will be about 10^4 ft³.

The fraction of open spaces in the crushed salt backfill, as charged, is expected to range from about .27 for mixtures of fine and medium salt to about .37 for medium salt.³³ Diffusion thru beds of as-charged medium salt is expected to be about three times slower than thru free space.³³ Consolidation of the crushed salt backfill will take place with accompanying dimunition of the fraction of open

spaces and possibly of the gas transport capabilities. The times after burial at which the backfill within a hole will have been consolidated have not been established.

The lower ignition limit for mixtures of H_2 in air or oxygen is about 4 vol \$.³⁴ In mixtures of water vapor and H_2 and O_2 , the lower limit is about 15 to 20 vol \$ H_2 plus O_2 .³⁵ The size of the container affects the ignition limit in the latter mixtures under at least some conditions;⁶ at 200°C the explosive limit increases from about 15 vol \$ of 2 H_2 + O_2 to about 50 vol \$ as the ratio of surface area to gas volume increases from about 1 to 10 in.⁻¹.³⁶ The ratio of surface area to gas volume in the crushed salt will be about 200 or more per in., and it is likely that the lower ignition limits will exceed the 4 vol \$ mentioned above by substantial factors. However, experimental verification of this hypothesis would be required before use could be made of a given ignition limit in an engineering design. The upper limit of inflammability of H_2 -air mixture is 75\$ H_2 . That for H_2 - O_2 mixture is 94\$ H_2 .³⁴

The permissible concentration of HCl in the air within working areas is 5 ppm.

The corrosion of stainless steel at high temperature by vapors containing HCl or Cl_2 is likely to be appreciable (several tens of mils per year)³⁸ whereas the rate of corrosion by water vapor alone likely would be negligible. The accelerating effects of HCl and Cl_2 on corrosion probably are comparable.³⁸ There is no information as to whether either Cl_2 or HCl catalyzes the reaction between water vapor and stainless steel, i.e. as to whether the chlorine species would form stable metal halides and whether corrosion would stop when the chlorine species were consumed.

8.3 Formation of Explosive Gas Mixtures With Hydrogen Gas

8.3.1 With Gas Transport Properties of Salt Beds Above Can Comparable to Those of Medium Crushed Salt

a. Within waste disposal hole

My estimates of the transport of H_2 thru beds sof medium crushed salt indicate that the maximum concertration of H_2 at any elevation above

The size of the container also affects the ignition limits in other gas mixtures.³⁷

the can would be < 3 vol % at the maximum rates of generation of H₂ listed in Table 4. Thermal and other bouyancy effects would play important parts in transferring the H₂ up thru the 8 ft deep beds and into the room. However, diffusion alone would suffice to hold the H₂ at < 3 vol % when radiolysis is the only source of H₂.

The situation below the top of the can is less obvious. However, for several reasons, it seems unlikely that an explosive composition would form. In general, gases will tend to be swept out and the remaining gases diluted by any steam which escapes reaction with the can. Any H₂ which is generated by reaction between the can and water will exercise similar sweeping and dilution effects. In addition it is likely that O_2 as well as water vapor would react with the can so that when diluent H₂O is removed from the gas-wapor phase, the O_2 would also be removed.

b. Room above waste disposal can

It can be shown that introduction of H₂ into a burial room at the maximum rates listed in Table 4 would present no problem from the standpoint of explosive gas-mixtures. Thus, introduction of H₂ at a rate of 4 x 10^3 mole/y (7.6 x 10^{-3} mole/min) from 10 5 Kw cans buried below a room would result in a maximum concentration of H₂ of 3 x 10^{-5} vol \$ within the ventilation-air. Even with no ventilation, the uniform concentration of H₂ within the volume of air associated with a burial hole would be only 3 vol \$ at the end of one year. If the room above a can is backfilled immediately after burial of the can, the uniform concentration of H₂ within the crushed salt would be 9 vol \$ after one year providing H₂ escapes the bole at the maximum rate listed in Table 4. As mentioned in Section 8.2, 3 vol \$ H₂ is at the lower limit for reaction in large containers. The lower ignition limit for gas mixtures within the crushed salt is unknown, but it is likely to be in excess of 9 vol \$ H₂.

8.3.2 With Burial Hole Scaled

In the event that a gas tight seal develops or is imposed within a salt bed above a waste can, there are possibilities that an explosive mixture of gases would collect below the plug. Thus for example, assume that a plug forms at an elevation of 2 ft above a can, and

assume also that the temperature of the 2 ft length of bed is still below that at which the vapor pressure of water is appreciable. Then gases would tend to accumulate in the 2 ft length of bed, and the maximum rate of increase of the partial pressure of radiolytic H₂ would be about .03 atm per day. The rate of partial pressure increase when H₂ is generated by corrosion at the maximum rate of 400 mole/y is about 4 atm per day. In order that the gas mixtures be combustible they must contain O₂. Oxygen is generated along with the radiolytic H₂, and providing this O₂ does not react with the can, it would accumulate along with radiolytic H₂ in the gas mixture. Atmospheric oxygen at a partial pressure of ~ 0.2 atm might be trapped below a plug and this limited amount might be available for reaction with corrosion H₂.

Considerations to date have indicated that an explosion below a plug after the space in the room above the can has been backfilled would not lead to ejection of the can from the bole. Also, an explosion at that time would not lead to serious dispersal of radioactivity even though the can is open for some reason at the time of the explosion. This latter conclusion follows from consideration of the maximum amounts of gases which would be available for expulsion from the hole and from the reasonable assumption that the expelled gases will quickly reach an approximate thermal equilibrium with the crushed salt in the room above the can. Thus, say 400 moles of H₂ (320 ft³, STP) accumulate within the space around a can for some unforseen reason, and say also that all of the 400 moles are expelled by an explosion. This amount of gas would occupy the gas space associated with a 4 ft length of room holding 5 Kw cans. The length of room associated with each can will be at least 40 ft, and it is very unlikely that any expelled gas would reach the room opening.

The considerations made to date have not led to any definite conclusions as to whether an explosion prior to backfilling would be of any concern.

BR. D. Cheverton and G. H. Jenks, unpublished analyses, July 1971.
8.4 Introduction of Moxious Gases Other Than Radioactive Species Into Working Area

It can be shown that introduction of HCl into the 10-can room at the maximum rate listed in Table 4 is of no concern from the standpoint of exceeding acceptable concentrations. With ventilation at 20,000 scfm and with HCl injection at 20 mole per year per can, the maximum HCl concentration in the ventilation air would be 0.015 ppm. Without ventilation the tolerance concentration of 5 ppm could be reached after one day. Prolonged loss of ventilation would be precluded by the cperational design.

Other species such as Br₂ and HNO₃ would be injected at much lower rates and would reach much lower concentrations in the working areas. 8.5 Effects of HCl and Other Active Species on Transport of Fission

Product Activities

Experts in this area have not ruled out the possibilities of forming volatile oxychlorides and they are investigating these possibilities.

8.6 Effects of HCl and Other Active Chemical Species on Corrosion of Waste Can

As mentioned in Section 8.2, it is likely that the corrosion rate of stainless steel is appreciable (several tens mpy) in contact with water vapor containing HCl or Cl_2 at high temperatures. The corrosion of carbon steel is also likely to be substantial. At a maximum, the average rate of corrosion could correspond to that at which the rates of inflow of water and of reaction of water with the can are equal. (Assuming maximum rates and uniform corrosion, the 1/4 in. walls on a 5 Kw can would be completely converted to oxide at 15 years after burial.)

8.7 Effects of Explosive Reactions of Chlorates and Perchlorates

Chlorates and perchlorates are explosives when they are in contact with oxidizable materials. However, it can be inferred that the explosive energy which could be developed from these materials within a waste hole would be tolerable after the burial room has been backfilled.^A The bases for this inference are the following.

^BNo analysis has been made of the situation prior to backfilling.

a. An explosive force equivalent to 1 lb of TNT within a burial hole is considered tolerable.³

b. The maximum rate of formation of chlorate is about 1.3 mole/y, Table 4. (The equivalent maximum rate of formation of perchlorate from chlorate is about 1.0 mole per year.) As stated in Section 6, it is believed that these compounds would decompose thermally to form O_2 and halides.

c. The explosive efficiency of the chlorates and/or perchlorates which might be present within a burial hole are unknown. It is conservative to assume that the material has an explosive efficiency equivalent to that of TNT and that the material has an atomic weight of 150.⁴⁰ Thus, the explosive force which could be developed from the maximum amounts of chlorates which could accumulate during one year, without any thermal decomposition during the year, would be equivalent to about 0.35 lbs of TNT.

d. The situation with respect to dispersal of radioactivity is the analogous to that discussed in Section 8.3.

