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**Effects of Gaseous
Radioactive Nuclides on the
Design and Operation of
Repositories for Spent LWR
Fuel in Rock Salt**

G. H. Jenks

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ORNL-5578
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Contract No. W-7405-eng-26

CHEMICAL TECHNOLOGY DIVISION

**EFFECTS OF GASEOUS RADIOACTIVE NUCLIDES ON THE
DESIGN AND OPERATION OF REPOSITORIES
FOR SPENT LWR FUEL IN ROCK SALT**

G. H. Jenks

With an Appendix by H. C. Claiborne

Date Published: December 1979

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The project was administered by the Office of Nuclear Waste Isolation,
Battelle Memorial Institute.

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ACKNOWLEDGMENTS

Helpful suggestions for this report were made by J. O. Blomeke, H. C. Claiborne, R. A. Lorenz, W. C. McClain, F. A. Posey, G. E. Raines, and A. J. Shor. G. E. Raines is associated with the Office of Nuclear Waste Isolation at Battelle Columbus Laboratories. The others are staff members of ORNL. The assistance and interest of these colleagues are gratefully acknowledged.

**EFFECTS OF GASEOUS RADIOACTIVE NUCLIDES ON THE DESIGN
AND OPERATION OF REPOSITORIES FOR SPENT LWR FUEL IN ROCK SALT**

G. H. Jenks

ABSTRACT

Information relating to the identities and amounts of gaseous radionuclides present in spent LWR fuel and to their release from canistered spent fuel under plausible storage and disposal conditions was assembled, reviewed, and analyzed. Information was also reviewed and analyzed on several other subjects that relate to the integrity of the carbon steel canister in which the spent fuel is to be encapsulated and to the expected rates of transfer of gaseous radionuclides through crushed salt backfill within a disposal room in a reference repository in rock salt. The advantages and disadvantages were considered for several different canister-backfill materials, and recommendations were made regarding preferred materials. Other recommendations relate to encapsulation procedures and specifications and to needs for additional experimental studies.

The objective of this work was to provide reference information, conclusions, and recommendations that could be used to establish design and operating conditions and procedures for a bedded salt repository for spent LWR fuel and that could also be used to help evaluate the safety of the repository. The results of this work will also generally apply to spent fuel repositories in domal salt. However, because the domal salt may have little or no brine inclusions within it, there may be little or no possibility that brine will migrate into open spaces around an emplaced canister. Accordingly, some of the concerns that result from the possible occurrence of brine migration in bedded salt may be of no importance in domal salt.

1. INTRODUCTION

Spent fuel (SF) from light water reactors (LWRs) contains all of the long-lived and stable nuclides that result from in-reactor operation of the fuel. These nuclides include isotopes of the noble gases helium, krypton, and xenon and also include some elements that are readily volatile or that can form readily volatile compounds in certain environments (viz.,

carbon, hydrogen, and iodine). Essentially none of these elements are present in solidified high-level waste (HLW) because they are separated during reprocessing and then disposed of in other waste forms. Their presence in SF leads to questions about the possibilities of release of gaseous and volatile radioactivities in repositories containing this waste and about the effects of possible releases on the design and operation of the repository.

The available literature contains much information that deals with these questions. I have assembled, reviewed, and analyzed information relating to the identities and amounts of gaseous radionuclides present in spent LWR fuel and have analyzed their release from canistered SF under plausible storage conditions. I have also reviewed and analyzed information on the integrity of the carbon steel canister in which the SF is encapsulated and on the rates of transfer of gaseous radionuclides through the crushed salt backfill within a disposal room in a reference repository. The advantages and disadvantages of several different canister-backfill materials are considered, and preferred materials are recommended. Other recommendations relate to encapsulation procedures and specifications and to needs for additional experimental studies.

My objective in this work was to provide reference information, conclusions, and recommendations that could be used to establish design, operating conditions, and procedures for a SF repository in bedded salt and that could also be used to help evaluate the safety of the repository.

The results of this work will also generally apply to SF repositories in domal salt. However, the domal salt may have little or no brine inclusions within it; hence, there may be little or no possibility that brine will migrate into open spaces around an emplaced canister. Accordingly, some of the concerns that result from the possible occurrence of brine migration in bedded salt may be of no importance in domal salt.

2. SUMMARY

The objective of this work was to provide reference information and conclusions and recommendations that could be used to establish design, operating conditions, and procedures for a bedded salt repository for spent LWR fuel and that could also be used to help evaluate the safety of the repository.

Information on the identities and amounts of gaseous radionuclides present in SF and on those that could be released from canistered SF under plausible storage and disposal conditions was assembled, reviewed, and analyzed. Information was also reviewed and analyzed on several other subjects that relate to the integrity of the carbon steel canister in which the SF is encapsulated and to the rates of transfer of gaseous radionuclides through crushed salt backfill within a disposal room in a reference repository in bedded salt. The advantages and disadvantages were considered for several canister-backfill materials, and recommendations were made regarding preferred materials. Other recommendations relate to encapsulation procedures and specifications and to needs for additional experimental studies.

The conclusions and recommendations include the following:

The canisters must be constructed to meet specifications and quality controls designed to ensure that they will remain mechanically intact throughout the period of retrievable storage in a repository. The specifications should include a value for the maximum acceptable leak rate from a sealed canister; this rate will depend very strongly on whether or not the total pressures of gases within the canister remain below atmospheric throughout the period of retrievability. Leak rates up to about 5×10^{-5} atm·cm³/sec could be acceptable if the initial pressure at maximum temperature is ≤ 0.5 atm and if the gases escaping from the fuel pins after the canister is sealed do not exceed an amount (~50 liters) which could cause the pressure to increase to ≥ 1 atm during the retrieval period. No significant leakage of radioactive gases would occur at pressures < 1 atm. Escape of more than ~50 liters from the fuel pins appears very unlikely, but experience with encapsulation, transportation, and emplacement of SF is needed to verify predicted behavior.

Escape of >50 liters could be accommodated without exceeding 1 atm pressure if the space around an assembly within the canister is left open (i.e., unbackfilled) or if the helium that is charged to the canister prior to sealing is at a pressure <0.5 atm.

Initial internal pressures >1 atm would require that the canister leak rate be $<4 \times 10^{-9}$ cm³/sec in order to ensure that the level of ⁸⁵Kr activity in unventilated disposal rooms does not exceed the recommended concentration guide level (RCG) within two or three years after emplacement of canistered 10-year-old SF. Ventilation of the disposal rooms was not precluded but was not evaluated.

Review and analysis of the corrosion characteristics of a carbon steel canister exposed to the corrosive environments that might be encountered after emplacement in bedded salt led to the conclusions that relatively rapid, localized corrosion is the most likely avenue through which the 1/2-in.-thick wall of such a canister could be breached in a relatively short period (2 to 30 years) after emplacement and that localized corrosion is a strong possibility unless special provisions are made to avoid it. Backfilling the space around the canister with a mixture of quicklime (CaO) and sand might prove to be a satisfactory means of preventing rapid, localized corrosive attack (as well as preventing generalized corrosion of the canister), and use of this backfill mixture was tentatively recommended. The period after emplacement for which the canister with this backfill would remain unbreached could exceed a century.

The recommendation to use a mixture of quicklime and sand for backfilling extended also to backfilling around the carbon steel sleeve, which might be used during retrievable storage of SF. If this recommendation is adopted, the thickness of the sleeve should be increased to 1/2 in. to ensure that it will not be collapsed by hole-closure stresses during the required period of retrievability.

On the basis of currently available information, there are no apparent reasons to expect that the suitability of the quicklime-sand mixture will prove to be inadequate. However, the chemical and physical properties are uncertain for the systems that would result if brine solutions came into contact with hydrated quicklime on the edges of the

backfill or on the surface of cracks within the backfill. These properties, along with radiation effects and carbon steel corrosion in this backfill material, must be established before the quicklime-sand mixture can be unequivocally recommended as backfill for the canister in salt.

Sand alone is a second choice for backfilling around SF canisters and sleeves. The suitability of this material would depend on the amount of in-migration of brine which will take place and on the length of time for which the canisters should remain unbreached. The use of other types of desiccants for backfilling around a canister was not precluded but was not examined.

The Zircaloy cladding on the fuel pins within a fuel assembly may undergo stress cracking if the Zircaloy is contacted by brine solutions. Accordingly, this cladding cannot be relied on for containment after the canister is breached. Stainless steel cladding could also be subject to stress cracking in brine solutions.

Evaluations of mechanisms by which a radioactive gas could be transported through crushed salt backfill within a disposal room showed that unconsolidated backfill will not provide an effective long-period retention of the gases within a room. Diffusion values calculated for krypton-air within crushed salt indicate that large fractions (~10%) of any krypton that leaks into the 1000-ft-long reference disposal room, which is open at each end, will have diffused out of the room into connecting corridors in about 60 years or less, depending on the initial location of the krypton within the room. Other radioactive gases such as tritium would diffuse more rapidly than krypton.

Breathing action, which results from changes in atmospheric pressure that are transmitted to a disposal room, will promote movement out of the backfill that is located within several feet of the open face of the backfill. This breathing would vitiate the room-sealing provisions that could be breached at the difference between ambient pressures which prevail within the repository from one time to another.

Other transport mechanisms, such as forced flow of stable gases that might be generated within the emplacement cavities or room, are unlikely to be as important in the transport of radioactive gases as diffusion and breathing.

3. PHYSICAL CHARACTERISTICS OF LWR FUEL ASSEMBLIES

3.1 Introduction

Information on the physical characteristics of unirradiated LWR fuel assemblies has been summarized by several workers.^{1,2} My list (Table 1) is based primarily on information obtained in refs. 1 and 2 and pertains to reactors using Zircaloy-clad fuel rods and, generally, the most recent core designs. Stainless steel rather than Zircaloy cladding was used in some early LWRs, and in 1977, stainless steel was still in use in three U.S. power LWRs: Connecticut Yankee [PWR, 600 MW(e)], San Onofre Unit 1 [PWR, 450 MW(e)], and La Crosse [BWR, 56 MW(e)].³ Additional information on the fuel assemblies used by several U.S. vendors of nuclear steam systems is given below.

3.2 Pressurized Water Reactors

Most of the information for PWRs in Table 1 pertains specifically to Westinghouse PWRs, and as stated in ref. 1, most of the information was obtained from RESAR-3.⁴ The 17×17 array assembly described in Table 1 was designed as a replacement for the 15×15 array assembly.⁵ There were no significant changes in either the outer dimensions or the fuel loading between the 17×17 and 15×15 arrays. Assemblies with 14×14 arrays have also been supplied by Westinghouse, and these were somewhat smaller in cross section (19.7 by 19.7 cm) and fuel loading than the 15×15 and 17×17 assemblies.⁶ The overall length was the same for all assemblies.³⁻⁶ The outer diameter of the fuel pins in the 14×14 and 15×15 arrays was greater than that in the 17×17 arrays — 1.072 cm compared with 0.95 cm in the latter arrays (see ref. 3, Table A-1).

The fuel assemblies used in the nuclear steam systems manufactured by Combustion Engineering⁸ had external dimensions a little smaller than those listed in Table 1. Those used in the nuclear steam systems of Babcock and Wilcox^{9,10} had somewhat larger dimensions than those listed in Table 1; the maximum lateral dimension was 21.7 cm, and the maximum axial dimension was 449 cm. The uranium loading in the assemblies of these PWR manufacturers was about the same or a little less than the value listed in Table 1.⁸⁻¹⁰

Table 1. Characteristic dimensions and some other parameters of unirradiated LWR assemblies^a

	PWR	BWR
Overall assembly length, cm	406	447
Cross section, cm	21.4 × 21.4	14.0 × 14.0
Fuel rod pin length, cm	385	406
Active fuel height, cm	366	376
Void volume in fuel rod, cm ³	23 ^b	28 ^c
Fuel rod OD, cm	0.950	1.252
Fuel rod wall, cm	0.057 ^d	0.086 ^e
Fuel rod array	17 × 17	8 × 8
Number of fuel rods per assembly	264 ^f	63 ^f
Uranium, MT ^g per assembly	0.461	0.183
UO ₂ , MT per assembly	0.523	0.208
Zircaloy, MT per assembly	0.108 ^h	0.100 ⁱ
Hardware, MT per assembly	0.026 ^j	0.012 ^k
Total nonfuel metal, MT per assembly	0.135	0.112
Total weight of assembly, MT	0.658	0.320

^aUnless otherwise noted, this information is based on that in refs. 1 and 2.

^bMy estimate based on rod dimensions and weight loading of UO₂.

^cEstimated from information in ref. 7.

^dFrom refs. 3 and 4.

^eFrom ref. 7.

^fSome spaces within an assembly do not contain fuel pins and may be used for other purposes.

^gMT = metric ton.

^hIncludes Zircaloy control-rod guide thimbles.

ⁱIncludes Zircaloy fuel-element spacers and fuel channel.

^jIncludes stainless steel nozzles and Inconel-718 grids.

^kIncludes stainless steel tie-plates, Inconel springs, and plenum springs.

A 17×17 array assembly described by Westinghouse in 1973-1974 (ref. 11) had a fuel pin active length of 416 cm rather than the 366 cm listed in Table 1. Also, the overall length of an assembly was increased to 474 cm, but the fuel loading per unit active length of fuel pin was unchanged. The South Texas Plant reactors are apparently using the longer fuel pins.¹²

3.3 Boiling Water Reactors

Most of the information for BWRs in Table 1 pertains specifically to GE/BWR/6, and as indicated in ref. 1, most of the information was obtained from GESAR-238 (1973).⁷ The Grand Gulf BWR (not completed) is characteristic of this design,¹³ a principal feature of which is the 8×8 fuel pin array within an assembly.¹⁴ Earlier BWRs, including Browns Ferry^{14,15} and Dresden 2,¹⁴ had a 7×7 array of fuel pins within the assemblies. However, the external dimensions of the assemblies have not changed significantly since Oyster Creek (BWR/2),¹⁴ nor has the fuel loading per assembly changed appreciably from one reactor to another. The diameters of the fuel pins have, of course, changed as the number of fuel pins per assembly changed (viz., either 1.427- or 1.448-cm OD in the 7×7 arrays, and 1.252-cm OD in the 8×8 arrays) (see ref. 3, Table A1).

4. FUEL ASSEMBLIES IN POOL STORAGE

Information on the number of commercial fuel assemblies in pool storage at the end of 1976 and on pertinent characteristics of the stored assemblies has been reported by Johnson.³ According to this author, there were 8674 fuel assemblies in storage at that time, including 1526 BWR and 1413 PWR assemblies discharged in 1976. Approximately 90% of the stored assemblies have Zircaloy-2 or Zircaloy-4 fuel-pin cladding. The remainder has stainless steel cladding.

Maximum fuel burnup on the stored fuel was 33,160 and 25,000 MWd per metric ton of uranium (MTU) on the Zircaloy-clad PWR and BWR assemblies, respectively, and 33,200 and 22,000 MWd/MTU on the stainless steel-clad PWR and BWR assemblies respectively.³

5. AMOUNT OF POTENTIALLY GASEOUS AND VOLATILE ELEMENTS IN SPENT FUEL

5.1 Pressurized Water Reactors

Table 2 lists values for the number of gram-moles, and related quantities, of potentially gaseous and volatile elements present within PWR fuel that has undergone burnup to 33,000 MWd/MTU.* The amounts of radioactivity associated with these elements after the fuel has decayed 10 and 100 years are also shown. The gram-mole and radioactivity information was obtained from the results of an ORIGEN calculation¹⁶ in which the recently updated¹ ORIGEN code was used. The physical characteristics of fuel assemblies listed in Table 1 were assumed in this updated code. Other assumptions included (1) operation in equilibrium cycles, (2) a reactor thermal power of 3800 MW, and (3) an average specific power of 37.5 MW(t)/MTU. No detailed calculations for other combinations of reactor characteristics, burnups, etc., were available. In general, the total amounts of the reactor products will be approximately proportional to the burnup.