APPENDIX 1

Composition of Brine

Holser⁴ reported experimental values (Table 1.1) for the ratios of Mg, Br, SO₄ and Ca to Cl in the brine inclusions in salt from the mine at Hutchinson, Kansas, and from a core from the Maval Air Station at the same location.^A He did not report any ionic concentrations, but he stated that his results showed that the brine inclusions were formed by the evaporation of sea water and that the concentration factor was about 60.^b

Values for the concentrations of Mg, Ma, K, Cl and Br which I deduced from Holser's results and/or interpretations are listed in Table 1.2. The concentrations of Mg and Ma in columns 2 and 3 were obtained using the 25°C solubility data^{6,7} in Fig. 1.1 and also using the material balance relationships,

(C1) = 2(Hg) + (Ha) + (K) (1.1)

and

$$(H_{\rm G}) = (H_{\rm A}) + (K),$$
 (1.2)

with (K) equal to 0.3 mole/kg. Eqn. 1.2 was deduced from Eqn. 1.1 using Holser's data for (Mg)/(Cl). Holser did not report on (K), and the above value is that reported by Usiglio⁵ for sea water which was concentrated by 60X. In using Fig. 1.1, it was assumed that two KCl were the equivalent of one MgCl₂ with respect to the effects of these solutes on the solubility of MaCl. Concentration values were selected to give a best fit to Eqn. 1.2 while, at the same time, giving best agreement with the assumed equivalence between effects of MgCl₂ and KCl. The value of 1.28 for the density is that reported for 60X sea water.^{1.1}

The value for (Mg) in column 5 was established using Usiglio's value for (Mg) in sea water after concentration by 60%. The value for

^BThese deposits are thought to be substantially the same as those at Lyons, Kansas.

Belser further stated that the brine inclusions are probably unchanged samples of bitterns left behind in Permian time

TABLE 1.1 Reported^a Ratios of Concentration of Ions in Brine Inclusions

	Weight Basis	Mole Basis ^b
Mg/Cl	.231	.333
Br/Cl	.015	.0067
SO ₄ /Cl	.009	.003
Ca/Cl	0	0
Mg/Br ^b	15.6	49.6

^aW. T. Holser.

^bDerived from Holser's data.

Table 1.2.	Composition	of	Brine	Inclusions
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Species	From Solub: From Holse:)	llity Data and r's Rat , for Mg/Cl	From Solubility Data and From Usiglio's Value for (Mg) in 60X Sea Water		
	mole/kg	mole/\$ (d = 1.28)	mole/kg	mole/1 (d = 1.28)	
Mg	1.9	2.4	2.3 ^ª	2.9	
Na.	1.6	2.0	.8	1.0	
ĸ	.3	.4	.3 ^A	.4	
Cl	5.6	7.2	5.6	7.2	
Br		•048 ^b		.048	

^BFrom data reported by Usiglio⁵ for sea water after concentration by 60X. ^bFrom value for (C1) and from Holser's value of (Br)/(C1).



Fig. 1.1 - Solubility NaCl in Solutions of MgCl₂

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(K) was found as described above. The value for (Na) was then established using the solubility data in Fig. 1.1 with an effective concentration of Mg,

$$(Mg)_{eff} = (Mg) + \frac{(K)}{2}$$
. (1.4)

The concentrations of Mg, Na, Br, and Cl derived using these two different approaches are in reasonable agreement. I concluded that the composition of the brine is within the following range of compositions.

Ion	Molarity
Mg	2.3 to 3
ĸ	0.4
Na	2 to 1
Cl	7 to 7.5
Br	0.05
рН	Slightly basic

^ARef. 8. Encapsulated brine solutions at elevated temperatures would be glightly acid (several hundred μ molar H^{*}) due to hydrolysis of MgCl₂.

APPENDIX 2

Review and Discussion of Reported Information on g'-Values in Chloride Solutions; β - γ -Irradiations

2-1. Experimental Information

2-1.1 Neutral Chloride Solutions

2-1.1.1 g'(Cl₂)

Anbar and Thomas^{2.1} observed formation of Cl_2^- in neutral NaCl and they reported relative yields over a range of (NaCl) up to 3M. Savai and Hamil^{2.2} reported that the experimental results of Anbar and Thomas are expressed by the relationship shown in Eqn. 2.1,

$$g'(Cl_2^-) = \frac{3.8}{(Cl^-)} (Cl^-) + 2.63$$
 (2.1)

Values corresponding to this relationship are plotted in Fig. 2.1.

 $2-1.1.2 g'(H_2O_2)$

Matsuyama and Namiki^{2.3} measured $g'(H_2O_2)$ in NaCl solution at concentrations up to 4.0M. The values of $g'(H_2O_2)$ decreased in proportion to $(Cl^{-})^{1/3}$ starting at 0.14M Cl⁻; at 3.4M Cl⁻ $g'(H_2O_2)$ was about 0.18 of that in pure water.

Savai and Hamil^{2.2} reported the following experimental relationship between $g'(H_2O_2)$ and (NaCl) in neutral solution,

$$g'(H_2O_2) = 0.64 - \frac{0.83 (C1^-)}{(C1^-) + 2.52}$$
 (2.2)

Their experimental data extended to 3M MaCl. Values corresponding to Eqn. 2.2 are plotted in Fig. 2.2.

I find that the data of Matsuyama and Namiki and of Sawai and Hamil are in near agreement.

^AIn this paper, the g'-value for a species refers to the number of the species per 100 ev which appears in homogeneous distribution in the initial radiation process. The number of a species which appears as a final product of the radiolysis is referred to as the G-value.







Fig. 2.2 - g'-Values for H_2O_2 in NaCl Solutions (Savai and Hamil)

2-1.1.3 g'(H₂)

Brusentseva and Dolin^{2.4} studied γ radiolysis of neutral KCl solutions at concentrations up to saturation. Evolution of H₂ and O₂ took place in amounts which increased with increasing (KCl). The ratio of (H₂) to (O₂) was close to 2. Their data are represented in a plot of G(H₂)^A and G(O₂) vs (KCl) in Fig. 2.3. Additional information on their work is included in Table 3.1.

It may be noted here that the values of $G(H_2)$ which were reported by Brusentseva and Dolin for (KCl) > .07M exceeded that of $g^*(H_2)$ in pure water; at 4M KCl the factor was about 4. Evidence in support of the high $G(H_2)$ values of Brusentseva and Dolin is included in the discussion Section, 2-2.2.4.

Information on $g'(H_2)$ values mentioned by Savai and Hamil^{2.2} appears to conflict with that of Bruséntseva and Dolin.^{2.4} The former investigators stated that $g'(H_2)$ is nearly unchanged^b in 2M Cl⁻ with 0.002M NO₃⁻ and 0.02M isopropyl alcohol. However, Baybarz^{2.5} found that a small amount of methanol, < 3 vol \$, in 10M LiCl with 0.05M HCl reduced $G(H_2)$ under α irrediation (6 x 10⁴ rad/min) from 2.36 to a negligible value.⁶ This reduction has not been explained. However, the results of Baybarz suggest that isopropyl alcohol might have affected the results of Savai and Hamil. Accordingly, I discounted their results in the present considerations.

The above mentioned work of Baybarz^{2.5} was done with 6.1 Mev α -particles (Table 3.2). It can be assumed that his experimental values of G(H₂) were less than or equal to g'(H₂) in the same experiments (See Section 2-2). In pure water the value of g'(H₂) for 6 Mev α 's is about 1.5.^{2.6} Accordingly, the experimental values for g'(H₂) in the lOM LiCl solution are substantially greater than in pure water.

Presumably from that in water although this was not stated.

 $\frac{c}{d}$ (-HCl) was also reduced to a negligible value.

^BAs discussed in a later Section, 2-2.2.4, it is very likely that these experimental values of $G(H_2)$ were less than or equal to values of $g'(H_2)$ in the same experiment.





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2-1.1.4 g'(Cl₂)

No direct experimental information is available. Indirect and theoretical information is discussed in Section 2-2.

2-1.1.5 g'(e ag) and g'(OH)

No applicable experimental values for either g'(e aq), g'(H) or g'(GH) have been reported.

2-1.2 g'(Cl₂) in Basic Solutions

Anbar and Thomas^{2.1} measured relative Cl_2^- yields in 2M NaCl over the pH range 7 to 14. Between pH 7 and 11 there was no change in g'(Cl_2^-). However at pH 12 and above the values of g'(Cl_2^-) were less than those at pH 7 (Fig. 2.1).