Some information is included in Table 2 regarding the volumes and pressures of reactor-product gases that would result if 100% of the gases were released from the oxide fuel within a fuel pin. Information relating to the probable fractions of the gases that are released in practice is discussed in Sect. 6.

5.2 Boiling Water Reactors

Croff et al.¹⁶ conducted ORIGEN calculations for BWRs along with those for PWRs described in Sect. 5.1. Again, the physical characteristics of the fuel assemblies listed in Table 1 were assumed in the ORIGEN code, and the other assumptions included operation in the

*It is assumed that all spent LWR fuel that is considered for geologic storage or disposal will be of the UO₂ type. Mixed oxide (MOX) fuels will contain plutonium obtained by reprocessing reactor fuels, and presumably the spent MOX fuel will also be reprocessed and will not be placed in geologic storage.

Table 2. Amounts and radioactivity of potentially gaseous and volatile elements in spent PWR fuel

Amounts per PWR spent fuel assembly at several decay times ^a									
Element	Net yield at 1 year ^b (%)	Amount (g-moles)			Radioactivity (Ci)		Volume of gas at 10 years and at 100% release (liters, STP)	Pressure of gas at 100% release and 100°C ^c (psia)	Probable fractional amount as gas or volatile within gas space ^d (%)
		1 year	10 years	100 years	10 years	100 years			
Tritium	1.8 × 10 ⁻⁴	0.0123	0.00732	4.5 × 10 ⁻³	215	1.36			Very small (<0.01)
Helium	0.49	0.335	0.386	1.27	0	0	8.62	32	<50
Carbon	1.8 × 10 ⁻⁴	0.0125	0.0125	0.0123	0.779 ^e	0.770 ^e			<10
Bromine	0.18	0.124	0.124	0.124	0	0			Very small
Krypton	2.91	2.00	1.94	1.88	2.29 × 10 ^{3f}	6.79 ^f	43.5	159	<50
Iodine	1.23	0.841	0.842	0.842	0.0146 ^g	0.0146 ^g			Very small (<0.01)
Xenon	26.79	18.34	18.34	18.34	0	0	410.8	1495	<50
Cesium	13.37	9.18	8.15	5.33	3.82 × 10 ^{4h}	4.77 × 10 ^{3h}			Very small

^a33,000 MWd/MTU. 0.461 MTU charged to fuel assembly. Values for gram-moles and radioactivity from refs. 1 and 16.

^bNumber remaining in 1-year-old spent fuel per 100 fissions.

^cAssuming that the volume of the gas space within the 204-pin, 15 × 15 fuel assembly is 5.5 liters.

^dSee Sect. 6 of text.

^ePresent as ¹⁴C.

^fPresent as ⁸⁶Kr.

^gPresent as ¹²⁹I.

^hPresent as ¹³⁷Cs. In addition, 2.3×10^4 -year ¹³⁵Cs has 0.159 Ci at both times, and 2.06-year ¹³⁴Cs has 2.5×10^3 Ci at 10 years and negligible at 100 years.

equilibrium cycles and a reactor thermal power of 3800 MW. The assumed burnup was 27,500 MWd/MTU, and the average specific power was 25.9 MW(t)/MTU.¹

No tabulations for BWRs analogous to those in Table 2 are included here. For purposes of making rough estimates, the assumption may be made that the amounts of reactor products that form and remain after a given decay period are proportional to the burnup and are equal to those in PWR fuel at the same burnup.

6. PHYSICAL CHEMICAL STATE OF POTENTIALLY GASEOUS AND VOLATILE ELEMENTS WITHIN SPENT FUEL PINS FROM UO_2 -FUELED LWRs

6.1 Krypton and Xenon

Much experimental information has been published regarding the fractional amount of these fission product elements, which are found within the gas plenums of irradiated fuel pins. These experimental data show that the fractional release from the UO_2 fuel compacts depends on both the burnup and temperatures during irradiation, generally increasing with increasing values of either or both of these exposure parameters. Maximum values for fractional release indicated by the available experimental data and the reported^{17,18} correlations of these are listed in Table 3 for several ranges of burnups and temperatures to which the LWR fuel might be exposed.

Information on temperatures of LWR fuel during reactor operation is generally reported in terms of average and peak thermal power per unit length of fuel pin and, occasionally, in terms of peak temperatures. Some values for these parameters in several PWRs and BWRs are listed in Table 4.

During equilibrium cycle operation of an LWR, the assemblies comprising the reactor core are shifted from one location to another at intervals during the complete cycle. An assembly may operate at two or three different locations and power levels during its operating life. I found no available information on either the actual or predicted thermal exposure histories of given assemblies within a reactor. Furthermore, because the effects on the fractional release of xenon or krypton from operating at different temperatures have not been firmly established, knowledge of the thermal history of an assembly might not be sufficient for the estimation of reliable values for the fractional release.

The maximum fractional release of xenon and krypton would be that resulting from continued exposures at the maximum temperature (maximum power per unit length of pin). For the 15×15 PWR fuel assemblies with burnups of about 33,000 MWD/MTU, my estimate of the maximum fractional release

Table 3. Maximum values for fractional release of xenon and krypton during reactor operation of UO_2 fuel in LWRs at several burnups and temperatures^a

Volume average temperature (°C)	Burnup (MWd/MTU)	Fractional release
1000 (12 kW/ft) ^b	20,000	0.12
	25,000	0.15
	30,000	0.20
	35,000	0.30
	40,000	0.42
	45,000	0.55
1400 (16 kW/ft) ^b	20,000	0.35
	25,000	0.40
	30,000	0.50
	35,000	0.55
	40,000	0.65
	45,000	0.75
<1000 and with centerline less than 1250 ^c	20,000	0.0025
	25,000	0.0050
	30,000	0.010
	35,000	0.015
	40,000	0.030
	45,000	0.060

^aBased on information reported in refs. 17 and 18.

^bSee ref. 17, Fig. 3, and ref. 18, Fig. 3.

^cSee ref. 17, Fig. 6.

Table 4. Average and maximum thermal power per unit length of fuel pin in several LWRs

Reactor type and name	Thermal power per unit length of fuel pin (kW/ft)	
	Average	Maximum
PWR, 14 × 14 core		
Kewaunee ^a	(6.9) ^b	17.30
PWR, 15 × 15 core		
Turkey Point Units 3 and 4 ^a	(7.2) ^b	17.9
PWR, 17 × 17 core ^c	5.43	(13.6) ^b
South Texas Units 1 and 2 ^d	5.33	13.30
BWR/4		
Browns Ferry Units 1, 2, and 3 ^e	7.05	18.35
BWR/5		
Zimmer Units 1 and 2 ^f	7.1	18.5
BWR/6		
Grand Gulf Units 1 and 2 ^g	6.04	13.40

^aFrom ref. 19.

^bValues in parentheses were found by assuming a peak to average ratio of 2.5 (ref. 11).

^cFrom ref. 5.

^dFrom refs. 11 and 19.

^eFrom refs. 15 and 19.

^fFrom refs. 14 and 19.

^gFrom refs. 13, 14, and 19.

is 0.45 to 0.5.* Information in Table 2 can be used to show that a fractional release of 0.5 would produce a xenon and krypton gas pressure within the fuel pin of about 850 psi at 100°C. In addition, the helium gas that is charged to the pins during manufacture (Sect. 5.2) might add up to 500 psi at 100°C, bringing the total pressure to 1350 psi. This estimate is in near agreement with the estimate of Hann and Wilson²² of the maximum pressure that might be present within pins in a few of the PWR assemblies now in pool storage. These workers²² suggested that the majority of the stored PWR assemblies would have pressures of 250 to 550 psi and occasionally 800 psi. The temperatures at which these pressures prevail are presumably those at the surface of the fuel pins during pool storage, that is, <60°C.³ They did not describe the sources of their information nor their estimation methods.

For the BWR/3, BWR/4, and BWR/5 assemblies that are in pool storage, I have estimated that the maximum fractional release of xenon and krypton is about 0.4.* By calculating ratios of BWR maximum burnups, gas volumes,** etc. to those for the PWRs discussed above, I have estimated that the maximum pressure of xenon and krypton within the fuel pins of stored BWR assemblies is about 450 psi at 100°C.[†] Again, there is reasonable agreement with the maximum pressure suggested by Hann and Wilson (200 to 300 psi during pool storage).²² These workers also stated that typical pressures are much lower (about 30 psi), although they occasionally reach 75 psi, and that they only rarely reach the maximum.²² The bases for these statements and estimates were not given.

*It should be emphasized that the average value for the fractional release of xenon and krypton within all of the fuel pins within a LWR will probably be very much less than the maximum values of 0.4 to 0.5 assumed in these paragraphs. The reactor safety study, WASH-1400,²⁰ assumed that, on the average, 8% of the total inventory of xenon and krypton would be released to the gas plenums of the fuel pins. Others²¹ have assumed that the average release of these elements is even lower (~1.3%).

**The gas space within the fuel pins in these BWR assemblies is about 50 cm³.¹⁵

[†]Apparently, no high pressures of helium were used in these BWR assemblies.

6.2 Helium

No specific information is available on the release of helium during reactor operation. It seems reasonable to assume that the fraction will be about the same as those for xenon and krypton, discussed in Sect. 5.1. Most of the helium that forms after reactor operation will probably be retained within the oxide compacts at the relatively low temperatures that then prevail. (Diffusional release of xenon and krypton from UO_2 fuel compacts during reactor operation is believed to be negligible when the UO_2 temperature is less than about 900°C .^{17,23} Presumably, this would also be true for diffusional release of helium.)

As can be seen in Table 2, the total inventory of helium that is a product of reactor operation is small relative to the amounts of xenon and krypton produced during the reactor operation — about 2% of the total inventory of noble gases in the 10-year-old SF.

Helium comprises most or all of the gaseous atmosphere within the fuel pin prior to reactor operation, and this helium will remain within the intact pin. Varying amounts, ranging from pressures of a few to several hundred pounds per square inch at room temperature, have been used in PWR fuel pins.* The purpose of this added helium is to promote heat transfer across the gap between fuel and sheath.

6.3 Tritium

A large fraction of the tritium produced within the oxide fuel is released during reactor operation, but this is tightly absorbed within the Zircaloy cladding.²⁷⁻³⁰ Where stainless steel rather than Zircaloy is being used, most of the released tritium will probably have diffused

*Gas volume and pin void space data for H. B. Robinson 2 fuel pins, reported by Lorenz et al.,²⁴ correspond to helium pressures of 210 psi at room temperature.

General Electric began using 3-atm helium prepressurization in BWR fuel pins in late 1978 according to information presented at a recent topical meeting of the American Nuclear Society.²⁵ At the same meeting, Westinghouse verbally reported helium prepressurization as 450 to 500 psi, depending on plant.²⁶

through the steel cladding and into the reactor coolant during reactor operation.^{30,31} It seems reasonable to assume that less than 1% of the tritium produced within the reactor will be present as a gaseous material within the gas plenum of fuel pins.

6.4 Cesium

Part of the fission product cesium may escape the oxide fuel during reactor operation. The escaped cesium is expected to form CsI or other low-vapor-pressure compounds within the gap between sheath and fuel.^{28,32-34} Experimental results reported by Lorenz et al.³⁵ confirm this expectation for H. B. Robinson fuel pins.

6.5 Iodine

Inspections of Zircaloy-clad spent LWR fuel have shown that part of the iodine is retained in the fuel and that the remaining part is fixed by reaction with cesium or other metals at the Zr-ZrO₂ interface.²⁸ Theoretical considerations have shown that any iodine released during reactor operation will react with cesium to form CsI or with zirconium in the cladding to form zirconium iodides.³²⁻³⁴ All of these metal iodides have very low vapor pressures at the temperature expected during storage and disposal of SF assemblies (<250°C).³²

Reported experimental results show that iodine may be released, with low yield, from solid CsI during gamma irradiation at room temperature.³⁶ Because free iodine, I₂, is very reactive with most metals, any that is formed by radiolysis of CsI will likely back react with the accompanying radiolytically formed cesium metal or with other nearby metals at the temperatures that will prevail during geologic storage or disposal.

Experimental work reported by Lorenz et al.³⁵ shows that iodine (and cesium) purged from H. B. Robinson gas space by purified helium condensed at ~450°C, indicating that these nuclides were present as CsI. Very little iodine was present in volatile forms such as I₂, HI, and organic iodides.

6.6 Carbon

It is possible that most of the carbon, including that initially present as an impurity in the fuel (~100 ppm corresponding to 3.4 g-moles per FWR assembly),¹ will be retained within the fuel in the form of carbides or as CO.³⁷ It is also possible that some of the CO would be released to the gas space, from which some might react with the Zircaloy cladding to form ZrC and ZrO₂.³⁸ Apparently, no direct information is available on the CO or ¹⁴C content of the free gases within SF pins. However, a large amount of N₂ was reported from mass spectrometer analyses of gases from fuel pins irradiated in the T. B. Robinson 2 reactor,²⁴ and because N₂ and CO cannot be distinguished easily in the mass spectrometer, it is conceivable that most of the reported gas was, in fact, CO. Assuming that this was the case, the amount of CO in the gas corresponds to 2.5 to 3% of the carbon that is probably present initially in the fuel.¹

It is apparent that the possibility exists that a significant fraction of the ¹⁴C that forms during reactor operation (primarily from an n,p reaction on ¹⁴N) may be transferred to and remain in the gas phase as CO. However, it appears likely that this fraction will be less than 0.10.

7. CONCEPTS FOR RETRIEVABLE STORAGE AND/OR FINAL DISPOSAL OF LWR SPENT FUEL IN BEDDED SALT

7.1 General

The concepts favored in the United States for the geologic storage or disposal of spent LWR fuel have been developed around the assumption that the fuel assemblies will not be dismantled. One or more complete assemblies will be sealed within a suitable metal canister, and, in a salt repository, the canister will be emplaced in a vertical hole drilled in the floor of an excavated room within the salt formation.

It is generally assumed that the canisters will be stored in a readily retrievable manner for some period of time following the initiation of repository operation. "Readily retrievable" means that a given canister can be removed and transported to surface facilities with approximately the same effort and time that were required for the emplacement. It also implies that the canister can be stored safely in appropriate surface facilities for extended periods after retrieval. In order to guarantee this state of ready retrievability, the canister must be protected from any corrosive or mechanical effects which might lead to failure of the containment during the period of retrievability. A sleeve within the emplacement hole or an overpack on the canister are conceivable means of achieving the required protection.

For final disposal, the sleeve or overpack might not be needed depending on (1) the corrosive and mechanical environment around an emplaced canister and (2) the provisions within the repository for retaining radioactive gases prior to and after decommissioning.

7.2 Kaiser Engineers Conceptual Design

A conceptual design of a national waste terminal storage repository in bedded salt for spent LWR fuel has been prepared for the U.S. Department of Energy by Kaiser Engineers.³⁹ The dimensions and related information for waste packages, emplacement holes, and storage rooms will serve as references for use in this paper. I have assembled this

information in Tables 5 and 6 and in Figs. 1 and 2.* As can be seen, a sleeve is specified for use with retrievable emplacements, but none is specified for nonretrievable disposal.