2-1.3 Acid Solutions

2-1.3.1 g'(Cl₂")

No values for g'(Cl₂⁻) in acid solutions have been reported. Anbar and Thomas^{2.1} showed that Cl₂⁻ is formed in acid solutions by reaction in the bulk of the solution between OH, Cl⁻ and H⁺. The overall reaction and the rate constant were,

 $OH + C1^{-} + H^{+} \stackrel{C1^{-}}{\longrightarrow} C1_{2}^{-} + H_{2}O; k_{2,3} = 1.66 \times 10^{10}$ $M^{-2}, \text{ sec}^{-1}. \qquad (2.3)$

Presumably, some Cl_2 was formed in the initial radiolysis process as in neutral solution (Section 2-2), but the concentrations of NaCl which were studied were below those at which $g'(Cl_2)$ was expected to be detectable.

2-1.3.2 g'(H₂O₂)

Values of $g'(H_2O_2)$ in solutions containing up to 0.1M KCl along with 0.4M H₂SO₄ were determined by Sworski^{2.7}. The values decreased in proportion to (KCl)^{1/3} and were equivalent to 0.78 and 0.53 at 0.0 and 0.1M KCl, respectively.

I note that this rate of decrease exceeds that reported for neutral chloride solutions.

2-2. Discussion

2-2.1 Spur Diffusion Model of Radiation Chemistries of Water and Aqueous Solutions

The radiation chemistries of vater and aqueous solutions are usually described in terms of the spur diffusion model.^{2.8,2.9} Several pairs of radicals or ions (primarily e_{aq}^{-} , OH and $H_{3}0^{+}$ in pure vater) are formed in small, isolated volume elements (spurs) in the initial radiation process. Species within the spurs interact as they diffuse into homogeneous distribution, and these interactions result in the reformation of vater and in the formation of other molecular products. In pure vater under γ -irradiation, the decomposition products which appear in homogeneous distribution are principally,

$$e_{a0}^{-}$$
, OH, H₂ and H₂O₂.

The H_2O_2 and H_2 are formed, primarily, by the following reactions,

$$e_{aq}^{-} + e_{aq}^{-} + 2H_2^{-} \rightarrow H_2^{-} + 20H^{-},$$
 (2.4)

$$OH + OH \rightarrow H_2O_2. \tag{2.5}$$

Important water-reformation reactions are,

$$e_{aq}^{-} + H_2O_2 - OH + OH^{-},$$
 (2.6)

$$e_{a0}^{-} + OH \rightarrow OH^{-},$$
 (2.7)

$$0H^{-} + H_3 0^{+} \rightarrow 2H_2 0.$$
 (2.8)

Reactive solutes at high concentrations can react with radicals within the spurs and thus cause changes in g'-values from those in pure water and, at the same time, cause the formation of additional g'-species. For example, a solute such as Cl⁻ which presumably can react with OH within the spur would cause reductions in g'(OH) and g'(H₂O₂) from those in pure water. This solute would also promote increases in g'(e_{aq}^{-}) and g'(H₂) providing that the new products of the spur reactions (i.e. Cl₂⁻ and possibly Cl₂), do not remove e_{aq}^{-} as rapidly as do OH and H₂O₂ in the pure-water system. Solutes at high concentrations can also be affected by direct action of radiations, e.g., reaction 2.9 may occur in chloride solutions,

$$C1^{-} \stackrel{A}{\rightarrow} C1^{0} + e^{-}.$$
 (2.9)

The yields for reactions such as 2.9 .equently quite high; say 5 to 10 product-species per 100 ev o' $gy^{2.4,2.9}$ absorbed by the parent species (C1⁻ in this case)

Reactions which result in the formation of OH, e ag and Cl₂ are summarized below.

Set 1 - Action of radiation on water followed by reaction between

OH,
$$Cl^{-}$$
 and $H_{3}O^{+}$ to form Cl^{0}

$$H_20 \xrightarrow{A} H_20^+ + e^-$$
 (2.10)

$$H_20^+ + H_20 \rightarrow OH + H_30^+$$
 (2.11)

$$e^{-\frac{H_2 U}{2}} e^{-\frac{1}{2}} e^{-\frac{1}{2}} e^{-\frac{1}{2}} (2.12)$$

$$OH + H_3 O^+ + C1^- \rightarrow C1^0 + 2H_2 O$$
 (3.13)

$$C1^{0} + C1^{-} \rightarrow C1_{2}^{-}$$
 (2.14)

Set 2 - Direct action of radiation on Cl^- to form Cl^0

$$C1^{-} \stackrel{A}{\rightarrow} C1^{0} + e \tag{2.9}$$

$$C1^{0} + C1^{-} \rightarrow C1_{2}^{-}$$
 (2.14)

$$\begin{array}{c} H_2 0 \\ e \rightarrow e^- \end{array}$$
 (2.12)

Reactions 2.10 thru 2.12 in Set 1 are those resulting in the formation of OH, e_{aq}^{-} and H_20^+ within a spur in the initial radiation processes of the spur diffusion model. An OH and an H_30^+ are consumed in the reaction with Cl⁻ to form Cl⁰.

Neither OH nor H_30^+ are removed during formation of Cl_2^- by direct action of radiation on Cl⁻, Set 2. However, radiation energy which is dissipated in this way is not available for reaction with water, Set 1, and so the initial yields of OH and H_30^+ are reduced by the formation of Cl_2^- by direct action.

AFor comparison, the yield of OH in Reactions 2.10 and 2.11 $[g^{\circ}(OH)]$ in pure H₂O is thought to be near 5.7.^{2.8}

2-2.2 Discussion of g'-Values in Neutral Chloride Solutions 2-2.2.1 g'(Cl2)

There are no apparent reasons to question the reported experimental values. Extrapolations to concentrations greater than the maximum experimental concentration (3H) are, of course, uncertain.

2-2.2.2 g'(Cl₂)

It is reasonable to assume that some interaction of Cl^0 to form Cl_2 takes place within spurs. In comparison with the yield of H_2O_2 in pure water, the value of $g'(Cl_2)$ might exceed 0.5 at $(Cl^-) > 3H$. Experimental results which have been reported to date do not preclude the occurrence of appreciable initial yields of Cl_2 .

2-2.2.3 g'(H₂O₂)

The observed reductions in $g'(H_2O_2)$ from those in pure water are explained as discussed in Section 2-2.1.

2-2.2.4 g'(H2)

Oxygen and possibly H_2O_2 were present during the times that H_2 evolution took place in the experiments of Brusentseva and Dolin.^{2,4} Accordingly, it is very likely that all e^-_{aq} and H reacted with O_2 cr H_2O_2 (Reactions 2.6, 2.15, and 2.16) so that no H_2 -formation took place outside the spurs.

 $e_{a3}^{-} + 0_2 - (b_2^{-}), k = 1.9 \times 10^{10} \text{ M}^{-1}, \text{ sec}^{-1}.$ (2.15)

 $H + O_2 \rightarrow SO_2$ (= $H^+ + O_2^-$), $k = 1.9 \times 10^{10} H^{-1}$, sec⁻¹. (2.16) The only known reaction by which H_2 is removed from water or chloride solution is.

 $OH + H_2 - H + H_2O$, k = 4.5 x 10⁷ M⁻¹, sec⁻¹. (2.17)

Reaction 2.17 is relatively slow and it is suppressed by certain other solutes which react more readily with OH. Bromide ion is such a solute and it was probably present as a contaminant in the experiments of Brusentseva and Dolin^{2.4} as well as in experiments of others where no special purifications were made to remove bromide from the chloride solution (Table 3.1 and 3.2).

 $OH + Br^{-} \rightarrow Br^{0} + OH^{-}, k = 1 \times 10^{9} M^{-1}, sec^{-1}.$ (2.18)

In order to illustrate OH-removal by Br⁻, assume that Br⁻ was present at 100 ppm (9.3 x 10^{-5} moles per mole KCl) in the experiments of Brusentseva and Dolin, and assume also that the rate constants for reactions 2.17 and 2.18 were the same as those in pure water. Then it can be shown that 9.3 OH reacted with Br⁻ for each OH which reacted with H₂ when (KCl) was 3H and (H₂) was at saturation; about 10 cm³/s.

On the basis of the above considerations, I concluded that $G(H_2)$ equaled g'(H_2) at high (001) in the experiments of Brusentseva and Dolin.^{2.4}

As mentioned previously, the $G(H_2)$ values of these workers are very high compared with the $g'(H_2)$ in water. It can also be noted that the high values are not readily explained on the basis of the spur diffusion model.⁶ However, the high values are supported by the experimental values for $G(Cl_2)$ at pH ll reported by Kabakchi et al.,^{2.10} and by the reported^{2.11} values of $G(H_2)$ in iodide solutions.^b The reported results of Kabakchi et al., are listed in Table 3.1 and illustrated in Fig. 2.4. Note that very high values of $G(Cl_2)$ were reported and note also that $G(H_2)$ in these experiments must have equaled or exceeded $G(Cl_2)$. Explanations for the occurrence of appreciable values of $G(Cl_2)$ at pH 11 are discussed in Appendix 4.