*The purpose of the vent in Fig. 1 was not explained.

Table 5. Mine storage room dimensions and canister layouts
(Kaiser Engineers conceptual design)

Room height	19 ft
Room width	17.5 ft
Room length	4000 ft
Pillar width	142.5 ft
Number of canister storage rows per room	2
Spacing between rows	5.5 ft
Distance from row center- line to pillar	6 ft
Canister spacing along row	4 ft (on centers)
Average number of canisters per 1000 ft of room	481

Table 6. Dimensions and other information for canister,
sleeve, and emplacement hole
(Kaiser Engineers conceptual design)

<u>Canister</u>	
Length	15 ft, 1 in.
Outside diameter	14.5 in.
Inside diameter	13.5 in.
Material	Carbon steel
Contents	1 PWR or 2 BWR assemblies, remaining spaces filled with sand
<u>Emplacement holes in salt</u>	
Retrieval period	
Diameter	20 in.
Depth	22 ft
Counterbore	24-in. diam; 5 ft deep
Postretrieval period	
Diameter	18 in.
Depth	23 ft
Counterbore	24-in. diam; 1 ft deep
Sleeve during retrieval period	
Material	Carbon steel
Length	15 ft
Outside diameter	17.5 in.
Inside diameter	17 in.
Bottom	Closed
Top	Brazed to a cast iron alignment ring
Maximum temperatures (for systems emplaced in final disposal mode)	
Salt	
Initial	28°C
Peak	140°C at 5 years after storage of 10-year-old SF
Within stored PWR assemblies, peak	184°C at 4 years after storage of 10-year-old SF

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Fig. 1. Emplacement hole and waste package — retrieval period.

Fig. 2. Emplacement hole and waste package — postretrieval period.

8. FACTORS INFLUENCING LEAKAGE OF RADIOACTIVITY FROM EMPLACED SPENT FUEL CANISTER AND ACCUMULATION IN OVERLYING ROOM DURING RETRIEVABLE STORAGE

8.1 Introduction

The possibility of radioactivity leakage during this period will depend on several factors, including (1) gas tightness of the canister, (2) relative pressures of gases inside and outside the canister, and (3) the amounts of radioactive gases which leak from the fuel pins into the canister. These factors are considered below. The relative gas pressures are important because they will influence rates and direction of gas leakage across the walls of a canister. In particular, if the internal pressure is below that of the gas surrounding the canister, any leakage will be from the surroundings into the canister; no transfer of radioactivity out of the canister could take place until the internal pressure increases to almost the equal of the external pressure (see Appendix A).

8.2 Relative Pressures of Gases Inside and Outside the Canister

8.2.1 Sources and amounts of gases inside the canister

8.2.1.1 Helium charge. Helium gas should be charged to the loaded canister before it is sealed to permit leak testing of the sealed canister by sensitive helium leak detectors. The pressure of this added helium should not exceed ~ 0.5 atm at the maximum canister temperature in order to avoid contributing unnecessarily to the possibility of encountering internal pressures that equal or exceed the gas pressure outside the canister (~ 1 atm).

Sensitive leak testing of the canister containing helium at pressures less than 1 atm could be accomplished by placing the canister inside a suitable chamber which can be evacuated and from which the gases can be passed through a helium leak detector. This general method of leak testing is well established.

8.2.1.2 Solid backfill in canister. Several different materials, including sand,³⁹ have been suggested for backfilling the open spaces that remain within a canister after loading a spent LWR fuel assembly. Absorbed and occluded gases, water, and organics, which might contribute appreciably to total gas pressures under the irradiation and heating within an emplaced canister, should be stripped from the backfill material prior to charging into a canister.

8.2.1.3 Gases from fuel pins after encapsulation of assembly. The amounts and physical states of gaseous elements within intact LWR fuel pins were discussed in Sects. 5 and 6. The total volume of xenon, krypton, and reactor-produced helium within the fuel pins of PWR assemblies that have operated to a burnup of 33,000 Mwd/MTU is about 463 liters (STP). However, only a fraction of this volume will be in the gaseous state within the plenums of the fuel pins. I estimated a maximum of 50%. At this fraction a maximum of 230 liters of these gases could be released within the canister if the cladding on all of the fuel pins were breached. The probabilities of encountering breachments of the fuel pins after encapsulation of fuel assemblies during transportation to, and emplacement in, a repository have not been established. On the basis of the reported³ good experience with fuel assemblies in pool storage, I believe that the number of fuel pins that might be breached in these operations will be less than 10%, assuming moderate care in canister handling. Assuming 10% as a maximum, a maximum of 23 liters (STP) of xenon, krypton, and reactor-produced helium would be released to the canister. An equal fraction of the helium that was added to the pins during manufacture would also be released, so that the total gas volume released to the canister might be 37 liters (STP) (i.e., 23 + 14), assuming that 375 psi of helium was added to the pins at manufacture.

This estimated maximum volume of 37 liters would contribute a pressure of 0.34 atm within the canister at 75°C, assuming the dimensions of the reference canister described in Sect. 6 and also assuming that the canister is backfilled with sand.³⁷ Only 35% ($1.4 \times 10^5 \text{ cm}^3$) of the internal volume of the canister is open gas space in the presence of the sand backfill.

8.2.1.4 Release of gases from UO_2 fuel upon oxidation to U_3O_8 .

Oxidation of UO_2 to U_3O_8 is accompanied by about a 35% increase in volume of the oxide. This swelling could cause the sheath on fuel pins to split and could also cause the oxide to break up with release of some of the trapped gases. However, because oxidation of irradiated UO_2 by air at temperatures $\leq 200^\circ\text{C}$ is known to be extremely slow (e.g., it has been estimated that 50 to 100 years would be required for complete oxidation at 200°C of UO_2 within a breached Canadian fuel element exposed to air),⁴⁰ the stability of the irradiated LWR fuel is not expected to be affected by air oxidation during either retrievable storage or final disposal of spent LWR fuel in a salt repository (maximum pin temperatures $< 200^\circ\text{C}$).

8.2.1.5 Leaking fuel pins present prior to encapsulation of assembly.

The results of theoretical considerations and of experience with leaking fuel pins in pool storage³ show that very little gaseous radioactivity remains as gases within the fuel pin after the pin is breached; that is, escape of the gases from the pins takes place rather quickly following the break. Some information on the occurrence of leaking fuel pins while in a reactor and some results of my considerations of the events that follow a breach in reactor are listed below.

1. Leaking fuel pins are observed during exposure of a fuel assembly in reactor. The Nuclear Regulatory Commission assumes 0.25% leakers.⁴¹
2. These leakers will lose much or all of the pressurizing helium within the pin when the pressure external to the pin is reduced subsequent to the formation of the leak. Essentially all of the gaseous xenon and krypton present at the time of leak occurrence will escape with the helium.
3. The leaking pin probably fills with water at the onset of reactor operation following a reactor shutdown in which the pressure is reduced from the operating pressure to near atmospheric.
4. Some or all of the gaseous and other nuclides within the plenum inside the leaking fuel pin will escape with the steam and/or water during the reactor shutdown which precedes the removal of the fuel assembly that contains the leaker.

5. Some water might seep into the leakers during pool storage, which will precede encapsulation of an assembly. Care should be taken to ensure that not more than a few grams of water remain with the fuel assembly after encapsulation in order to preclude the occurrence of an appreciable partial pressure of water vapor within the sealed canister.

8.2.1.6 Diffusion of hydrogen through canister walls. At high temperature, hydrogen can diffuse into and through many metals, including carbon steel. Some reference information on H₂-Fe systems is summarized below.⁴²⁻⁴⁹ This is followed by a discussion of the possible importance of H₂ diffusion into a reference canister in salt.

The rate of diffusion of hydrogen from a gaseous environment through clean-surface carbon steel plate into a gaseous environment containing negligible hydrogen can be expressed, approximately, as

$$q = (k_0/d)(P^{\frac{1}{2}})\exp(-b_0/T) , \quad (1)$$

where

q = diffusion rate, cm³(STP)·cm⁻²·sec⁻¹;

P = pressure of H₂, mm Hg;

d = thickness of plate, mm;

T = temperature of metal, K;

k_0 and b_0 = constant characteristic of the gas-metal system. The values of these are determined experimentally. Values reported for H₂-Fe (all from experiments at temperatures >300°C) are $k_0 = 1.6 \times 10^{-3}$ and $b_0 = 4820$, with units consistent with those of the other parameters given above.

Although it is generally believed that hydrogen dissolves and diffuses as hydrogen atoms in steel as well as in some other metals, surface films can decrease the rate of transfer at a given temperature if the films inhibit formation and dissolution of atoms within the metal.⁴⁴ Also, hydrogen atoms are intermediate products in certain corrosion reactions (e.g., reduction of H⁺ or H₂O), and these may be

absorbed in and diffuse through a corroding metal, depending on the corrosion potential but more or less independent of the actual external pressure of gaseous H_2 .⁴⁸

Theoretical considerations^{43,44} and experimental evidence⁴⁴ indicate that the following relationship prevails if the metal-gas interfaces on both sides of the plate have identical characteristics aside from the pressure of H_2 :

$$q = (k_0/d)[\exp(-b_0/T)](P_1^{1/2} - P^{1/2}) , \quad (2)$$

where P_1 and P represent the higher and lower H_2 gas pressures respectively.

If the volume of the receiving system is V_c , the diffusion area is A , the pressure is expressed in atmospheres, and P_1 remains constant, we can write Eq. (2) in terms of dP/dt and integrate the resulting equation to obtain, with $P = 0$ at $t = 0$,

$$-P^{1/2} + P_1^{1/2} \ln \frac{1}{1 - (P_1/P)^{1/2}} = t(k_0/d)[\exp(-b_0/T_c)] \left(\frac{A}{V_c} \right) \frac{(760)^{1/2}}{2} (T_c/273) . \quad (3)$$

Using this equation with values for k_0 and b_0 given above and with values of A , V_c , d , and T_c appropriate to a reference SF canister in salt ($A = 5.3 \times 10^4 \text{ cm}^2$; $V_c = 1.4 \times 10^5 \text{ cm}^3$; $d = 12.7 \text{ mm}$; $T_c = 423 \text{ K max}$) and with $P_1 = 1 \text{ atm}$, we find that 1.5 years would be needed to increase the value of P from zero to 0.5 atm. At 80, 100, and 300°C, the similarly calculated values for the times required to achieve this P value are 17.2, 17.8 and 3.2×10^{-4} years respectively.

The above information and calculations indicate that rates of H_2 diffusion into a reference SF canister might be significant under certain special conditions, including (1) a constant supply of H_2 at about 1 atm partial pressure over the entire external surface of the canister and (2) rates of sorption of H_2 within the external surfaces greater than or equal to those of clean iron surfaces. In practice, the effective partial pressure of H_2 might be well below 1 atm for several reasons, including limited accessibility of the surfaces to ambient gases and to

corrosive solutions (Sect. 8), and low rates of H_2 formation around a canister. Also, the properties of the external surfaces may not favor absorption of H_2 .

The effects of any H_2 which diffuses into a canister gas space will depend on whether the H_2 remains within the gas space. In practice, this will probably depend on whether the canistered assembly has stainless steel or Zircaloy fuel-pin cladding. Any gaseous H_2 will probably be absorbed by the Zircaloy cladding but not by the stainless steel cladding.^{50,51} Although it seems unlikely that H_2 diffusion into reference SF canisters will occur at rates sufficient to produce significant effects within the canisters, verification of this should be sought by analyzing for gaseous and absorbed H_2 within canisters after they have been exposed to environments similar to those expected in a repository.

8.2.2 Rates of inflow of gases through capillary leaks in partially evacuated spent fuel canister and rates of pressure changes within canister

From equations presented in Appendix A, where this topic is reviewed and discussed in detail, it can be shown that about 90 years would be required to increase the pressure within a canister from 0.5 atm initially to 0.99 atm when the assumed capillary leak has a radius of about 6×10^{-4} cm and a length of 1.25 cm. If the initial pressure is 0.83 rather than 0.5 atm, the required time is 63 years. Larger diameter leaks require shorter times (see Fig. A.1 of Appendix A), and smaller diameter leaks require much longer times. As an example, if the assumed radius of the capillary is 8.7×10^{-5} cm, the time required for the leak to increase the pressure from 0.5 to 0.99 atm increases to 2×10^5 years.

Capillary leaks of the sizes assumed above would show helium leak rates of about 7×10^{-5} and 3×10^{-8} atm·cm³/sec, respectively, when the canister contains helium at 0.5 atm pressure and is placed in an evacuated chamber for leak testing. Leaks of these sizes are, of course, readily detected and measured by this testing method.

8.2.3 Rates of leakage of gases and radioactivity from pressurized spent fuel canister

Leakage rates of gases are reviewed and discussed in Appendix A.

Transport of radioactive gas from a pressurized canister by flow of pressurizing gas through a capillary leak can occur when one or more fuel pins have leaked gaseous radioactive nuclides into the gas space within a reference canister, and the radioactive gases mix with the pressurizing gas. A low rate of gas flow from the canister is assumed in the following analyses so that the pressure within the canister does not change appreciably over long periods of time (in practice less than about 10^{-5} atm·cm³/sec).

Let b_n equal the amount (μCi) of radioactive nuclide, n , transported out of canister in time, t (sec), and let L equal the rate of gas leakage from the canister (atm·cm³/sec) at 25°C. Then

$$b_n = (\alpha_n/V_g)Lt \exp(-\lambda_n t) , \quad (4)$$

and

$$L = Q(298/T_c) , \quad (5)$$

where

α_n = amount of radionuclide, n , within gas space in canister, μCi;

V_g = total volume of gas within canister at 25°C, atm·cm³;

Q = rate of flow of pressurizing gas through capillary leak, atm·cm³/sec, at temperature of capillary, T_c [value of Q given by Eq. (A.6) of Appendix A];

t = time during which leakage of gas from canister at rate L takes place, sec;

λ_n = decay constant of radionuclide, sec⁻¹;

T_c = temperature of canister at capillary during leakage period, K.

Now

$$V_g = V_o P_i(298/T_i) , \quad (6)$$

where

V_c = volume of gas space within canister, cm^3 ;

P_i = initial pressure at initial temperature, atm;

T_i = initial temperature, K.

Combining Eqs. (5) and (6) gives

$$L/V_g = (Q/V_c P_i)(T_i/T_c) . \quad (7)$$

Also, substituting for Q in Eq. (7) from Eq. (A.6) of Appendix A and letting P_i equal 1 atm yields

$$L/V_g = (3.978 \times 10^5 / \mu)(a^4 / 2l)(P_c^2 - 1) / P_c . \quad (8)$$

P_c , the pressure within the canister, is related to P_i as shown by

$$P_c = P_i(T_c/T_i) . \quad (9)$$

The symbols a , l , P_c , and μ in Eq. (8) are defined in Appendix A. Values for L/V_g from Eqs. (7) or (8) can be used with Eq. (4) in evaluations of b_n .

As stated above, it is assumed that the amount of pressurizing gas within the canister does not change significantly during the period in which b_n is evaluated. The change in the value of P_c from one period to another as a result of a given leak rate can be readily evaluated using Eq. (A.8) of Appendix A.

The amount of time required for leaked gaseous radionuclides in a disposal room to reach the RCG_n^* is a quantity of considerable interest. The amount of radionuclide, n , per unit volume in a disposal room depends on (1) the average value of b_n per canister for all of the canisters emplaced within the room and (2) the gas space within the room, as shown by

* RCG_n = recommended concentration guide for nuclide, n , for air that is inhaled 40 hr/week for 13 weeks per quarter (from Title 10, Code of Federal Regulations, Part 20, 1977, Appendix B, Table 1).

$$A_n = \bar{b}_n / V_r, \quad (10)$$

where

A_n = concentration of radionuclide, n , within the gas space in emplacement room, $\mu\text{Ci}/\text{cm}^3$;

V_r = gas space per canister within the emplacement room, cm^3 .

The time at a given value of $\bar{b}_n$ to reach the value of A_n which equals RCG_n can be found by setting RCG_n equal to A_n in Eq. (10), substituting for $\bar{b}_n$ from Eqs. (4) and (7), and solving the resulting equation for t :

$$t \exp(-\lambda_n t) = (\text{RCG}_n)(V_r)(a_n)^{-1}(Q/V_c P_i)^{-1}(T_i/T_c)^{-1}. \quad (11)$$

In doing this, it was assumed that the value of the quantity $(a_n)(Q/V_c P_i)(T_i/T_c)$ in Eq. (11) is equal to the average value of this quantity for all of the canisters emplaced in the room.

Some values for t which were estimated using Eq. (11) are shown in Table 7 together with values for several of the factors appearing in Eq. (11) and used in these estimates. A summary of the assumptions used in these particular estimates of t are listed below.

1. The emplaced canisters contain PWR SF 204 pin assemblies.
2. Twenty (20%) fuel pins per assembly are breached after the assembly is sealed within the canister.
3. The emplacement room is open but unventilated. Gases from leaking canisters mix immediately and uniformly with room gases ($V_r = 2.0 \times 10^7 \text{ cm}^3$).
4. Assumed values for Q range from 1×10^{-6} to $1 \times 10^{-3} \text{ atm}\cdot\text{cm}^3/\text{sec}$ (at 1 atm).
5. P_i is 1.6 atm ($V_c = 1.4 \times 10^5 \text{ cm}^3$).
6. Values for the total amount of radioactive gases within a fuel pin and for the maximum fraction of these which are within the gas phase, as gases, in a fuel pin are those given in Table 2.
7. The leaks start at emplacement of the 10-year-old SF₆, and all canisters leak at rate Q .

Table 7. Estimated time necessary for an unventilated disposal room to reach RCG^a values due to release of gaseous radionuclides from spent PWR fuel assemblies in leaking, pressurized canisters

Nuclide	Decay constant (sec ⁻¹)	RCG ^a (μCi/cm ³)	Radioactivity per 10-year-old PWR fuel pin (μCi)	Radioactivity from 20 PWR fuel pins aged 10 years at maximum value of F ^b (μCi)	Assumed rate of gas leakage from canister, Q (cm ³ /sec)	Time after start of leak necessary to reach activity level in unventilated room equal to RCG (years)
⁸⁵ Kr	2.05 × 10 ⁻⁹	1 × 10 ⁻⁵	1.12 × 10 ⁷	1.2 × 10 ⁸ (F _{max} = 0.5)	1 × 10 ⁻⁹	∞
					1 × 10 ⁻⁸	1.3
					1 × 10 ⁻⁷	0.12
					1 × 10 ⁻⁶	0.012
³ H	1.78 × 10 ⁻⁹	5 × 10 ⁻⁶	1.05 × 10 ⁶	2.1 × 10 ⁵ (F _{max} = 0.01)	1 × 10 ⁻⁸	∞
					1 × 10 ⁻⁷	∞
					1 × 10 ⁻⁶	3.4
¹⁴ C	3.84 × 10 ⁻¹²	4 × 10 ⁻⁶	3.80 × 10 ³	7.6 × 10 ³ (F _{max} = 0.1)	1 × 10 ⁻⁸	∞
					1 × 10 ⁻⁷	825
					1 × 10 ⁻⁶	75
¹²⁹ I	1.38 × 10 ⁻¹⁵	2 × 10 ⁻⁹	71.2	14 (F _{max} = 0.01)	1 × 10 ⁻⁸	1970
					1 × 10 ⁻⁷	197
					1 × 10 ⁻⁶	20

^aRCG = recommended concentration guide for air inhaled 40 hr/week for 13 weeks per quarter.

^bF represents the fraction of the radionuclide which occurs in a gaseous material within the plenum of the fuel pin. This fraction has escaped the oxide fuel and has also escaped reaction with the fuel pin sheath or other binding reactions. Estimates of the maximum values of F are discussed in Sect. 6.

^cThe activity level never reaches the value of RCG in this case because of radioactive decay of the nuclide.

As can be seen in Table 7, ^{85}Kr is the only gaseous radionuclide which would reach the RCG level of activity within the room in less than several hundred years when the canister leak rate is $\leq 10^{-7} \text{ cm}^3/\text{sec}$; ^{85}Kr reaches the RCG level at 0.12 and 1.3 years at leak rates of 10^{-7} and $10^{-8} \text{ cm}^3/\text{sec}$ respectively. Of course, the bases for these estimated values are very conservative, and if the average rate of leakage of gases from the canisters is assumed to be $10^{-9} \text{ cm}^3/\text{sec}$, or alternatively, if the assumed leak rate remains at $10^{-8} \text{ cm}^3/\text{sec}$ and fewer of the canisters are breached so that the assumed concentration of ^{85}Kr within the open spaces of the canisters is reduced by a factor of 10, the activity level of ^{85}Kr never reaches the RCG level because of the effects of radioactive decay at these lower transfer rates. This assumed reduction by a factor of 10 might also result from an average release of only 5% rather than 50% of the krypton from the inventory within the oxide fuel.

Radioactive decay also precluded the accumulation of RCG levels of ^3H activity at Q equals $10^{-7} \text{ cm}^3/\text{sec}$ and of ^{14}C at Q equals $10^{-8} \text{ cm}^3/\text{sec}$.

8.3 Gas Tightness of Canister

The SF canisters can and should be constructed with specifications and quality controls designed to ensure that they will remain mechanically intact throughout the period of retrievable storage in the repository. As stated previously the canisters will be protected from mechanical and corrosive actions of the surrounding salt and brines during this period.

The specifications for the canisters should include a value for the maximum acceptable leak rate from a sealed canister. This maximum acceptable rate will depend very strongly on whether or not the pressures of gases within the canisters are below atmospheric initially and will remain so throughout the period of retrievability. As discussed in Sect. 7.2, initial leak rates of about $5 \times 10^{-5} \text{ atm}\cdot\text{cm}^3/\text{sec}$ or somewhat larger could be acceptable if the initial pressure at maximum temperature is $\leq 0.5 \text{ atm}$ and if the gases escaping from the fuel pins after the canister is sealed do not exceed about 50 liters (STP) during the retrieval period. Escape of more than 50 liters appears very unlikely, but experience with encapsulation, transportation, and emplacement of SF is needed to verify predicted behavior. Larger volumes of leaked gases

could be accommodated without exceeding 1 atm pressure if the free volume within the canister is made larger by eliminating the sand backfill or if the initial pressure of helium charged to the canister prior to sealing is <0.5 atm.

9. FACTORS INFLUENCING LEAKAGE OF RADIOACTIVITY AND TRANSPORT FROM SPENT FUEL CANISTER EMPLACED IN FINAL DISPOSAL MODE

9.1 Introduction

The concepts that have been reported for final disposal of SF in salt differ from those for retrievable storage in several important ways:

1. The canister that encapsulates the assembly might not be protected from the corrosive and mechanical attack of the surrounding salt and brines by a sleeve or overpack.
2. The rooms overlying the emplaced canisters might be backfilled with crushed salt.
3. The open spaces remaining in an emplacement hole might also be backfilled with crushed salt or other material.

Subjects that then must be included in considerations of leakage and transport of radioactive gases from emplaced SF are (1) rates of corrosion of the emplaced canister, (2) period of time after emplacement before the canister is breached as a result of corrosion, (3) mechanical effects imposed by the salt formation and period of time after emplacement before mechanical effects would damage the canister, (4) susceptibility of fuel-pin cladding to corrosion and breaching in the environments prevailing after the canister is breached, and (5) rates of diffusion and flow of gases from breached canisters through backfilled and open rooms. Some pertinent information on each of these topics is summarized below.

9.2 Corrosion of Carbon Steel Spent Fuel Canister Emplaced in Bedded Salt Repository and Preferred Backfill Material

Information on the corrosion of the reference steel canister emplaced in bedded salt, as well as information relating to radiation and mechanical effects, is presented and analyzed in Appendixes B through D. A summary of the results of this work and recommendations for backfill material are presented in this section.

The characteristics of corrosion of carbon steel (the material from which the reference canister is fabricated) are well established for the several environments that might be encountered around a canister in bedded salt. A principal feature of the corrosion characteristics is

that aqueous solution (either bulk or condensate) must be in contact with the surface of the carbon steel for corrosive attack to take place at an appreciable rate. It is generally believed that some brine will migrate into an emplacement cavity in bedded salt from surrounding solid salt and that some of this brine might come into contact with and corrode the canister. The rates of in-migration of brine and their dependence on time after emplacement of a reference canister have not been firmly established. Estimates based on existing temperature and brine migration information indicate that inflow rates will correspond to <100 g of water per year and will not change appreciably with increasing time after emplacement, up to a period of 35 years (the period for which temperature calculations were available). Accidental flooding of the repository is another conceivable source of water which should be included in safety considerations.

My review and analysis of the corrosion characteristics of an emplaced reference canister led me to conclude that relatively rapid, localized corrosion is the most likely avenue through which the 1/2-in.-thick canister wall could be breached in a relatively short time after emplacement (2 to 30 years), and also that rapid localized corrosion is a strong possibility unless special provisions are made to avoid it.

The localized corrosion could occur as a result of the vapor pressure, temperature, and concentration properties of the brines. The brines in bedded salt are rich in $MgCl_2$, and the presence of this salt causes a lowering of the vapor pressure of the NaCl-saturated solution by factors that increase with increasing concentration of $MgCl_2$. A solution that contains $MgCl_2$ and that is in contact with solid NaCl becomes more concentrated in $MgCl_2$ as water is lost from the solution. Then, because of the relatively low vapor pressure of the concentrated solution, water vapor could diffuse from adjacent, lower-temperature regions (if a diffusion path exists) to replenish the lost water. Therefore, it is conceivable that a rapid attack on the local area could continue until a large fraction of the inventory of water in brines around the canister is consumed in the attack.

Rapid, localized attack could also be associated with the formation of radiolytic O_2 in any liquid brine that might accumulate in the

irradiated backfill regions surrounding the canister. Reduction of dissolved O_2 can be part of the processes by which iron is rapidly corroded in brine, and no net consumption of water takes place at the corrosion site when the O_2 reduction is the cathodic reaction part of the processes. Accordingly, when only a small fraction of the canister surface is wetted with brine, it is conceivable that most of the available O_2 in the surroundings would diffuse to and react corrosively at this semipermanently wetted surface. Again, diffusion paths for the O_2 must be present.*

Hole-closure stresses on the canister might also influence the time to canister breaching if the stresses are great enough to buckle the canister walls; these stresses will probably be about 2000 psi when the repository is located at a depth of 2000 ft. The results of stress calculations made using standard formulas indicate that the reference canister (1/2-in.-thick walls) will withstand more than 2000 psi without buckling. However, to avoid buckling after corrosion, allowance must be made for the amount of corrosion weakening which can be expected during the required time that the canister should remain unbreached. Although no significant amount of weakening would probably result from scattered, localized corrosion, weakening would result when an appreciable, continuous area of the surface is thinned by corrosion.

After reviewing the properties and probable advantages and disadvantages of several different materials for backfilling around the canister at emplacement, I concluded that a backfill comprised of a strong desiccant mixed with sand could provide high probability of long-term integrity of the canister. Quicklime (CaO) is a strong desiccant that might prove suitable for this use; 1.5×10^5 g of powdered CaO contained in the backfill around a 12-ft length of the reference canister could bind 45 kg of H_2O as $Ca(OH)_2$. Because swelling by a factor of 1.89 occurs upon complete hydration of quicklime, the backfill would tend to become impervious when the initial density of the powdered CaO as mixed

*It is assumed that no significant amount of air will diffuse into the backfill after emplacement of the canister and, also, that the emplacement cavity will be deaerated as part of the emplacement operations.

with the sand is $\geq 55\%$ of the theoretical for the solid. It seems likely that brine would only have access to the canister from the surrounding salt through cracks that develop in this backfill and that have surfaces on which all CaO has previously reacted with H_2O . However, diffusion paths would be almost nonexistent within this backfill material, and the maximum rate of localized attack at the end of a crack would be limited to the locally available supply of corrodents (i.e., water and/or O_2). The local supply would probably limit the local corrosion rate to < 5 mils/year.

The chemical and physical properties are uncertain for the systems that would result if brine solutions came into contact with hydrated quicklime on the edges of the backfill or on the surface of cracks within the backfill. These properties must be established before a final recommendation can be made to use the quicklime-sand mixture as backfill for the canister in salt. Also, experimental tests of radiation effects and of carbon steel corrosion in this backfill material are required for final verification of the suitability of the material. However, on the basis of currently available information, there are no apparent reasons to expect that the suitability of the quicklime-sand mixture will prove to be inadequate.

Other types of desiccants for use around waste canisters in salt are under investigation by others.⁵² A system of chemical additions that would promote the formation of tachyhydrite ($2MgCl_2 \cdot CaCl_2 \cdot 12H_2O$) is one of these. The factors that must be investigated prior to using any one of these desiccants are probably about the same as those outlined above for quicklime.

As implied above, I tentatively recommend the use of a quicklime-sand mixture for backfilling around reference SF canisters emplaced in bedded salt. This recommendation also applies to backfilling around the carbon steel sleeve which might be used during retrievable storage of SF. If this recommendation is adopted, the thickness of the sleeve should be increased to $1/2$ in. to ensure that it will not be collapsed by hole-closure stresses during the required period of retrievability.

9.3 Corrosion of Zircaloy Fuel-Pin Cladding in Brines

Zircaloy is very resistant to general corrosion in brines at temperatures of interest in SF disposal in bedded salt.⁵³ However, Zircaloy is known to be subject to stress cracking in brine solutions at 25°C when anodically polarized by galvanic coupling with alloys such as stainless steel.⁵⁴ It thus seems likely that the Zircaloy cladding on fuel pins within an assembly would be subject to stress cracking when in contact with brines.

Accordingly, it must be assumed that the Zircaloy cladding on fuel pins within a canistered fuel assembly will crack soon after the cladding is contacted by brine solution entering a breach in the canister.

9.4 Corrosion of Stainless Steel Fuel-Pin Cladding in Brines

Because austenitic stainless steel is subject to stress cracking in chloride solutions at elevated temperatures, especially when O₂ is present, it must be assumed that the stainless steel cladding on fuel pins within a canistered fuel assembly will be breached by cracking soon after the cladding is contacted by brine solution that enters through a breach in the canister.

9.5 Movement of Fission Gases Through Salt Backfill in Spent Fuel Disposal Room

9.5.1 Introduction

Radioactive gases that might escape from an emplaced SF canister can move through the crushed salt backfill within the overlying storage room by several processes, including (1) diffusion through connecting air passages, (2) breathing action resulting from changes in atmospheric pressure, (3) flow of corrosion H₂ or radiolytic gases from emplacement cavity, and (4) room closure or temperature changes. Effects of these processes on the rates of gas transport are discussed below.