^BThe initial yield of reduced species within a spur in pure vater is thought to be $5.7^{2\cdot8}$ (measured as e_{aq}^{-}), while the values of g'(H₂) and g'(e_{aq}) are 0.43 and 2.7.^{2.8} Nov at g'(H₂) equal to 2, as indicated for chloride solutions, the maximum possible value of g'(e_{aq}) would be 1.7 providing that the yield of reduced species within a spur does not exceed 5.7. In addition, an increase in the value of g'(e_{aq}) would be expected to accompany an increase in the value of g'(H₂) providing that the rate constant for interaction of e_{aq} to form H₂ does not change and also providing that the lifetime of a spur does not change. It can be speculated that increased values of g'(H₂) in chloride solutions result from effects of chloride ions on one or more of the parameters which have been mentioned, i.e., initial yield of e_{aq}, rate constant for interactions between e_{aq}, and lifetime of spur. However, additional experimental and theoretical work would be needed to verify effects of chloride on any of these parameters.

 ${}^{D}G(H_2) \approx 1 \text{ at } (I^-) = 4 \text{ M}.$



Fig. 2.4 - G(Cl₂) in Solutions of KCl, of NaCl, and of BaCl₂ at pH ll (Kabakchi, Gramolin, and Evokhin)

2-2.3 Expected Effects of Elevated Temperatures on g'-Values in Chloride Solutions

Increasing temperatures (to at least 250° C) have negligible effects on g'-values in pure water.^{7,2,12} This temperature insensitivity can be explained qualitatively in terms of a balance between the increase in the rates of diffusion-limited thermal reactions within a spur and the increase in the rates of diffusion into homogeneous distribution. Assuming that this qualitative explanation is correct, I would expect that g'-values in Cl⁻-solutions would also be insensitive to increasing temperatures.

APPENDIX 3

Summary of Reported Information on $G(Cl_2)$, $G(H_2)$, and $G(O_2)$ in Chloride Solutions and in Salt-Mine Erines^B

1. Tubulated Information

Information pertaining to neutral and basic solutions is set forth in Table 3.1; information on acid chloride solutions is in Table 3.2. 2. Evolution of Oxidant in Salt-Vault-Experiment

As part of the salt-vault-experiment reported^{3.7} by others, sweepair passing between the irradiated bedded salt and the hole-liner was monitored for gaseous oxidants by means of commercial chloride detectors. When oxidants were indicated, the gases were conducted through a cold trap, and the contents then analyzed to determine the oxidizing species. The gas sweep rate was about 7 liters per min. per hole, and the residence time of air within the hole was about 8 min. at $170^{\circ}C$ (~ 76 g of air within hole at $170^{\circ}C$). The hole was kept more or less free of liquid by the air-sweep. The irradiation intensity in the air was about 10^{5} rads per hr. The salt within 6 in. of the edge of the hole was exposed to 10^{8} to 10^{9} rads total.

The commercial detector showed gaseous oxidants at 0.5 to 1 ppm. after the temperature at the walls of a hole exceeded $175^{\circ}C$. The indicated oxidant concentrations were roughly proportional to dose rate. The concentrations decreased with exposure time, and were in the range 0 to 0.3 ppm when the arrays were shutdown 5 months later.

No chlorine was found in the cold traps; presumably no bromine was found either since the analytical methods likely would have detected bromine.^{3.1} The experimenters suggested that the oxidant was an organic peroxide which was stable enough to react with the chlorine detector but which decayed during the times required to collect it in the cold trap and to analyze the contents.

^AAlso some information on radiolytic formation of bromine in KBr solution.

				1					
Invest leaters	Concentration	n Chloride	Туре	Dese	Deee	Tamp.	G(C1 ₂)	c(=_)	c(0 ₂)
	NC1 (N/L)	LIC1 ()(/1)		Rate (Lad/min)	(Red)	(*c)	-		
Kubet "ª	1.4	-	Υ	2 x 10 ⁴	te 10 ⁵	204-25	.03 <u>b</u>	•	•
Kubet s ⁴	6	•	۲	2 ± 10^{4}	105	35-40	.07	-	-
Kubet a ⁸	6	•	۲	2 x 10 ¹	105	35-40	.12	-	-
Kubet a ⁰	t	•	۲	2 x 10 ⁴	10 ⁵	35-40	.17	•	•
Allen <u>et al^d</u>	1 <u>ť</u>	-	X-pile	3 x 10 ⁴	1.3 x 10 ⁸	200	-	. m ^e	-
Alles <u>et al</u>	.12	•	X-pile	3 x 10 ⁴	1.3 x 20 ⁸	² 00	•	.63 ⁴	-
Bugsonko and Horslov ^R	2 b	-	X-say	6 m 10 ³	2.5 x 10 ⁵	R.T.	.47 *	-	-
Bugaenko and Horalov ^E	2	-	X-tay	6 m 10 ³	2.5 x 10 ⁵	R.T.	.69	-	•
Buganako and Heralev ^E	3	-	X-ray	6 x 10 ³	2.5 x 10 ⁵	R.T.	. 74	•	•
Bugaenke and Horalev ^B	3	-	X-197	4 ± 10^{3}	2.5 x 10 ³	R.T.	.95	-	-
Sugsonko and Horalova	6	-	X-rey	6 x 10 ³	2.5 x 10 ⁵	B.T.	1.19	-	•
Kubota ^g	0.2	11.0	Y	2 = 10 ⁴	2 = 10 ⁷	204-5(0.22 C(-# ⁴)44	-	-
Beybarol	Neutral to 0,4	10	0 6.1 Hev	5 x 15 ⁴ te 14 x 10 ⁴	-	12-35	C(-H ⁺) = 1.0	2.341	0.38 C(x ₂ 0 ₂) = 0

.

Table 3.1. Summary of Some Literature information on $G(Cl_2)$ and $G(R_2)$ for Solutions of Acid Chloride

a Ref. 3.4

- <u>b</u> The reported values of $G(Cl_2)$ increased linearly with increasing (HCl) in this concentration range. I read these values from the reported plot of the data.
- c My estimate.
- <u>d</u> Ref. 3.3.
- <u>e</u> These values compare with a value of 0.89 for $g'(H_2)$ in pure water in the same irradiation facility. Ref. 3.5.
- <u>f</u> Reagent grade HCl.
- g Ref. 3.6.
- h Treated with KMnO4 and then distilled.
- <u>1</u> Ref. 2.5.
- <u>i</u> In pure water, the value of $g'(H_2)$ for 6 Mev a's in about 1.5 (See Section 1.1.3, Appendix 2).

		Solution			Irradiatio	b			
Investigators	Salt	Concentration (M/L)	рн	Туре	Dose Rate (Rad/Min)	Doee (Rad)	G(.1 ₂)	с(H ₂)	c(0 ₂)
Kubota ⁸	NaC1-	up to sat.	Neutral	۲	~2 x 10 ⁴	to > 10 ⁷	0	•	
Kubota ^A ·C	XaC1ª	Sat.	Neutral	Y	~2 x 10 ⁴	-	•	<u>d</u>	<u>d</u>
Brusentseva and Dolin-	KC1 [®]	0.02	Neutral	۲	-	-	0	0	0
Brueentseva and Dolin	KC1 [®]	3.3	Feutral	۲	•	•	.09	1.8	.9
Brusontseva and Dolin	KC1 <u>b</u>	<.01 to ~4	Meutral	ř	-	•	-	0 to 2.2 ^f	0 to 1.1 ^f
Kabakchi, Gramolia and Rvokhin ⁴	NaCla Dr NaCla Dr NaCla	1 2 3 4	11 11 12 11	Y Y Y	- - -	to 2×10^6 to 2×10^6 to 2×10^6 to 2×10^6	.6 .8 1.3 .1.6	- - -	- - -
Allen ot alh	NaCl [®]	1	Neutral	X-File	3 × 10 ⁴	2.7 x 10 ⁷	•	.69 ¹	•
Allen <u>et al</u>	XaC1	1	Meutral	X-7110	3 x 10 ⁴	1.3 x 10 ⁸	•	.481	•
Allen <u>et al</u>	NACIL	0.1	Weutral	X-Pile	3 x 16 ⁴	~ 10 ⁷	•	0	-

Table 3.2. Summary of Literature Information on $G(C1_2)$, $G(H_2)$ and $G(O_2)$ in Meutral and Basic Chloride Solutions

Notes to Table 3.2

- a Ref. 3.1.
- b I estimate that the temperature was 30-40°C in each of these experiments.
- c Ref. 3.2.
- d A steady-state pressure of about 10 atus was observed in gas phase over the saturated solution; Ref. 3.2.
- e Reagent grade.
- f See Fig. 2.3. $G(H_2)$ and $G(O_2)$ increased with increasing (KCl) starting from zero at (KCl) $\cong .01M$.
- g Ref. 2.10. See Fig. 2.4.
- h Ref. 3.3.
- <u>i</u> This compares with a value of 0.89 for $g'(H_2)$ in pure water in the same ir:adiation facility.
- j Specially purified to remove browide ion.
- k Ref. 2.4.

Radiolytic Formation of Br in KBr Solutions

a. Brusentseva and Dolin^{2.4} found that Br_2 was formed by -irradiation of deaerated KBr solutions at (KBr) > 0.1M. The value f G(ΣBr_2)^B was 0.04 and .35 at (KBr) equal to 0.1 and 1.0M, respectively. b. Rafi and Sutton^{3.8} found G(ΣBr_2)^B equal to 0.08 and 0.38 at

KBr) equal to 0.1 and 1.0M, respectively, in pH 2 solutions (pH djusted with H_2SO_4). G(ΣBr_2) was zero at (KBr) < 0.1M.

c. Kubota^{3.1} found no bromine formation during γ -irradiation of leutral bromide solutions at concentrations up to about 1M.

^BCBr₂ signifies the sum of all bromine with oxidation number zero.

APPENDIX 4

Identities of the Oxidized Species Formed Radiolytically Within Chloride Solutions and Salt-Mine-Brine

4-1. Introduction

Formation of reduced species in the radiolysis process must be balanced by formation of a stoichiometrically equivalent number of oxidized species. For chloride solutions, this balance is expressed by the following relationship between G-values when it is assumed that Cl_2 and ClO_3^- are the only final chlorine species,

 $G(H_2) = 2G(O_2) + G(H_2O_2) + G(Cl_2) + 3G(ClO_3).$ (4.1)

Eqn. 4.1 is valid regardless of the identity of the reduced species. For example, it is valid if reduction of O_2 to H_2O takes place instead of release of H_2 . The sign of $G(O_2)$ would be negative in this case. The g'-products could include radicals and Cl_2 as shown in the following oxidation-reduction balance relationship,

 $2g'(H_2) + g'(e_{aq}) + g'(H) = g'(OH) + 2g'(H_2O_2) + g'(Cl_2^-) + 2g'(Cl_2).$ (4.2)

Values of $g'(H_2)$ and $G(H_2)$ in chloride solutions were discussed previously, Appendixes 2 and 3. Information on the identities of the balancing species is reviewed and discussed below.

4-2. Neutral Chloride Solutions

The experimental data \square showed that O_2 is formed along with H_2 in the approximate ratio of one O_2 to two H_2 (small excess of H_2) and that $G(Cl_2)$ is small or negligible out to saturation concentrations of NaCl and KCl. Accordingly, reactions must occur in which chlorine species oxidize H_2O to form O_2 . In amplification of this statement, it can be noted that in the absence of reactions between chlorine and H_2O , the

^BThe salt mine brines contain Br, and accordingly, the oxidized species include bromine species with oxidation number > -1. ^bSee Table 3.2 and Fig. 2.3.^b only source of O_2 is that H_2O_2 which is formed as a g'-product. The H_2O_2 would release O_2 thru reactions of the following types,

$$H_{2}O_{2} + Cl_{2}^{-} \rightarrow H^{+} + 2Cl^{-} + HO_{2} (\stackrel{\text{res}}{=} H^{+} + O_{2}^{-})$$
(4.3)^b
$$O_{2}^{-} + HO_{2} \rightarrow HO_{2}^{-} + O_{2}$$
(4.4)^c

$$D_2 \rightarrow HO_2 \rightarrow HO_2 + O_2$$

Overall,

 $H_2O_2 + 2Cl_2 \rightarrow 2H^+ + 4Cl^- + O_2$ (4.5)

and $G(O_2)$ would equal $g'(H_2O_2)$ if H_2O_2 were the only source of O_2 . The experimental data at high (C1⁻) where $g'(H_2O_2)$ is < .12^d show that $2G(O_2) \cong G(H_2) > .24$. It follows that O_2 must be formed by reactions between $Cl^{>-1}$ and H_2O .

The most likely reactions of chlorine species with water are of the types which have been proposed by others^{4.3} to explain the photolytic behavior of solutions of Cl₂ and/or HClO. With neutral solutions containing Cl at high concentrations, the likely reactions are,

> $Cl_2 + H_20 - Cl^{-} + H^{+} + HCl0 (= H^{+} + Cl0^{-}),$ (4.6) $C1_2^{-} + HC10 \rightarrow H^+ + 2C1^- + C10^0$, (4.7)

$$C10^{0} + EC10 - H^{+} + C1_{2}^{-} + O_{2},$$
 (4.8)

Reaction 4.7 and 4.8 comprise a chain reaction. Reactions 4.6 to 4.8 give overall,

$$2C1_2 + 2H_20 \rightarrow 4H^{\dagger} + 4C1^{\dagger} + 0_2. \qquad (4.9)$$

^BThe OH radical does not contribute to $G(O_2)$ because it reacts with Br to form Br⁰ (Appendix 2). In the absence of Br, the OH would react with H₂; reaction 2.17.

BRef. 4.1.

 $\frac{c}{The}$ rate constant for formation of O_2 and H_2O_2 in solutions containing HO_2 and O_2 is pH-dependent (Ref. 4.2). Some values for the rate constant in water at 25°C are listed below.

$\begin{array}{ccc} 11 & 8.5 \times 10 \\ 7 & 8.5 \times 10^5 \end{array}$	
7 8.5×10^{5}	
5 2.1 x 10^{7}	
<<5 6.7 x 10 ⁵	

^aSee Fig. 2.2.

4-3.

. Chloride Solutions at pH 11

The experimental data of Kabakchi et al, tuken together with data of others for $g'(Cl_2^-)$ indicate that $2G(Cl_2) = g'(Cl_2^-)$ in chloride solutions at pH 11.^A Their value of 1.6 for $G(Cl_2)$ at 4M Cl⁻ is near the value of 1.9 for $G(H_2)$ reported by Brusentseva and Dolin at the same chloride concentrations. Accordingly, it can be inferred that reactions in which chlorine species are reduced by H₂O are inhibited at pH 11. This might be explained by assuming that Cl₂ hydrolyzes rapidly at pH 11 and that ClO^{-G} does not react with Cl₂; possibly because of like charges on the reactants.

$$HOC1 - H^{T} + C10^{T}$$
 (4.10)

$$Cl_2 + Cl0 + 2Cl + Cl0^0$$
 (4.11)

Without reactions between chlorine and water, the relationship shown in Eqn. 4.12 would be expected,

$$0 \leq G(H_2) - G(CL_2) \leq 2g'(H_2O_2). \tag{4.12}$$

The various experimental data indicate that Eqn. 4.12 is approximately valid at pH 11.

^ASee Appendixes 2 and 3. See also Figs. 2.2 and 2.4. ^bSee Fig. 2.3.

Server information on equilibrium constants, it can be shown that the following values for concentration-ratios obtain at equilibrium in 4% Cl⁻ at 25°C and at pH ll and 6.

	pH 11	рН 6
(HC10) (C1 ₂)	5.7 x 10 ⁶	57
(C10 ⁻) (HC10)	3 x 10 ³	0.3
(C10 ⁻) (C1 ₂)	1.7 x 10 ¹⁰	1.7
$\frac{(C1_3)}{(C1_3)}$	0.8	0.8

4-4. Acid Chloride Solutions

The data of Kubota^B indicate that $G(Cl_2)$ is negligible during γ -irradiation of aerated HCl solutions at (HCl) < 1M. Above about 1M his values of $G(Cl_2)$ increased linearly with increasing (HCl) up to about 8M where $G(Cl_2)$ equaled 0.10. Above 8M HCl, $G(Cl_2)$ increased more rapidly, and the value of $G(Cl_2)$ at 11M HCl was about 0.15.

The $G(Cl_2)$ values reported by Bugaenko et al.,^H for x-irradiation of deaerated solutions of 1 to 6M HCl are much higher than those of Kubota; $G(Cl_2)$ was l.l at 6M HCl.