9.5.2 Diffusion

The gas transport properties of dry, crushed salt were studied by Evans et al.⁵⁵ Relationships that they reported for the interdiffusion of a gas pair 1-2 in the crushed salt are

$$D_{12} = (\epsilon'/q)D_{12} , \quad (12)$$

$$\epsilon'/q = (\epsilon_t)^2/(1 - \epsilon_t) , \quad (13)$$

where

ϵ' = flow porosity,

ϵ_t = total porosity or fractional void volume of a porous system,

D_{12} = binary diffusion coefficient of the gas pair 1-2 in free space,

D_{12} = effective coefficient for mutual diffusion of the gas pair 1-2 in a porous system,

q = tortuosity factor.

Evans et al.⁵⁵ determined the value of ϵ_t for several grades of crushed salt and found that the minimum value was 0.27 for a 50-50 mixture of medium and fine grades. The other three grades studied had ϵ_t values between 0.34 and 0.38. Using a minimum initial value of $\epsilon_t = 0.30$ for the salt backfill within a disposal room, we find from Eq. (13) that $\epsilon'/q = 0.13$. The value of D_{12} for krypton-air at 40°C and 1 atm approximately equals 0.16 cm²/sec.⁵⁶ Then with $\epsilon'/q = 0.13$, the value of D_{12} for krypton-air at this temperature and pressure is 0.021 cm²/sec.

Of course, the porosity of the backfill will decrease from the initial value as room closure and reconsolidation of the backfill take place. Estimates of the volumetric closure (and reconsolidation) of a high-level waste (HLW) repository at 25 years after emplacement of 10-year-old HLW have been reported by Ratigan and Wagner⁵⁷ to be between 11 and 22%. Their calculations applied to somewhat higher thermal loadings and mine extraction ratios than those which prevail in the reference repository, but no calculations more pertinent to the repository are available. For discussion purposes, I assumed 15% reconsolidation at 25 years of the backfill in the reference repository, which would correspond to a decrease in the porosity to 0.15 from 0.30. If we now assume that the relationship shown in Eq. (13) prevails for the

partially reconsolidated backfill, the value ϵ'/q would become 0.026, and the value of $D_{\text{Kr-air}}$ would become 0.0042 at 40°C and 1 atm.

Estimates of the rates of escape by diffusion of radioactive gases from a backfilled emplacement room were made using

$$Q/S_0 = 1 - \frac{4}{\pi} \sum_{n=1}^{\infty} \frac{(-1)^{n+1}}{(2n-1)} \exp \left[-\frac{D(2n-1)^2 \pi^2 t}{4L^2} \right], \quad (14)$$

where

Q = cumulative flow of nuclide out of the open end of a backfilled emplacement room, amount per unit cross-sectional area of the room;

S_0 = amount of nuclide occurring as an instantaneous source within the backfill, amount per unit cross-sectional area of the room;

L = horizontal distance between location of instantaneous source and open face, cm;

D = diffusivity of nuclide-air within porous backfill, cm^2/sec ;

t = time after initial occurrence of the source of nuclide within the backfill, sec.

It is assumed that the concentration of radionuclides in the gas within the plane of the open face of the room remains negligible at all times — a result of diffusion, gas ventilation, etc., within the gas that contacts the open face.

The relationship in Eq. (14) was derived by Claiborne⁵³ for a system in which diffusion movement from the source takes place in only one direction.* In practice, the 1000-ft-long emplacement room in the reference SF repository is open at each end, and the source gas will diffuse in both directions. It can be shown qualitatively that diffusion in both directions would reduce the value of Q given by Eq. (14) by a factor of 2 when the source is located in the exact longitudinal center of the room. For a source located very near one of the faces, the value of Q would not differ appreciably from that given in Eq. (14). The

*Claiborne's derivation is described in Appendix E.

effects of the two-directional diffusion on the fractions of S_0 which have flowed out of the nearest face at a given time will also differ from those shown by Eq. (14) by factors ranging from 1 to 0.5: 1 for a source very near one of the open faces, and 0.5 for a source in the longitudinal center of the room.

Values for Q/S_0 , which were calculated for krypton with $D = 0.021$ and $0.0042 \text{ cm}^2/\text{sec}$, are plotted in Fig. 3. The value calculated with $D = 0.021 \text{ cm}^2/\text{sec}$ indicate that at the initial porosity of the backfill, large fractions ($\sim 10\%$) of any krypton that leaks into the room will have diffused out of the room in 60 years or less, depending on the initial location of the krypton within the room. The longest periods will be required when the krypton enters the backfill at a location near the longitudinal center of the 1000-ft (305-m) room. Possible effects of a partial reconsolidation of the backfill are illustrated by the increased diffusion times that result when the assumed value of D is decreased to 0.0042 from the initial $0.021 \text{ cm}^2/\text{sec}$.

Other radioactive gases could have diffusion characteristics appreciably different from those of krypton. For example, the value of $D_{\text{HT-air}}$ at 40°C and 1 atm is $\sim 0.58 \text{ cm}^2/\text{sec}$,⁵⁶ 3.6 times greater than that of $D_{\text{Kr-air}}$ at the same temperature and pressure. Values of Q/S_0 for other gases with other values of D can be roughly estimated from the plots in Fig. 3 by noting that an increase in the value of D by a given factor is equivalent to a decrease in the value of L by the square root of the factor. Thus, an increase in the value of D from 0.021 for krypton-air to $0.076 \text{ cm}^2/\text{sec}$ for hydrogen-tritium-air would be equivalent to a decrease in the value of L by a factor of 1.9 (with no change in the value of D).

The effects of some other factors on the transport of gases through the backfill are considered in the following sections.

9.5.3 Breathing action resulting from changes in atmospheric pressure

Changes in atmospheric pressure at the repository site which are transmitted to a disposal room will result in expansion and contraction of gases within the room. Such changes in gas volume within a backfilled room could result in the forced exchange of gases contained in backfill

Fig. 3. Fractional escape of radioactive gas by diffusion from backfilled emplacement room after pulse injection at several distances from the open end of the room versus time after pulse; D units are square centimeters per second.

near the open face of the room with those in the adjacent corridor. The extent of the forced exchanges would depend on the amount and frequency of the changes in atmospheric pressure and on the volume of gases within the backfilled room.

Information on the first of these parameters was obtained by reviewing the barograms for Oak Ridge, Tennessee, for the past year. These barograms were recorded by and are in the files of the Atmospheric Turbulence and Diffusion Laboratory at Oak Ridge.⁵⁹ My summary of the pressure changes shown in the barograms is as follows: During the winter months, the pressure varies regularly about 0.5 in. Hg over periods of 2 or 3 days. Sometimes the variation is as much as 1 in. Hg, and on one occasion this year the variation was 1-1/2 in. Hg (January 1979). During the other seasons, the pressure variations are lower than 0.25 in. Hg. Oncoming storms cause only small changes in pressure (<0.25 in. Hg). No comparable information was obtained on atmospheric pressure variations at other U.S. locations.

A 0.5-in. Hg decrease in ambient pressure within the 1000-ft-long room in the reference repository would result in the expulsion of the gases from the backfill within a distance of about 8 ft at each of the two open ends of the 1000-ft-long room. A subsequent increase in ambient pressure to the original value would pull gases from the connecting corridor into the backfill a distance of about 8 ft. These breathing actions would have obvious effects on the movement of radioactive gases out of the backfill that is located within 10 to 15 ft from the face. More importantly, this breathing would vitiate the room-sealing provisions that could be breached at the prevailing differences between ambient pressures from one time to another. The breathing action would probably have negligible effects on the rates of transport of gases from distances greater than 20 to 30 ft from the open faces of the rooms.

Control of repository pressure probably could be accomplished with the ventilation system if such control is deemed necessary.

9.5.4 Forced flow of H₂ originating around emplaced canister

The effects of corrosion and radiolytic H₂ on the transport of gases through a backfilled room will, of course, depend on several factors, including (1) the rates of evolution of H₂ from the many emplacement cavities within the room, (2) the distance between the site at which H₂ enters the backfill and the open face of the room, and (3) the flow area within the backfilled room. For reference and discussion purposes, the simplest assumptions are:

1. H₂ is evolved from each emplacement cavity at the same given rate, R .
2. The evolved H₂ flows as a slug toward the nearest open end of the backfilled room.
3. The area of the flow path is equal to the product of the cross sectional area of the room and the porosity of the backfill.

With these assumptions, the relationship between the time, t_i , required for the evolved gases to flow from site i to the open face is

$$t_i = \frac{PA\epsilon_t}{aR} \frac{273}{T_r} [1/N + 1/(N-1) + \dots + 1/(N+1-i)] , \quad (15)$$

where the sites (i) are numbered in order starting with the one nearest the open face and continuing to the one nearest the middle of the reference room, which is open at each end, and where

P = longitudinal distance between emplacement sites in room, cm
(Site 1 is located a distance P from the face; site i is located a distance i times P from the face.);

A = cross-sectional area of emplacement room, cm²;

ϵ_t = porosity of backfill;

a = number of rows of emplaced canisters within emplacement room;

R = rate of H₂ evolution from each emplacement cavity, cm³(STP)/sec;

N = one-half the total number of emplacement sites per row within emplacement room;

t_i = time after start of evolution of H₂ from canisters, sec;

T_r = temperature of gas in backfill, K.

Plotted in Fig. 4 are smoothed values for t_i versus distance, iP , which were calculated using Eq. (15) with assumed values for R , T_r , and ϵ_t of 3.6×10^{-3} cm³/sec, 313 K, and 0.3, respectively, and with values of a , P , A , and N germane to an emplacement room in the reference repository (see Sect. 6).

The assumed value for R corresponds to the H₂ evolution rate that would result from 90 g of water per year migrating into each emplacement hole and undergoing decomposition to form H₂, which is then evolved into the room. The values of t_i are inversely proportional to the assumed value of R . For example, if the brine inflow and decomposition rate is 30 g of water per year rather than 90 g/year, the calculated values of t_i in Fig. 4 would all be increased by a factor of 3. The values of t_i are also proportional to porosity and inversely proportional to absolute temperature, and the calculated values will change with changes in these quantities.

Comparisons between the calculated values plotted in Figs. 3 and 4 indicate that diffusive transport of any radioactive gases will probably not be appreciably affected by forced flow of stable gases that may be generated within the emplacement cavities (or room). Of course, the possibility cannot now be ruled out that rates of in-migration of water and of its subsequent decomposition to form H₂ might be substantially greater than the 90 g of water per year assumed for the Fig. 3 calculations. In situ experiments at the proposed repository site would be needed to establish actual rates of H₂ production in a disposal room.

9.5.5 Changes in temperature and consolidation within crushed salt backfill

These long-term changes will have the effect of expelling gases from the backfill. It is unlikely that these effects will be as important to the transport of radioactive gases as the mechanisms discussed in Sects. 9.5.2 through 9.5.4.

Fig. 4. Smoothed values of time required for H_2 evolved at a constant rate from each emplacement site within a disposal room to flow from a given site to the open face of the room versus distance of site from face. [$R = 3.6 \times 10^{-3} \text{ cm}^3/\text{sec}$; $T_r = 313 \text{ K}$, and $\epsilon_t = 0.3$ (see Eq. 11)].

**Appendix A. RATES OF FLOW OF GASES THROUGH CAPILLARY LEAKS IN
REFERENCE SPENT FUEL CANISTER AND RATES
OF PRESSURE CHANGES WITHIN CANISTER**

A.1 Poiseuille Law

At normal pressures the rate of flow of gases through cylindrical capillaries is given by the Poiseuille law.⁴⁷ This law can be written

$$Q = \frac{(3.978 \times 10^5)(a^4/l)}{\mu} \frac{(P_2 + P_1)(P_2 - P_1)}{2}, \quad (\text{A.1})$$

where

- Q = rate of flow of gas through capillary, $\text{atm} \cdot \text{cm}^3/\text{sec}$ at T_c ;
- T_c = temperature of capillary, K;
- P_2 = pressure on high-pressure side of capillary, atm;
- P_1 = pressure on low-pressure side of capillary, atm;
- a = radius of capillary, cm;
- l = length of capillary, cm;
- μ = viscosity of gas at T_c , P.

A.2 Reference Canister with Initial Pressure Less Than Atmospheric

For this case, P_2 equals 1 atm, and Eq. (A.1) can be written

$$Q = (3.978 \times 10^5/l)(a^4/2l)(1 - P_c^2), \quad (\text{A.2})$$

where P_c is the pressure within the canister in atmospheres ($P_c \leq 1 \text{ atm}$).

The rate of pressure change within the canister corresponding to a given value of Q in Eq. (A.2) is given by Eq. (A.3) if the temperature of the gas within the canister is equal to that of the canister wall, T_c ,

$$dP_c/dt = Q/V_c, \quad (\text{A.3})$$

where V_c is the volume of gas space within the canister.

Substituting from Eq. (A.2) into Eq. (A.3) and integrating yields

$$\tanh^{-1} P_c = (3.978 \times 10^5 / V_c \mu) (a^4 / 2l) (t) + \tanh^{-1} P_i, \quad (\text{A.4})$$

where

P_i = initial pressure within canister, atm ($P_i < 1$ atm);

t = time after development of leak described by the values of a and l .

Let us now evaluate the time to reach 0.99 atm pressure within the reference canister versus the values of the capillary radius starting with P_i equals 0.5 atm. For this illustrative evaluation, assume the following:

$P_c = 0.99$ atm,

$P_i = 0.5$ atm,

$\mu = 2.10 \times 10^{-4}$ P (viscosity of air at 75°C),

$V_c = 1.4 \times 10^5$ cm³ (assumes that only 35% of internal volume of canister is unoccupied by assembly and other fillers such as sand),

$l = 1.27$ cm.

Introducing these values into Eq. (A.4) and rearranging yields

$$t = (3.94 \times 10^{-4}) a^{-4}. \quad (\text{A.5})$$

A plot of values of t (in years) versus a (0.0004 to 0.0014 cm) is shown in Fig. A.1. The time ranges from 3 to 450 years between the largest and smallest values assumed for the capillary radius.

A.3 Reference Canister with Initial Pressure Greater Than Atmospheric

For this case, P_i equals 1 atm, and Eq. (A.1) can be written

$$Q = (3.978 \times 10^5 / \mu) (a^4 / 2l) (P_c^2 - 1), \quad (\text{A.6})$$

where P_c still represents the pressure within the canister in atmospheres, but in this case $P_c \geq 1$ atm.

Fig. A.1. Time to reach 99% of atmospheric pressure within reference canister versus radius of capillary leak in canister wall (initial internal pressure, 0.5 atm).

The rate of pressure change within the canister corresponding to a given value of Q in Eq. (A.6) is given by the following equation if the temperature of the gas within the canister is equal to that of the canister wall:

$$dP_c/dt = -Q/V_c . \quad (A.7)$$

Substitution of Eq. (A.6) into Eq. (A.7) and integrating yields

$$\coth^{-1}P_c = (3.978 \times 10^5/\mu)(a^3/2l)t + \coth^{-1}P_i , \quad (A.8)$$

where, again, the symbols have meanings stated in Sects. A.1 and A.2; however, in this case $P_i > 1$ atm.

Eqs. (A.6) and (A.8) are used or referred to in Sect. 8.2.3 in connection with the discussion of rates of leakage of gases and of radioactivity from pressurized canisters.

**Appendix B. REVIEW OF SOME THEORETICAL AND EXPERIMENTAL
INFORMATION ON THE ELECTROCHEMISTRY OF CORROSION***

B.1 Corrosion Reactions

Corrosion of a metal in an aqueous environment involves two electrochemical reactions: (1) an anodic reaction in which the metal is oxidized and (2) a cathodic reaction in which some component of the solution is reduced by the electrons released in the anodic reaction.