The negligible values of $G(Cl_2)$ below 1M HCl might be explained by assuming the occurrence of certain reactions between chlorine and water of the types discussed in Section 4-2. The occurrence of significant values of $G(Cl_2)$ above 1M HCl might then be explained by assuming that these reactions are inhibited by hydrogen ions and that the degree of inhibition becomes significant at 1M H⁺. In acid solutions, the chain reactions leading to oxidation of H₂O must be,

$$Cl_2^{-} + Cl_2 + H_2 0 \rightarrow 2H^{+} + 3Cl^{-} + Cl0^{0}$$
 (4.13)

$$C10^{0} + C1_{2} + H_{2}0 \rightarrow 2H^{+} + 2C1^{-} + C10^{0} + O_{2}$$
 (4.14)

to give the overall reaction 4.9. It is easy to speculate that hydrogen ions inhibit one or both of these reactions (4.13 and 4.14).

No explanation is offered for the substantial difference between the reported results of Kubota and those of Bugaenko et al. However, it can be noted that oxidized species other than Cl_2 are possible products of radiolysis (see below), and some difference between results of different investigations might have resulted from the undetected occurrence of some of these.

^ASee Appendix 2 and 3.

^bIt can be mentioned that little difference between the g'-species and-g'-values of x- and γ -rays would be predicted from theory.

Data reported by $Baybarz^{\underline{B},2.5}$ for G(-H⁺), G(H₂), G(O₂) and G(H₂O₂) during α -irradiation of concentrated LiCl solutions which also contained HCl at 0.4 to 0 molar are of interest because it can be inferred that appreciable amounts of Cl₂ and/or Cl₂⁻ were converted into ClO₃⁻ during Baybarz's irradiations. Considerations which lead to this inference are summarized below.

Eqn. 4.15 shows the oxidation-reduction balance relationship which must prevail between G-values for oxidized and reduced species in this system when all conceivable oxidized species are included.

$$2G(H_2) = 2G(Cl_2) + 5G(Cl_2) + 2G(Cl_20) + 4G(O_2) + 2G(H_2O_2) + 6G(Cl_2) + 8G(Cl_2) + 4G(Cl_2)$$
(4.15)

Charge balance requires the following relationship involving G(-H⁺),

$$2G(Cl_2) + 5G(Cl_2) + 2G(Cl_20) = G(-H^+)$$
(4.16)

Hypochlorous acid and hypochlorite ions were omitted from Eqn. 4.15 because the amounts of these in equilibrium with Cl_2 is very small in solutions containing a small amount of HCl. Chlorous acid, $HClO_2$, rather than ClO_2^- would have been present in the acid solutions. However, the acidity of the solution was measured by titration, and the measured value would not have been affected by formation of either ClO_2^- or $HClO_2$ (the pK of $HClO_2$ is 2.0 at 25°C).

Now substituting from Eqn. 4.16 in Eqn. 4.15, we have,

 $2G(H_2) = G(-H^+) + 4G(O_2) + 2G(H_2O_2) + 6G(C1O_3) +$

 $8G(C10_{4}) + 4G(C10_{2})$

(4.17)

The experimental G-values were:

Species	G-value
H ₂	2.36
H+	-1.0
02	0.38
H2O2	0

-See Appendix 3.

Introducing these values into Eqn. 4.17 we find,

 $3G(C10_{2}) + 4G(C10_{4}) + 2G(C10_{2}) = 1.10$

Chlorous acid and chlorites are fairly strong oxidizing agents. Also, they are unstable with respect to decomposition to form chlorate and chloride^{4.4} thru reactions such as reaction 4.19.

 $3HC10_2 \rightarrow C1^- + 2C10_3^- + 3H^+.$ (4.19)

(4.18)

Accordingly, it is unlikely that chlorous acid was present at any significant concentration. Ferchlorate is not formed by thermal decomposition at 25°C of aqueous solutions of Cl₂, HClO, HClO₂ or ClO₂. These decomposition transformations stop at chlorate.^{4.4} Also, it is unlikely that perchlorate was formed during irradiation since it is not formed by photolysis of solutions containing Cl₂ or HClO; O_2 and ClO₃⁻ are the exclusive products of photolysis of these solutions.^{4.4}

On the basis of Eqn. 4.18 and the above arguments, I concluded that the value of $G(ClO_3^-)$ was 0.37 in the experiments of Baybarz. The fraction of the $G(H_2)$ which was balanced by ClO_3^- was then 0.47. Radiolytic reactions such as the following may have accounted for part of the formation of ClO_3^- ,

$$Cl_2^- + Cl_2 + H_2 0 \rightarrow 2H^+ + 3Cl^- + Cl0^0,$$
 (4.13)
 $HO_2 + Cl0^0 \rightarrow H^+ + Cl0_3^-.$ (4.20)

These results and conclusions indicate that chlorate may be formed in concentrated chloride solutions during γ - as well as *a*-irradiations. In general, G(ClO₃⁻) should be measured along with other G-values for complete delineation of a system.

-5. Salt-Mine-Brine

4-5.1 Brine Inclusions

Because of the high temperatures and long irradiation times, it is very likely that all Cl_2 and Br_2 which does not react with H_2O or with H_2O_2 to form O_2 will be converted into ClO_3^- and BrO_3^- before the inclusions reach the hole around the can. The conversionreactions would include reactions 4.19-4.24 as well as radiolytic and other thermal $^{4.4-4.6}$ reactions mentioned previously. $3C10^{-} \rightarrow C10_{3}^{-} + 2C1^{-}$ (+.21)

$$2C10^{-\frac{810}{2}}C10_{2} + C1^{-1}$$
 (4.21a)

$$C10_{2}^{-} + C10^{-125} C10_{3}^{-} + C1^{-}$$
 (4.21b)

$$Br_2 + 2ClO_3 \rightarrow 2BrO_3 + Cl_2$$
 (4.23)

$$3BrO^- \rightarrow BrO_3^- + 2Br^-$$
 (4.24)

The maximum value of G(ClO₃" + BrO₃") would be,

$$G(C10_3 + Br0_3)_{max} = \frac{G(H_2)}{3}$$
 (4.25)

Taking $G(H_2)_{max}$ equal to 2.1, $G(ClO_3 + BrO_3)_{max}$ would be 0.7.

As discussed in Appendix 5, the pyrolysis of chlorates and bromates within the hot, dry open spaces around a can would produce halides, perchlorates and oxygen. Some bromine might be formed by pyrolysis of $Mg(BrO_3)_2$. The indicated absence of Cl_2 and Br_2 in sweep-gas of the salt-vault experiment (Appendix 3) supports the idea that all Cl_2 and Br_2 within brine-inclusion will react with H_2O and H_2O_2 to form O_2 and/or chlorates and bromates and that only very small amounts of Cl_2 and Br_2 would be formed within the open spaces. 4-5.2 Acid Brine Around Waste Can

The products of radiolysis of any liquid brine in the open spaces around a can may differ from those of encapsulated brine for two reasons: (1) the liquid around the can may contain HCl and also some of the HNO₃ which may be formed radiolytically within the gasvapor mixture in contact with the liquid, and (2) radiolytic gases will readily escape from the une offined hot liquids. I have concluded that the possible radiolytic products under these conditions include Cl_2 , Br_2 , ClO_3 , BrO_3 , ClO_2 , ClO_4 and ClO_2 along with H_2 and O_2 . The Cl_2 would react radiolytically to form HCl within the vapor phase. The ClO_2 would decompose thermally or by reaction with reducing agents including the metal can.

The possible importance of the radiolysis of brine around a can will depend upon the residence time for the brine and this in turn will depend upon the rate of heat up of can and surroundings.

With a 5 Kw can, the temperatures at the ends of the can will exceed the boiling temperature of brine at times subsequent to about 14 hr after burial. Because of the short exposure time, it can be assumed that radiolysis of liquid around a 5 Kw can will be of negligible importance.

The temperatures at the ends of a 2 Kw can do not exceed the boiling temperature of brine until after a period of about six months following burial. If it is assumed that water vapor does not escape from the can region for some reason (e.g., plugs in the crushed salt backfill) essentially all liquid which entered the can region during this period would remain as liquid. A conservative estimate is that one-half of the amount (0.6 liters max) which enters the region remains and is irradiated for the entire 6 month period. At 10^5 rad/hr, the rate of production of H₂ is 0.3 mole/yr at G(H₂) equal to 2.1, and the total production of H₂ is 1.5 moles during a 6 month period. As shown in Table 4, the 0.3 mole/yr rate for H₂ is well below the maximum rate at which radiolytic H₂ would appear around a can as a result of the migration of brine to the can. The maximum amounts of O₂, ClO₃⁻, BrO₃⁻ and Cl₂(HCl) would also be well below those associated with the migrating brine.

APPENDIX 5

Hydrolysis and Pyrolysis of Brine-Salts Around Waste Can

5-1. Pyrolysis of Chlorates and Bromates

As discussed in Appendix 4, it is possible that chieretes and bromates will be formed within the migrating brine inclusions.

Upon passage of the brine inclusions into the open spaces around a can, the water will vaporize leaving precipitated salts which include any chlorates and bromates. Providing that the temperatures around the can are high enough, the chlorates and bromates will undergo thermal decomposition. Information bearing on thermal decomposition of particular chlorates and bromates which may be present is summarized below:

a. NaClOj

Decomposition starts at temperatures slightly above the melting point;^{5.1} 263°C. The decomposition at 300°C was reported to amount to 0.5% during two days exposure.^{5.2} The onset of rapid decomposition took place at 465°C.^{5.2} The temperature of decomposition is lowered by many types of catalysts including sand and KCl.^{5.1,5.3}

The decomposition products are NaCl, NaClO₄, and O₂.^{5.1-5.3} The perchlorate decomposes into NaCl and O₂ near the fusion temperatures $482^{\circ}C$.^{5.1,5.2}

b. $Mg(C10_3)_2$

Thermal decomposition of this compound yields $MgCl_2$, $Mg(ClO_4)_2$ and O_2 .^{5.3} The hydrate, $Mg(ClO_3)_2$ °6H₂O, melts at 35°C and decomposes at 120°C.^{5.4} The products of decomposition of $Mg(ClO_4)_2$ include, under some conditions, MgO and Cl₂ along with MgCl₂ and O₂. It has been suggested^{5.5} that these products are in equilibrium,

 $M_{gO}_{(6)} + Cl_{2}_{(g)} - M_{gCl_{2}} + 1/2 O_{2}_{(g)}$ (5.1)

I concluded that the formation of Cl_2 under the conditions prevailing around a can would be unlikely.

The decomposition temperature for $Mg(ClO_4)_2$ is 250°C.^{5.4}

c. NaBrO3

Thermal decomposition produces NaBr and O_2 .^{5.5} Decomposition takes place readily in the temperature range 300 to 368°C.^{5.5}

f. $Mg(BrO_3)_2$

The principal products of thermal decomposition are MgO, Br₂ and O_2 .^{5.5} The decomposition temperatures are in the neighborhood of 300°C.^{5.5}

It should be emphasized that decomposition temperatures within the mixture of salts from the brine might be substantially below those for the pure compounds.5.3

It may be noted that it is unlikely that irradiation of any oxygen-containing salts around a can will have important effects on the stabilities of these salts. In order to illustrate this idea, assume that the dose rate is 10^5 rad/hr and that the G-value for decomposition is 4.^{5.6} Then the fractional decomposition per year is about 0.5. It seems likely that thermal effects will outweigh radiation effects on decomposition.

5-2. Hydrolysis of MgCl₂ to form HCl

Magnesium chloride reacts with water (including water of hydration) or steam at high temperatures to form HCl. 5.7-5.10 The overall reactions are usually represented as, 5.8,5.10

$$M_{gCl_{2}} + H_{2}0 = M_{g}(OH)Cl + HCl$$
 (5.2)

and

 $2M_g(OH)C1 = M_gC1_2 + M_gO + H_2O$ (5.3)

The available fragmentary information on these equilibria indicate that reaction 5.2 will go to completion to the right at temperatures above about 180° C (Table 5.1) providing that the HCl moves away from the MgCl₂. Complete hydrolysis through reaction 5.3 takes place only at temperatures over 520°C.^{5.10}

Table 5.1. Compositions of Steam-HCl Mixtures Over Mixtures of MgCl₂ and the Hydrolysis Product

(Vol \$)
99.2
92.1
79.0
33.5
30.3
37.85

AW. Moldenhauer, Z. Anorg. Chem. <u>51</u>, 369 (1907), Refs. 5.8 and 5.9.

b_{System} probably not at equilibrium.
APPENDIX 6

Brine Inflow by Cavity Migrati ...

Introduction

Theoretical calculations and experimental observations led Bradshav and coworkers^{6,1} to conclude that the rate of migration of a brine cavity is directly proportional to temperature gradient at the site of the cavity and that the proportionality constant is dependent upon temperature. Their conclusions can be expressed as shown in Eqn. 6.1,

$$X_{\Delta t} = \frac{\Delta T}{\Delta X} f(T) (\Delta t)$$
 (6.1)

where X_{A+} = migration distance of cavity during time interval Δt ,

 $\frac{\Delta T}{\Delta X} = \text{average temperature gradient at cavity, and}$ f(T) = cavity migration rate per unit temperature gradient at average temperature, T.

Theoretical and experimental values of f(T) presented by these vorkers^{6.1} are reproduced in Fig. 6.1. These workers also reported^{6.1,6.2} estimates of brine inflow for the following particular system: reference dimensions for waste can as shown in Fig. 1 of text; 1.66 Kw initial heat output with 3 1/3-year aged waste; cans positioned on 10-ft. centers; and temperatures and temperature gradients as shown in Fig. 6.2. They used their theoretical values of f(T), Fig. 6.1 in making these estimates. These particular characteristics of the wastes and of the temperatures and temperature distributions do not conform to those which are presently under consideration.

I made estimates of brine inflow to two different waste can systems which are presently under consideration and for which temperature-time-position information was available. The reference dimensions for these cans were the same as those used by Bradshaw et al., $^{6.1,6.2}$



Fig. 6.1 - Values of f(T) vs Temperature



Fig. 6.2 - Temperature-Time-Distance Relationship Used by Bradsbaw and Cowoikers

(Fig. 1 of text). Some other characteristics of these waste-can systems are summarized below.

	Case C-1	Case B-2	Case C-2
Heat output at burial	2 Kv	5 Kw	5 Kv
Age of waste at burial	10 years	10 years	10 years
Layout in mine	Cans on 22 ft centers. Two rows of cans per room.	Cans on 17 ft centers.	Cans in one row in middle of 30 ft room 42 ft between cans.

Temperatures for Cases C-1 and C-2 were available for times out to 50 years-three dimensional calculations.²

Temperatures for Case B-2 were available for times out to 5 years and for the horizontal midplane only-two dimensional line source calculations.¹⁷

The method which I employed in making the estimates of brine inflow was basically the same as that of Bradshaw et al. However, my method differed in two important respects; (1) I used the more conservative estimates of f(T) which are shown in Fig. 6.1 and replotted in Figs. 6.3 and 6.4, and (2) I assumed that the salt fractures at high temperatures starting at 250°C,²⁰ and that the edge of the open spaces around the can follows the 250°C front within the salt.^b In the event that the salt does not reach 250°C, I assumed that the edge of the open spaces remains at the original distance of 5 inches from the center of the can.

Details of the estimation method are presented below together with results of estimation for the two waste-systems, Case C-1 and Case B-2.

⁸The results of temperature calculations for this case became available after this report was drafted.

^bT. R. Anthony and H. E. Cline working at G. E. in Schenectady have recently published several papers dealing with their experimental and theoretical work on brine migration in KCl.^{6,7-6,11} Their theoretical analyses is applicable also to NaCl, and is more complete than that of Bradshaw. We will discuss the possible applications of their findings to waste repository in another paper.



Fig. 6.3 - Cavity Migration Rate vs Temperature





 6-2. Summary of Procedures for Accomplishing Estimates of Inflow of Brine, and Summary of Data and Results for Cases C-1 and B-2. My step-by-step procedures for accomplishing estimates of brine inflow at a given elevation are set forth below together with

results of estimates:

- I. Make linear plot of T vs X^D at various times of interest. Values of X go to maximum radius of interest. Examples; Case C-1, midplane, Fig. 6.5, Case B-1, midplane, Fig. 6.6.
- II. Plot T <u>vs</u> time at various radii using plots from No. I. Examples; Case C-1, midplane, Fig. 6.7, Case B-1, midplane, Fig. 6.8.
- III. Plot $\frac{\Delta T}{\Delta X}$ vs time using plots from No. I. Examples; Case C-1, midplane, Fig. 6.9 and B-1, midplane, Fig. 6.10.
- IV. Estimate time required for cavity starting at given redius, X₀, to reach edge of hole. The following steps are involved. IV-1. Select value of X.
 - IV-2. Select appropriate time interval during which T and $\frac{\Delta T}{\Delta X}$ at site of cavity does not change by too large a factor so that graphical estimations of average T and $\frac{\Delta T}{\Delta X}$ is feasible.
 - IV-3. Estimate average T and $\frac{\Delta T}{\Delta X}$ during selected time interval using plots from Nos. II and III.
 - IV-4. Estimate average f(T) during selected time interval using average ? from No. IV-3 and also using plots of f(T) vs T (Figs. 6.3 and 6.4).
 - IV-5. Evaluate estimate of migration distances, $\Delta X_{\Delta t}$, during selected time interval, Δt , using Eqn. 6.1.
 - IV-6. Repeat above steps IV-1 through IV-5 using new value of X_o equal X_o^1 $X_a^1 = X_o - \Delta X_{\Delta t}$

^ABasically the same as that of Bradshav.^{6.3} ^bHorizontal distance from the center of the can.