The general formulation of the anodic reaction is⁶⁰⁻⁶²

A more realistic formulation for ordinary aqueous corrosion is

The ions formed in reaction (B.2) may precipitate in the form of a stable oxide and/or hydroxide on the surface and thus stifle further corrosion:

A more protective oxide or hydroxide may be formed directly:

or

Reactions such as (B.4) and (B.5) are favored by higher anodic potentials.^{**,62}

*Based in large part on my previously published review (ref. 49).

**With the convention used, an increase in electrode potential, $\Delta\phi$, refers to a change in potential in the anodic (or noble) direction. A decrease is in the cathodic (or active) direction.

Another anodic reaction is one in which the cations enter the solid oxide film directly:

This type of reaction must prevail when the metal surface is covered with an oxide that is impervious to solution and in which only the anions are mobile.

The cathodic reactions of possible importance in aerated aqueous solutions include the following:

Reaction (B.9) represents the reduction of protons to form H_2 . The hydrogen atom is a probable intermediate. Reaction (B.10) represents the direct reduction of water to form H_2 . Again, the hydrogen atom is a probable intermediate. Although there is no thermodynamic difference between reactions (B.9) and (B.10), reduction of H^{+} is usually the more favored reaction due to kinetic factors. Reduction of H_2O is usually encountered at potentials well below the equilibrium potentials for reaction (B.10).

Reactions (B.7) and (B.8) represent the reduction of O_2 to form OH^{-} . Hydrogen peroxide is an intermediate,⁶³ and its reduction may require lower potentials than needed for reduction of O_2 . Accordingly, under some conditions, it is possible for H_2O_2 to accumulate in aerated solutions in which a metal is corroding.

The potentials for O_2 reduction are normally above those for H^{+} reductions.

B.2 Factors That Affect the Rates of Anodic Reactions

The rate of the anodic (corrosion) process in aqueous solutions is basically dependent on three factors: (1) the protective properties of solid films that may form on the metal surface, (2) the concentrations of any solutes that take part in the dissolution or in the film-building reactions, and (3) the potential differences between the metal and adjacent solution and between the surface of the film and adjacent solution. The latter quantities may differ because of the resistance of the film to passage of ions. In the general case, the film could have any composition, but the usual protective films in aqueous solutions are oxides and hydroxides. The term "protective properties" refers to the properties of (1) permeability to ions from the solution, (2) permeability to solution, and (3) ionic and electronic conductivity of the film. With a freely corroding system, the potential is that for which the anodic and cathodic rates are equal.

In some cases, the anodic and cathodic reactions can be studied separately using electrical polarization methods. The types of anodic potential-current relationships which may be encountered in polarization measurements are illustrated in Fig. B.1. The different regions are described more fully below.

Region i. In this region of low potential, little or no protective film is formed with some metals for a variety of reasons, possibly because the solid products of the reaction are porous and/or permeable to the solution. In addition, hydride formation may occur and have a detrimental effect on protective properties of the film. The expected current-potential relationship in this region of active corrosion has the form*

$$i_a = i_{corr} \exp \left[\frac{\alpha_a ZF}{RT} (\Delta\phi - \Delta\phi_0) \right], \quad (B.11)$$

*The general relationship between current and potential, $\Delta\phi = a + b \log i$, where a and b are constant, is called a Tafel relationship.

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Fig. B.1. Types of relationships between potential and anodic current.

where

- i_a = anodic current,
- i_{corr} = corrosion current at open circuit,
- $\Delta\phi$ = polarized electrode potential (the difference between potentials of metal and solution),
- $\Delta\phi_o$ = electrode potential at open circuit (the corrosion potential),
- Z = charge on the metal ion,
- α_a = effective anodic transfer coefficient (values for this quantity at all temperatures studied are usually in the range 0.5 to 2),
- F = Faraday constant,
- T = temperature,
- R = gas constant.

Regions 2 and 3. With some systems, protective oxide formation begins and continues above a certain potential, as indicated for regions 2 and 3 in Fig. B.1. The formation of a protective oxide may result from the occurrence of reactions such as reactions (B.3) through (B.6).

If the film is nonconductive and does not break down, the current may remain low as the potential is increased to very high values (several hundred volts) while protective film (barrier layer) continues to grow at a low rate. This growth is a result of the movement of anions or cations through the film under the influence of the applied potential.

Region 4. This region indicates breakdown of film and pitting due to the presence of aggressive anions such as Cl^- .

Regions 5, 6, and 7. If electrons can pass through the oxide, redox reactions can take place at the oxide-solution interface as the potential is increased. If the oxide is a good conductor of electrons, these reactions would be expected to occur near the potentials at which they become thermodynamically possible.

The redox reactions that might occur include oxidation of H_2O and solutes and oxidation of the protective oxide to a higher oxide. In the latter case, the higher oxide may be nonprotective, or soluble, and the formation of this oxide would then result in active corrosion of the

metal. This behavior is referred to as overpassivation, and the potential region is referred to as the transpassive region.

B.3 Theoretical and Experimental Information on Kinetics of Reduction of Hydrogen Ions and Water* on Clean Metal Surfaces

B.3.1 Theoretical relationships for charge-transfer overvoltage

The theoretical relationship for the cathodic current from reduction of ions in a single-charge-transfer redox reaction at an electrode is

$$i_- = -kC_o' \exp\left[-\frac{\alpha_c F}{RT} (\Delta\phi - \zeta)\right], \quad (\text{B.12})$$

where k is a constant characteristic of the metal; C_o' is the concentration of the oxidized species at the interface between compact and diffuse double layers on the surface; α_c is the cathodic transfer coefficient; ζ is the zeta potential, that is, the potential across the diffuse double layer; and the other symbols have the usual meanings.

The value of C_o' is related to the concentration of the oxidized species in the bulk of solution C_o through

$$C_o' = C_o \exp\left[(-Z_o F/RT)\zeta\right], \quad (\text{B.13})$$

where Z_o is the ionic valence of the oxidized species.

Applying Eqs. (B.12) and (B.13) to reduction of H^+ and of H_2O , we have, for H^+ reduction,

$$\Delta\phi = \frac{-RT}{\alpha_c F} \ln|i| + \frac{RT}{\alpha_c F} \ln[H^+] - \left(\frac{1 - \alpha_c}{\alpha_c} \zeta\right) + \text{constant}, \quad (\text{B.14})$$

and for H_2O reduction,

$$\Delta\phi = -\frac{RT}{\alpha_c F} \ln|i| + \zeta + \text{constant}. \quad (\text{B.15})$$

*See section beginning on p. 129 of ref 61.

If the solution contains a large excess of inert electrolyte (supporting electrolyte), the ζ potential does not change with change in pH.* Accordingly, in this case the H_2O reduction current at a given potential is independent of pH, and H^+ reduction current is directly proportional to the molar concentration of H^+ ($[\text{H}^+]$) in the bulk solution.

If the solution is a pure acid or alkaline electrolyte, the potential does change with change in pH, and the expressions for H^+ and H_2O reductions in these cases, which are given by Vetter,⁶¹ are

$$\Delta\phi = \frac{-RT}{\alpha_c F} \ln|i| + \left[\frac{RT}{F} \ln[\text{H}^+] \right] + \text{constant}, \quad (\text{B.16})$$

or

$$|i| = \text{constant}' [\text{H}^+]^{\alpha_c} \exp\left(-\frac{\alpha_c F}{RT} \Delta\phi\right) \quad (\text{B.17})$$

for the H^+ reduction. For H_2O reduction,

$$\Delta\phi = \frac{-RT}{\alpha_c F} \ln|i| - \left(\frac{RT}{F} \ln[\text{H}^+] \right) + \left(\frac{RT}{F} \ln K_w \right) + \text{constant}^0, \quad (\text{B.18})$$

or

$$|i| = \frac{\text{constant}''}{[\text{H}^+]^{\alpha_c}} \exp\left(-\frac{\alpha_c F}{RT} \Delta\phi\right), \quad (\text{B.19})$$

where the ionization constant of water, K_w , is included in the constant term. Theoretical values for α_c range between 0 and 1; the measured values are usually near 0.5.

Eqs. (B.17) and (B.19) show that in these cases the H^+ reduction current at a given potential is directly proportional to about the square root of $[\text{H}^+]$, and the H_2O reduction current is inversely proportional to about the square root of $[\text{H}^+]$.

Incidentally, the concentration of H^+ at the interface between the compact and diffuse double layers is, theoretically, independent of pH in pure acid solution. The same is true for the concentration of cations in basic solution. The ζ potential changes with pH to effect these

*The ζ potential is dependent on the value of $\Delta\phi$. However, the variation of ζ potential with $\Delta\phi$ is small if the ζ potential is small.

constant concentrations. With excess of supporting electrolyte, the $[H^+]$ at the inner double layer is directly proportional to $[H^+]$ in the bulk solution. It is also worthwhile to note that in all but the most concentrated solutions, the concentration of ions at an interface is probably small compared with the concentration of water at the interface.

B.3.2 Diffusion-limited currents

The concentrations of reactants and products at the surface of an electrode can be affected by limitations on the rates of diffusion of these species to or from the surface. In particular, the maximum rate at which a solute can be reduced cannot exceed the rate at which the solute diffuses to the surface. This diffusion-limited current can be estimated from the expression

$$i_d = \frac{nFCD}{\delta}, \quad (B.20)$$

where

- i_d = limiting diffusion current, A/cm²;
- n = number of electrons taking part in the reduction of the species;
- F = Faraday constant;
- C = concentration in the bulk solution of the species undergoing reduction, moles/cm³;
- D = diffusion coefficient of species, cm²/sec;
- δ = effective thickness of diffusion layer on specimen surface, cm; this thickness will depend on specimen shape and on the amount of agitation of the solution. A typical thickness is $\sim 5 \times 10^{-3}$ cm.

B.4 Experimental and Theoretical Information on Kinetics of Reduction of Oxygen

B.4.1 Clean metal surfaces

Theoretical understanding of the kinetics of O₂ reduction is not as complete as that for H⁺ reduction. Experimentally, the following relationships have been found for reduction of O₂ on silver:

$$i = -k[O_2]\exp\left(-\frac{\alpha_c F}{RT} \Delta\phi\right) \quad (B.21)$$

in acid and neutral solutions,⁶¹ and

$$i = -k[O_2][H^+]\exp\left[-\frac{(1 + \alpha_c)F}{RT} \Delta\phi\right] \quad (B.22)$$

in alkaline solutions.⁶¹ At each pH, the value of α_c was 0.5. Equation B.21 was also found to be applicable with mercury in acid and neutral solutions.⁶¹

B.4.2 Surfaces coated with porous oxide

The presence of porous oxides on an electrode would undoubtedly affect the kinetics of a reduction process on the electrode. In the simplest case, the reaction would take place only on the bare metal or on thin oxide at the bases of the pores or crevices. The effective area of the surface would then be less than the apparent area. Also, the thickness of the solution-diffusion layer might be increased depending on the film thickness.

B.5 Corrosion Potentials and Currents on a Freely Corroding Specimen

The corrosion potential of a freely corroding specimen is that at which the rates of the anodic and cathodic processes are equal. This potential can be measured directly. It can also be established in some cases from the results of polarization measurements, as illustrated in Fig. B.2; the corrosion potential is the point at which the anodic and cathodic polarization curves intersect. Additionally, the rates of anodic and cathodic processes on the freely corroding specimen can sometimes be estimated from polarization information. For example, if the cathodic polarization data form a straight line plot as illustrated in Fig. B.2, the cathodic rate at open circuit (which is the corrosion rate) can be estimated by extrapolating the straight line to the known open circuit potential. Also, small current polarization can be used to establish the corrosion rate.⁶⁴

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Fig. B.2. Illustrative plots of cathodic and anodic polarization.

B.6 Effects of Localized Corrosion on the Local Corrosion Potential and Solution Composition

Localized corrosion in regions of restricted access to the bulk solution (e.g., pitting corrosion, crevice corrosion, and stress corrosion cracking) results in local changes of the corrosion potential and the solution composition. In particular, when the anodic rate exceeds the cathodic rate within a restricted region, the electrode potential will be less than that at exposed surfaces, and anions from the bulk solution will be concentrated in the restricted region. Hydrogen ions and/or metal ions, which are produced in the anodic reactions, will also be concentrated within the restricted region. Additional definitions and explanations which may aid in understanding the effects of localized corrosion are presented below.

The potential of a solid metal test electrode immersed in solution is the difference between the potentials of the metal and solution phases; this is illustrated in Fig. B.3 and can be expressed as

$$\Delta\phi = \phi_m - \phi_s . \quad (\text{B.23})$$

The potentials represented by ϕ are the Galvani or inner potentials of the phases. The Galvani potential is the sum of (1) the potential due to excess charge and (2) the surface potential due to oriented dipoles. The value of $\Delta\phi$ is measured by combining the test electrode system with a reference electrode and measuring the voltage between them. Neglecting contact potentials in the lead wire systems and also neglecting solution-junction potentials, the measured voltage, E , is the difference between $\Delta\phi$ and $\Delta\phi_R$ as expressed by

$$E = \Delta\phi - \Delta\phi_R , \quad (\text{B.24})$$

where $\Delta\phi_R$ represents the arbitrarily assigned potential of the reference electrode. This is zero for the hydrogen electrode:

$$E = \Delta\phi \text{ (with hydrogen reference)} . \quad (\text{B.25})$$

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Fig. B.3. Setup used to measure electrode potential.

The setup commonly used to measure the potential of a specimen electrode when current flows through the solution is also illustrated in Fig. B.3. The current is ionic, and it may flow between the specimen and a counter electrode or between different regions on the surface of the specimen. A salt-bridge probe is placed adjacent to the specimen surface so that ϕ_s appearing in the measurement will approximate that at the specimen surface. With localized high corrosion rates, as within a pit or crevice, the probe will not generally measure the solution potential within the pit or crevice.

The possible situation for a pit (or crevice) is illustrated in Fig. B.4. Assuming a net anodic current within the pit, the solution potential exceeds that at the surface by the voltage drop between pit and surface solutions. Accordingly, the $\Delta\phi$ in the pit is given by the expression

$$\Delta\phi = (\phi_m - \phi_s) - \delta\phi_{IR} \quad (B.26)$$

where $\phi_m - \phi_s$ represents the electrode potential measured at the exposed surface, and $\delta\phi_{IR}$ is the difference between potentials of surface and crevice solutions. The relative levels of the potentials at different locations are also illustrated in Fig. B.4. Estimates and additional discussion of potential and solution composition changes in restricted-access corrosion are presented in Appendix 4 of ref. 49.

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Fig. B.4. Effects of restricted-geometry corrosion on solution and electrode potentials.

**Appendix C. REVIEW OF INFORMATION ON CORROSION OF CARBON STEEL
IN ENVIRONMENTS THAT MIGHT PREVAIL AROUND REFERENCE
CANISTER EMPLACED IN BEDDED SALT**

C.1 Dry Air and/or Dry Salt, Unirradiated

Available experimental information shows that carbon steel is very resistant to corrosive attack in dry air (less than about 1 mil/year is expected at temperatures that will prevail around SF canisters). Contact with dry salt does not increase the rate of attack.^{65,66}

Dry air as used in this report means that no liquid phase is in contact with the metal, either as bulk liquid or as surface condensate.