Fig. 6.5 - Salt Temperature vs Distance from Center of Can at Several Different Times After Burial, Midplane (Case C-1, 2 Kw Can)









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Fig. 6.8 - Temperature vs Time After Burial at Several Different Radii, Midplane, Case B-2 (5 Kw Can)





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Fig. 6.10 - Temperature Gradient vs Time After Burial at Different Radii, Case B-2 (5 Kv Can)

IV-7. Repeat steps IV-1 through IV-6 until cavity which started at X_n reaches edge of open spaces around can.

V. Make a plot of the estimated time, t, required for a cavity to reach edge of hole <u>vs</u> the value, X_0 , of the radius at the initial location of the cavity.

Plots for Cases B-2 and C-1 are in Figs. 6.11 and 6.12. VI. Make a list of t and of V at given values of X_0 and then plot V <u>vs</u> t. Values of t at the given values of X_0 are obtained from No. V. Values of V at the same values of X_0 are calculated from Eqn. 6.2,

$$V = bh\pi (X_0^2 - X_1^2)$$
 (6.2)

vhere

V is the volume of brine within a right cylindrical annulus of height, h, and of radii X_0 and X_1 . The latter radius, X_1 , is the distance between the center of the can and the edge of the hole. The b in Eqn. 6.2 is the fractional volume of brine within the salt at the time of burial (the value of b is taken as 0.5%).

Plots of V vs t for Cases C-1, B-2 and C-2 are set forth in Figs. 6.13, 6.14 and 6.17. The assumed value of h is 10 ft in each case. Note that estimated values of inflow for Cases B-2 cod C-2 are in fair agreement at times up to about 2 years.

VII. Estimates of inflow rate vs time obtained from plots No. VI are plotted in Fig. 6.15 and 6.16 for Cases C-1 and B-2.

6-3. Comments and Discussion

6.3.1 Temperature Symmetry Around Can

Consideration of the calculated temperature values for Case C-1 showed that temperatures are distributed nearly symmetrically around the center line of a can out to distances and times of at least 3 ft and 30 years, respectively. This despite the fact that the separation between nearest-neighbor-cans is much greater in one direction than in any of the other three directions-38 ft vs 22 ft.

ⁿI did not consider longer times or greater distances.



Fig. 6.11 - Time Required for Inclusion Starting at Given X, to Migrate Into Hole, Midplane, Case B-2 (5 Kw Can)











Fig. 6.14 - Total Cumulative Brine Inflow vs Time After Burial, Nidplane, h = 10 ft, Case B-2 (5 Kv Can)









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Temperatures within the horizontal planes passing through the top and bottom of a can are less than those in the midplane. The planes which are midway between the end and midplanes are about equivalent in temperature to the midplane.

6-3.2 Brine Inflow from Salt Above Top of Can,^E Case C-1.

I estimated that brine inflow to the top of the can from hemispheres above the top would be about 24 during the first 25 years; see Fig. 6.13. Similar: ', inflow to the bottom of the can from salt below the bottom would be 24 during the same period of time. 6-3.3 Effective Values of h for Brine-Inflow Estimates, Case C-1

The estimated values of total brine inflow which correspond to midplane conditions and to an assumed h-value of 10 ft are too high because of the lower migration rates at the end-planes. However, the middle one half or more of the can is at midplane conditions (Section 6-3.1 above), and if it is assumed that the inflow rates decreased linearly from this middle one-half to the ends, it can be shown that the inflow values estimated as stated above are in error by only 5 to 10%. This is well within the overall uncertainty of the estimates.

6-3.4. Changes with Time in the Brine Content of Salt at Edge of Hole, Case C-1.

Estimates of the brine content of the salt at the edge of the hole at exposure time, t, were made for Case C-1 using Eqn. 6.3,

$$b_t = \frac{(inflow rate)_t}{(nigration rate)_t}$$
 (6.3)

where (migration rate)_t is the value of this quantity at the edge of the hole estimated as described in Section IV-3 and IV-4 above, and b_t in the brine content of the salt at the edge of the hole at the given time, t.

Values of inflow and migration rates and of the resulting values of b₁ at certain times ranging up to 50 years are listed in Table 6.1.

^BAnd from below bottom of can.

These values indicate that the brine concentration within the salt at the edge of the hole remains approximately constant during the exposure times considered (50 years).

No estimates were made for Case B-2 because of the limited times for which temperature data were available and because the diameter of the hole was presumably changing with time. Values for Case C-2 were not available at the time these estimates were made.

Table 6.1. Lists of Migration Rates at Edge of Hole, Brine Inflow Rates and Resulting Values of Brine Concentrations in Salt at Edge of Hole

Exposure Time (year)	Migration Rate (ft/year)	Inflow Rate ^C (1/year)	b (1/ft)
·0			3.66
.73	.17	.62	3.6
1.4	.19	.62	3.3
3.3	.25	.76	3.0
3.8	.24	• 80	3.4
7.6	.32	.88	2.8
13.4	.26	.85	3.2
26.8	.33	•55	1.7
50.0	•036	•30	3.5

ACalculated for 0.5 vol \$ brine; radius = .417 ft and h = 10 ft. CBases for these values included the assumed values: radius of hole, .417 ft; brine volume in salt, 0.5 vol \$; h = 10 ft.

APPENDIX 7

Estimation of Dose to and Total Hydrogen Generation in Migrating Brine; Procedure and Results

7-1. Procedure

Prepare a plot of dose rate <u>vs</u> position within salt over the ranges of time which are of interest, Fig. 7.1.

Estimate the dose absorbed by brine within a cavity starting at given X_0 and moving through a small distance ΔX in time Δt . Use ΔX , Δt relationships which were obtained as part of the estimates of brine inflow which were discussed in Appendix 6. Repeat this process until the cavity which started at X_0 reaches the particular radius of interest. Sum the doses received by the migrating brine during its migration between the given radial positions.

7-2. Results for Case C-1

A list of estimated values of dose $\underline{vs} X_0$ for brine moving into the open spaces around a can for Case C-1 is set forth in Table 7.1. Figure 7.1 was employed in these estimates. It was assumed that the dose rate remained constant during the 27 years exposure period.

The results show that the great majority of the dose is accumulated at the high dose rates in the salt adjacent to the hole. Accordingly, the dose to the brine is approximately independent of the value of X_{a} .

Values for the concentration of radiolytic H₂ which correspond to the listed dose values when G(H₂) equals 2.1 and when all H₂ is retained in the brine are listed in the final column of Table 7.1. 7-3. Results for Case B-2

A list of estimated values for dose to the migrating brine and for the hydrogen concentration within the brine, calculated as described above for Case C-1, is set forth in Table 7.2.



Fig. 7.1 - Dose Rates in Salt at Midplane, Case C-1, 2 Ky, 10 Year Aged Waste, 1 Year After Burial

Table 7.1. List of Doses Received by and Hydrogen Generated in Brine Which Starts at Different Radial Positions, X₀ and Migrates to Edge of Hole, Case C-1 Midplane^b

X ₀ (ft)	Time to Reach Edge of Hole (year)	Dose (rads) x 10 ⁸	Conc. of H_2 at $G(H_2) = 2.1$ (mole/4)
.5	.73	5.8	1.6
•6	1.4	8.5	2.2
.8	3.3	10.9	2.9
1.2	7.6	8.8	2.4
1.6	13.4	9.2	2.5
1.2	26.8	7.9	2.1

Described in Appendix 6.

^bDose rates illustrated in Fig. 7.1 were assumed to remain constant throughout the 27 year exposure period.

Table 7.2. List of Doses Received by and Hydrogen Generated in Migrating Brine Entering Edge of Open Spaces Around Can, Case B-2ⁿ, Midplane^b

Time After Burial (year)	Dose (Rad x 10 ⁸)	Conc. H_2 at $G(H_2) = 2.1$ (mole/#)
.25	2.0	.54
.75	1.9	.50
1.0	1.7	.45
2.0	1.3	.35
3.0	1.3	.35
4.0	1.3	.35

^ADescribed in Appendix 6.

^bDose rates were those in Fig. 7.1 multiplied by 2.5. Dose rates assumed to remain constant with time.

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