C.2 Aqueous Salt Solutions, Unirradiated

A summary of theoretical and experimental information on the electrochemistry of corrosion is presented in Appendix B.

Electrochemical studies of corrosion of carbon steel in deaerated, concentrated NaCl solutions (up to 4 M at 25°C) were reported by Posey and co-workers.⁶⁷⁻⁷⁰ The pH of their solutions varied from 2 to 7 (measured at 25°C), and the exposure temperatures varied from 22 to 200°C. The solutions were stirred mildly. A summary of their findings that are pertinent to considerations of corrosion of SF canisters in salt is given below.

1. The corrosion rates in the 4 M NaCl solutions varied with pH and temperature as shown in Eq. (C.1) (from refs. 69 and 70):

$$i_{\text{corr}} = 1.90 \times 10^5 \exp(-3.98 \times 10^3/T) \\ + 4.19 \times 10^6 (10^{-\text{pH}}) \exp(-2.10 \times 10^3/T) , \quad (\text{C.1})$$

where i_{corr} is the corrosion rate in mils per year and T is absolute temperature (K).

The rates at a given temperature decreased with increasing pH to about pH 5 and then remained unchanged to pH 7. All rates increased with increasing temperature. Illustrative values for i_{corr} calculated using Eq. (C.1) are:

	Temperature (°C)	i_{corr} (mils/year)
pH = 3.1	25	2.9
	100	12
	150	25
pH = 5 to 7	25	0.3
	100	4.5
	150	16

2. No protective oxide or hydroxide is formed in concentrated brines. However, the chloride ion at high concentration slows the corrosion rate to an appreciable extent, and the rates at concentrations greater than 4 M will probably be significantly less than those found with 4 M NaCl. The beneficial effects of increasing chloride concentration might result from a displacement of intermediates of the iron dissolution and hydrogen evolution reactions from the corroding surface by absorbed chloride ions.⁷⁰

3. The principal cathodic reaction in the pH range 5 to 7 in the 4 M deaerated solutions is the reduction of H₂O [Reaction (B.10), Appendix B]:

At pH < 5, the predominant cathodic reaction is the reduction of H⁺ [Reaction (B.9), Appendix B]:

The principal anodic reaction is the oxidation of Fe to Fe²⁺:

Some magnetite, Fe₃O₄, is usually formed along with the Fe²⁺ but this is nonprotective⁷¹ (see Sect. C.4).

In aerated, concentrated brine solutions, some reduction of O_2 [Reactions (B.7) and (B.8), Appendix B] will be included among the cathodic reactions:

This O_2 reduction will increase the potential and the rate of the anodic reaction at the corroding steel surfaces. The corrosion product will probably be primarily magnetite, but this product forms a porous oxide layer rather than a protective oxide in the brine solutions. Corrosion rates of ~50 mils/year have been observed in aerated NaCl brine at room temperature, and higher rates would occur at higher temperatures.*⁶⁶

C.3 Water-Availability Limit to Average Corrosion Rate of Canister Emplaced in Salt - Deaerated Environments

As implied in the above discussion, the corrosion of iron in the deaerated environment around a waste canister in salt is, in fact, a reaction between the iron and water in which an iron oxide or hydroxide is formed together with H_2 . Negligible corrosion takes place in the absence of water.

Assuming that the migration of water into the spaces around the emplaced canister takes place at average rate I , the following relationship prevails:

$$\alpha \bar{R} \leq I , \tag{C.3}$$

where $\bar{R}$ is the average corrosion rate of the canister and α is a proportionality constant - the value of which depends on the surface area of the canister and also on the iron to oxygen ratio in the corrosion product oxide.

*There is no net consumption of H_2O when the cathodic reactions are those shown as Reactions (B.7) and (B.8) in Appendix B.

The value of α for the reference canister (area = $5.3 \times 10^6 \text{ cm}^2$) and Fe_2O_3 as the corrosion product is $\sim 455 \text{ g(H}_2\text{O)} \cdot \text{year}^{-1} \cdot (\text{mils/year})^{-1}$.

Then

$$\bar{R}/I \leq 0.0022 (\text{mil/year}) \cdot \text{g(H}_2\text{O)}^{-1} \cdot \text{year} . \quad (\text{C.4})$$

The rate of migration of brine into an SF emplacement hole from surrounding salt is uncertain although it is expected to be much less than 450 g/year for more than 35 years after emplacement of 10-year-old SF in unbackfilled holes in the salt.⁷² If this is the case in practice and if there are no inflows of water or brine or oxidants from other sources, the average corrosion rate will be $\ll 1 \text{ mil/year}$.

However, as discussed in later sections, a small amount of brine can support very high localized corrosion rates when the brine is concentrated at the localized areas or when the contacting brine is oxygenated so that the cathodic corrosion reaction might not lead to the consumption of H_2O [e.g., Reactions (B.7) and (B.8)].

C.4 Considerations of pH and Hydroxy Complex Concentrations in Desaturated MgCl_2 -Rich Brines Adjacent to Canister in Salt

C.4.1 Introduction

Brines that occur as inclusions within bedded salt will probably be rich in MgCl_2 ; for example, those occurring within the halites found near Lyons, Kansas, and in New Mexico are about 2 m each in Mg^{2+} and in Na^+ , and they contain only traces of other cations.⁷² The brines are, of course, saturated in NaCl . Any inclusions that enter the open spaces around a waste canister will lose water by several processes, including reaction with the iron canister, radiolytic decomposition, and evaporation. The loss of water from the MgCl_2 -rich, NaCl -saturated solutions results in the precipitation of NaCl and an increase in the concentration of MgCl_2 (refs. 73-76) (Fig. C.1). With continued loss of water, the solutions become saturated in MgCl_2 , and a solid hydrate precipitates; this can be $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ or $\text{MgCl}_2 \cdot 4\text{H}_2\text{O}$ depending on the temperature of the system (Fig. C.2). These hydrates exert sensible vapor pressures of

Fig. C.1. Vapor pressure of water over NaCl and MgCl₂ solutions and over MgCl₂ solid hydrates versus temperature.

Fig. C.2. Concentration of NaCl versus concentration of MgCl₂ in NaCl-saturated solutions at 60, 80, 100, 120, and 140°C.

water, and they can be converted to still lower hydrates at suitably low partial pressures of water vapor^{73,74,76} (Fig. C.2). The hydrates can also undergo hydrolysis to form solid hydroxy chloride, MgOHCl , and HCl gas. However, this hydrolysis reaction will probably be very slow at the relatively low temperatures around SF canisters in salt.⁷⁷

The MgCl_2 -rich solutions will undergo hydrolyses to some extent at temperatures around reference canisters ($<150^\circ\text{C}$) with the formation of soluble hydroxy complexes and hydrogen ions. At first glance, it might seem that these hydrolytic reactions could reduce the pH and thus influence the rate of corrosion of any mild steel surfaces in contact with deaerated brine since the corrosion rate increases with increasing $[\text{H}^+]$ in these solutions (Sect. C.2). However, the products of iron corrosion also affect $[\text{H}^+]$, and their hydrolytic and/or dissolution reactions must be included in consideration of the probable composition of the corrosive brines. As shown below, it is likely that the maximum $[\text{H}^+]$ in saturated MgCl_2 solutions which are in equilibrium with iron corrosion products in deaerated systems will be $<2 \times 10^{-5} \text{ m}$ at 140°C and $<3 \times 10^{-6} \text{ m}$ at 100°C . The corrosion rates at these concentrations of H^+ would probably be <13 mils/year and <4.5 mils/year at the respective temperatures (Sect. C.2).

C.4.2 Hydrolytic reactions of Mg^{2+} and values for stability constants at 100 and 140°C

The hydrolytic reactions of Mg^{2+} at 25°C have recently been reviewed by Baes and Mesmer.⁷⁸ They concluded that the principal hydrolytic species are $\text{Mg}_4(\text{OH})_4^{4+}$ and $\text{Mg}(\text{OH})_2(\text{c})$. They showed tables of values for the formation quotient, Q , for each of these species at zero ionic strength, I , and also showed the formulations and the values for the constants to be used to evaluate Q at $I > 0$. Values at 1 m MgCl_2 ($I = 3$) which were found using their information and calculational methods were $-\log Q_{11} = 12.12$, $-\log Q_{44} = 38.85$, and $-\log Q'_{s_{10}} = 17.48$. Q_{xy} represents the formation constant for the hydroxy complex in which the subscripts x and y refer to the number of Mg and OH , respectively, which comprise the complex. $Q'_{s_{10}}$ refers to the reaction in which the Mg^{2+} in solution reacts with H_2O to form hydrogen ions and precipitated hydroxide.

Baes has also extrapolated existing 25°C data to obtain estimates of the values for Q for the hydrolytic species at higher temperatures.⁷⁹ His extrapolated values at 100 and 140°C are $-\log Q_{11} = 9.9$ and 9.1 ; $-\log Q_{44} = 30.8$ and 27.8 ; and $-\log Q_{s10} = 13.5$ and 11.8 .

Very recently, information from Russian workers on the hydrolysis of Mg^{2+} at 100 and 140°C was reported in *Chemical Abstracts*.⁸⁰ These workers studied $Mg(ClO_4)_2$ solutions (0.4 to 1.4 M) at 100 and 140°C at $I = 3$ ($NaClO_4$) by titration with a base. They reported the formation of the hydroxy complexes $Mg(OH)^+$, $Mg_2(OH)^{3+}$, and $Mg_4(OH)_4^{4+}$ with values for $-\log Q_{xy} = 10.5$, 10.0 , and 31.0 at 100°C and 9.9 , 9.0 , and 27.0 at 140°C. This information is presented in tabular form in Table C.1. The Russian values were apparently in molar units, and I multiplied their values by 1.16, where appropriate, to convert to molal units. $C_{x,y}$ represents the concentration of the x,y species.

The occurrence of the 2,1 hydrolytic species among those reported by the Russian workers is an obvious difference from the species reported by Baes. Baes believes that the presence of the 2,1 species has not been firmly established and that the 1,1 species might account for the experimental observations.⁷⁹ However, the Russian values will provide higher, and thus more conservative, estimates of $[H^+]$ in concentrated brine solutions, and I have used these values in the calculations reported in subsequent paragraphs.

The values of Q'_{s10} indicate that no $Mg(OH)_2$ would form in saturated $MgCl_2$ solutions at $[H^+] > 1.0 \times 10^{-6} m$ at 100°C and $> 7.1 \times 10^{-6} m$ at 140°C. As will be shown in subsequent sections, the $[H^+]$ resulting from the formation of the other soluble, hydrolytic species will exceed these amounts. Accordingly, the hydroxide was omitted from the estimates of $[H^+]$ resulting from hydrolysis in brine solutions.

C.4.3 Hydrolytic reactions of Fe^{2+}

The hydrolytic reactions of Fe^{2+} have recently been reviewed by Baes and Mesmer.⁸¹ Magnetite, Fe_3O_4 , is the stable solid phase in the presence of H_2 (H_2 will probably be present during corrosion of iron in deaerated systems). Sweeton and Baes⁸² studied the solubility of Fe_3O_4 over wide ranges of solution composition between 50 and 300°C at 1 atm H_2 . The dissolution reaction in which Fe^{2+} is formed is

Table C.1. Values for formation quotient
of Mg^{2+} hydrolysis products (molal units)

Relationship	Russian values ^a		Baes extrapolated values ^b	
	100°C	140°C	100°C	140°C
$Q_{1,1} = C_{1,1}[\text{H}^+]/[\text{Mg}^{2+}]$	3.7×10^{-11}	1.5×10^{-10}	1.2×10^{-10}	7.9×10^{-10}
$Q_{2,1} = C_{2,1}[\text{H}^+]^2/[\text{Mg}^{2+}]^2$	1.0×10^{-10}	1.0×10^{-9}		
$Q_{4,4} = C_{4,4}[\text{H}^+]^4/[\text{Mg}^{2+}]^4$	1.2×10^{-31}	1.2×10^{-27}	1.6×10^{-31}	1.6×10^{-28}
$Q'_{s_{10}} = [\text{H}^+]^2/[\text{Mg}^{2+}]$			1.5×10^{-13}	5.2×10^{-12}

^aSee ref. 80.

^bSee ref. 79.

The equilibrium constant, K_0 , for this reaction is,

$$K_0 = [\text{Fe}^{2+}]/[\text{H}^+]^2 \cdot [P_{\text{H}_2}]^{1/3} . \quad (\text{C.6})$$

Their least-squares average values for K_0 were represented by

$$R \text{ and } K_0 = (2.688 \times 10^3/T) + 9.81 \ln(T - 1) - 81.21 . \quad (\text{C.7})$$

Equilibrium constants for formation of other hydrolytic species, including FeOH^+ and $\text{Fe}(\text{OH})_3^+$, were reported. At equilibrium, the amounts of these at $[\text{H}^+] > 10^{-6} \text{ m}$ would be negligible.

C.4.4 Procedures for calculating $[\text{H}^+]$ and other hydrolytic species in concentrated MgCl_2 solutions in equilibrium with solid Fe_3O_4

We first write the charge balance relationship,

$$\begin{aligned} 2[\text{Mg}^{2+}] + C_{1,1} + 3C_{2,1} + 4C_{4,4} + [\text{H}^+] + 2[\text{Fe}^{2+}] \\ = [\text{Cl}^-] + [\text{OH}^-] . \end{aligned} \quad (\text{C.8})$$

Let M represent total moles of magnesium in solution per kilogram of H_2O ; then

$$M = \frac{[\text{Cl}^-]}{2} = [\text{Mg}^{2+}] + C_{1,1} + 2C_{2,1} + 4C_{4,4} . \quad (\text{C.9})$$

Substituting from Eq. (C.9) into Eq. (C.8) and collecting terms yields

$$-C_{1,1} - C_{2,1} - 4C_{4,4} + [\text{H}^+] + 2[\text{Fe}^{2+}] = [\text{OH}^-] . \quad (\text{C.10})$$

Substituting relationships into Eq. (C.10) for $C_{1,1}$, $C_{2,1}$, and $C_{4,4}$ from Table C.1; for $[\text{Fe}^{2+}]$ from Eq. (C.6); with $[\text{Mg}^{2+}] \approx M$; and with $[\text{OH}^+] = K_w/[\text{H}^+]$, and rearranging,

$$\begin{aligned}
 & -Q_{1,1}M[H^+]^3 - Q_{2,1}M^2[H^+]^3 - K_w[H^+]^3 + 2K_0P_{H_2}^{1/3}[H^+]^6 \\
 & + [H^+]^5 = 4Q_{4,4}M^4.
 \end{aligned}
 \tag{C.11}$$

This equation can be used to evaluate $[H^+]$ when the values of $Q_{1,1}$, $Q_{2,1}$, $Q_{4,4}$, and K_w are known and when those for M and P_{H_2} are given. The concentrations of the other species can be determined from their relationships to $[H^+]$ given in Sects. C.4.2 and C.4.3.

C.4.5 Results of calculations of values for $[H^+]$ and other hydrolytic species in saturated $MgCl_2$ solutions in equilibrium with solid Fe_3O_4 at 100 and 140°C

These calculations were made using Eq. (C.11) and parameter values and relationships from Sects. C.4.2, C.4.3, and C.4.4. P_{H_2} was assumed to equal 1 atm for one set of calculations and 0.1 atm for the other set. The value of M for the saturated solutions was 7.7 m at 100°C and 9.6 m at 140°C. The results are listed in Table C.2.

As stated in Sect. C.4.1, the $[H^+]$ indicated by these results is $< 2 \times 10^{-5}$ m at 140°C and $< 3 \times 10^{-6}$ m at 100°C. The P_{H_2} has only small effects on the concentration of the different species because it enters as $P_{H_2}^{1/3}$.

C.5 Hydrolytic Reactions and pH in Aerated, $MgCl_2$ -Rich Brine Adjacent to Caulister in Salt

Some of the iron that is oxidized in aerated, $MgCl_2$ -rich brines in the reference repository will be oxidized to the ferric state. The hydrolytic reactions of ferric iron in concentrated chloride solutions at elevated temperatures are uncertain. It is probable, however, that the ferric ions and complexes will be less soluble than the ferrous ones.⁸¹ If this is the case, the $[H^+]$ resulting from hydrolysis of Mg^{2+} will exceed that in deaerated systems. At the extreme, with no soluble iron, the $[H^+]$ would be established by the Mg^{2+} hydrolysis alone. Using calculations procedures and parameter values and relationships discussed in Sect. C.4, it can be shown that the $[H^+]$ in saturated solutions of $MgCl_2$ with no dissolved iron would be about 3×10^{-5} m at 100°C and about 3×10^{-4} m at 140°C.

Table C.2. Results of calculation of concentrations of hydrolytic species in saturated MgCl_2 solutions in equilibrium with Fe_3O_4

Species	Equilibrium concentration, <i>m</i>			
	100°C		140°C	
	1 atm H_2	0.1 atm H_2	1 atm H_2	0.1 atm H_2
H^+	2.0×10^{-6}	2.5×10^{-6}	1.3×10^{-5}	1.7×10^{-5}
Fe^{2+}	1.6×10^{-3}	1.2×10^{-3}	3.6×10^{-3}	2.8×10^{-3}
MgOH^+	1.5×10^{-4}	1.1×10^{-4}	1.1×10^{-4}	8.5×10^{-5}
$\text{Mg}_2(\text{OH})^{3+}$	3.0×10^{-3}	2.3×10^{-3}	7.0×10^{-3}	5.5×10^{-3}
$\text{Mg}_4(\text{OH})_4^{4+}$	2.8×10^{-5}	1.0×10^{-5}	3.4×10^{-4}	1.2×10^{-4}

The effects of this lower $[H^+]$ on the rate of corrosion of the iron is likely to be negligible relative to the effects of the higher corrosion potential that occurs in the presence of O_2 .

C.6 Localized Corrosion of Canister Emplaced in Salt with Bedded Salt Backfill

A large fraction of the brine within the bedded salt is released during crushing, and the crushed salt will contain essentially all of this brine, probably spread out on surfaces within the crushed salt. Also, any water remaining as brine inclusions within crystals or as hydrates within the crushed salt could be released rapidly when the backfill is heated.⁷⁰ The brines in bedded salt are rich in $MgCl_2$,⁷² and the presence of this chemical causes a lowering of the vapor pressure of the $NaCl$ solutions by factors that increase with increasing concentration of $MgCl_2$ (Sect. C.4).^{73,74,76} A solution that contains $MgCl_2$ and is in contact with solid $NaCl$ becomes more concentrated in $MgCl_2$ as water is lost from the solution (Sect. C.4).⁷³⁻⁷⁶ Consideration of these factors led me to conclude that (1) liquid brine might remain in contact with the canister wall at one or more points of contact between backfill and canister, (2) this brine would be of moderately low pH (5 to 6), and (3) localized penetration of the canister (1/2-in.-thick wall) might occur at a point of contact at rates ranging up to about 15 mils/year in deaerated backfill depending on temperature ($\sim 150^\circ C$, max) of the solutions contacting the canister wall and on whether the gamma radiation that emanates from the canister will alter the corrosion rate from that prevailing in the absence of radiation. As discussed in Appendix D, it is possible that radiolytically formed oxygen could lead to localized corrosion rates ranging from 200 to 300 mils/year on the reference carbon steel canister if only a small fraction of the canister surface were wetted by brine. This is true even though the amount of radiolytic O_2 would not be sufficient to significantly alter the average corrosion rate that would prevail should the entire canister surface be wetted with brine.

C.7 Effects of Emplacement Hole Closure on Canister Corrosion and Integrity

It is generally believed that the solid salt surrounding an emplaced canister will undergo inward displacement as a result of plastic creep in the salt and that the hole will eventually be closed around the canister by this process.^{57,83} This inward displacement could affect the corrosion of the canister if the displacement and any accompanying changes in the compressive stresses on crystal aggregates result in release of appreciable amounts of brine from crystal boundaries within the salt. Also, the number and characteristics of contacts between salt and canister wall and, hence, the possibilities of rapid, localized corrosion (Sect. C.6) could be affected by the inward displacement. Furthermore, depending on the strength of the canister walls and on the overburden pressure at the repository, the canister walls might collapse as the full overburden pressure is applied through the salt and backfill.

Neither theoretical calculations nor experimental tests of rates and characteristics of hole closure have been made for the reference repository in bedded salt. The reported⁵⁷ results of calculations of closure rates around widely spaced HLW canisters in domal salt at a depth of 2000 ft suggest that the closure in an air-backfilled emplacement hole in the repository will be ≤ 2 in. on the radius at five years after emplacement of the reference canister. If the space around the canister is backfilled, the closure will probably be appreciably less than 2 in., but the pressure on the canister walls may approach the maximum overburden pressure — about 2000 psi at a depth of 2000 ft.

The results of stress calculations made using standard formulas indicated that the reference canister (1/2-in.-thick wall) will withstand more than 2000 psi without buckling.^{57,84}

The experimental information available from Project Salt Vault showed that the 1/4-in. radial hole closure that took place during the heating phase of the experiment did not cause any significant breakup of the solid salt walls.⁸⁵

C.8 Possible Benefits of Using Sand Backfill Around Canister in Salt

Although the use of sand rather than crushed bedded salt backfill around a canister in a bedded salt repository would help to minimize the possibility that brine would contact the canister in only a few local areas, local brine contacts might still take place within short periods of time after emplacement of a canister. High rates of localized corrosion would probably take place at these sites by the processes described in Sect. C.6.

C.9 Possible Benefits of Mixing Quicklime with Sand Backfill Around Canister in Salt

Quicklime (CaO) is a strong desiccant, and the product of the reaction with H_2O , $\text{Ca}(\text{OH})_2$, is stable at very high temperatures (e.g., the vapor pressure of H_2O over $\text{Ca}(\text{OH})_2$ is 0.0035 atm at 300°C .⁸⁶ A 12-ft length of the annular region around a reference canister (see Table 6) has a total volume of $2.1 \times 10^5 \text{ cm}^3$. About $1.5 \times 10^5 \text{ g}$ of powdered CaO could fit into the otherwise open spaces within the sand or crushed salt backfill. Complete reaction of this amount of CaO with water would bind 2500 moles of H_2O (45 kg H_2O) as $\text{Ca}(\text{OH})_2$. Swelling by a factor of 1.89 occurs upon complete hydration of quicklime so that the backfill would tend to become impervious when the initial density of the powdered CaO as mixed with the sand is $\geq 55\%$ of the theoretical for the solid.

It seems likely that access of brine to the canister from the surrounding salt would be limited to cracks that develop in this backfill and that have surfaces in which all CaO has previously reacted with H_2O . However, diffusion paths would be nearly nonexistent within this backfill material, and the maximum rate of localized attack at the end of a crack would be limited to the locally available supply of corrodents, that is, water and O_2 . The local supply would probably limit the local corrosion rate to $< 5 \text{ mils/year}$.

The chemical properties and phase behavior are uncertain for the systems that would result if brine solutions came into contact with hydrated quicklime on the edges of the backfill or on the surface of cracks within the backfill. These properties must be established before

a final recommendation can be made to use the quicklime-sand mixture as backfill for the canister in salt. Also, experimental tests of radiation effects and of carbon steel corrosion in this backfill material are required for final verification of the suitability of the material. Other factors that should be investigated experimentally include (1) identities, physical properties, and phase behavior of the products of reaction between the CaO and the MgCl_2 -rich brines; (2) the fraction of the CaO which would actually be available for reaction with brine water over the long periods of time which are of interest; and (3) determining whether paths develop in the backfill through which brine could migrate to the canister without contacting CaO.

C.10 Possible Benefits of Mixing Quicklime with Crushed Bedded Salt for Backfill Around Canister in Bedded Salt

The possible benefits are comparable to those described above for the mixture of quicklime and sand, and the quicklime-salt mixture might prove to be comparable in suitability. However, there are additional uncertainties about the quicklime-salt mixture because of (1) the presence of brine on the surface of the crushed salt, (2) the nonuniform sizes and shapes of the particles within the crushed salt, and (3) the occurrence of radiation damage in the salt.

C.11 Other Types of Desiccants Around Canister in Salt

Other types of desiccants for use around waste canisters in salt are being considered,⁵² including chemical additions that would promote the formation of tachyhydrite ($2\text{MgCl}_2 \cdot \text{CaCl}_2 \cdot 12\text{H}_2\text{O}$).⁵² The factors that must be investigated prior to the use of any of these desiccants are likely the same as those outlined for quicklime.

C.12 Use of Air Backfill Around Canister in Salt

As stated in Sect. C.1, the oxidation rate of the carbon steel canister in dry air will be very low. At the low rates of in-migration of brine which appear likely in a repository, it should be possible to keep any accumulated liquid away from the canister for several years

after emplacement and thus maintain low corrosion rates for several years. However, an air backfill has several possible disadvantages:

1. Refluxing of water may take place, resulting in shifting of salt around the emplacement cavity. This shifting might result in some loss of support for the sleeve in the retrievable storage concept of Kaiser Engineers (Sect. 6.2).
2. Hole closure would probably take place over a period of 5 to 10 years after emplacement of the reference canisters (Sect. C.7), and in-migrating brine might then contact the canister surface at isolated areas.
3. The relatively large hole-closure movements might entail release of relatively large amounts of brine from the solid salt.
4. Mixtures of gases, if present, could react explosively within the large, open unbackfilled spaces around a canister. These gases would probably not be able to react explosively within sand or crushed salt backfill or within other backfill materials of similar type.
5. If some area of the canister becomes wetted with brine, corrosion on that area could proceed very rapidly in an aerated environment (Sect. C.6 and Appendix D).

C.13 Summary and Conclusions

An appropriate summary and some important recommendations are presented in Sect. 8.2 of the text. Additional recommendations for in situ experiments are presented below.

In situ experiments with canisters in bedded salt should be conducted to verify the conclusions relating to the corrosion and integrity of the reference canister emplaced with a given backfill in bedded salt. The information that could and should be sought in these experiments includes the following:

1. rates of closure as functions of time and of radial and axial locations within the cavity;
2. stability of cavity walls during closure movements;
3. effects of closure movements of solid salt on release of brine from the solid salt surrounding the waste package;

4. pressures on walls of waste package exerted by backfill when it is compressed by closure movements of surrounding salt, and measures of these pressures as functions of time and of circumferential and axial locations around the waste package;
5. porosity of backfill as functions of time and of radial and axial locations within the backfill (The porosities might be determined with suitably located tubes through which gases could be passed into the backfill.);
6. rates of emission of H_2 and other gases from backfill into overlying room determined throughout the in-cavity portion of the experiment;
7. total corrosion and general corrosion characteristics of waste package during the experiment determined using corrosion coupons or other means;
8. visual appearance of backfill material upon removal of experiment from cavity; and
9. chemical composition of backfill material at representative locations within the cavity determined upon removal of experiment and backfill from cavity.

Appendix D. RADIATION CHEMISTRIES OF FLUIDS AND SOLID SALT
AROUND EMPLACED CANISTER AND EFFECTS OF RADIATION
ON CORROSION OF CANISTER IN SALT

D.1 Brines

Available theoretical and experimental information⁷⁷ indicates that any liquid brine that collects in the irradiated spaces around a waste canister will undergo radiolysis with production of H₂ and balancing amounts of one or more of the oxidized species shown in the oxidation-reduction balance relationships in Eq. (D.1):*

The interpretation of Eq. (D.1) is sometimes elusive but can be understood from the following illustration: Assume that H₂ and O₂ are the only products formed in the radiolysis and subsequent chemical reactions. Then Eq. (D.1) reduces to

$$2G(H_2) = 4G(O_2) , \quad (D.2)$$

or

$$G(O_2) = \frac{1}{2}G(H_2) ; \quad (D.3)$$

that is, the yield of O₂ is one-half that of H₂ corresponding to the products of decomposition of H₂O into H₂ and O₂.

An additional relationship resulting from charge balance requirements is

*The symbol $G(X)$ represents the number of species X occurring within or evolving from an irradiated solution at any given time after the start of irradiation, per 100 eV of radiation energy absorbed in the solution. These species include those which are formed as initial products in homogeneous distribution in the solution and also the products of subsequent reactions of these within the solution.

The symbol $G(-\text{H}^+)$ in Eq. (D.4) represents the yield for loss of H^+ which results from the formation of the Cl and/or the other neutral species that are set out in this equation.

The estimated maximum value for $G(\text{H}_2)$ in the body of a brine solution is 2.1.⁷⁷

The identities and relative yields of the oxidized species are uncertain. In general terms, it seems likely that O_2 and ClO_3^- will predominate when the pH (measured at 25°C) is between 3 and 8 and when the brine temperature is between 50 and 150°C. At lower values of pH, it is likely that appreciable yields of Cl_2 will occur. Small amounts of the other chlorine species shown in Eq. (D.1) may also occur at the lower pH. Bromine species are included in Eqs. (D.1) and (D.4) because the brine might contain a significant concentration of Br^- (about 0.05 M in Lyons salt).^{72,77}

D.2 Gas-Vapor Phase

The principal radiolytic reaction will be the reformation of H_2O from H_2 and O_2 within the gas space.^{87,88} The value of $G(\text{H}_2\text{O})$ will probably be between 3 and 6 based on energy absorption in all of the species present with the gas-vapor phase.

If N_2 is present, some HNO_3 and/or other nitrogen oxides may also form.⁸⁹ If Cl_2 enters the gas space, it will react radiolytically with H_2 to form HCl .⁹⁰ Subsequent dissolution of this HCl in the brine will result in recovery within the brine of the H^+ that was lost when the Cl_2 was formed.

D.3 Solid Salt

Gamma irradiation of solid NaCl under SF emplacement conditions will result in the formation of radiation defects which are chemically equivalent to colloidal sodium and to colloidal chlorine. Upon dissolution of the salt in brine, the sodium will react to form H_2 , while the chlorine will react in ways dependent upon the solution composition and

temperature.^{91,92} It is likely that the identities and relative yields of the oxidized species will be similar to those produced by direct absorption of gamma-ray energy in the given brine solution.

The amount of H₂ produced by dissolution of salt which was irradiated under SF conditions corresponds to that for a $G(\text{H}_2)$ value of 0.0070 based on the gamma energy deposited in the salt up to the time that the salt was dissolved.^{91,92}

It is conceivable that irradiation-damaged salt will have a significantly higher chemical potential and thus be more soluble than unirradiated salt. If this proves to be the case, it is likely that surfaces of irradiated salt in contact with brine would dissolve, while precipitation would take place on adjacent fresh surfaces.⁷² The radiation defects would, of course, dissolve as the salt dissolves.

D.4 Gamma-Ray Dose Rates Around Emplaced Canister

Croff et al.⁹³ have recently reported detailed calculations of the gamma-ray dose rates around spent PWR assemblies. Their values correspond to about 2.5×10^4 rems/hr in salt at the midplane outer edge of a 10-year-old assembly and about 50 rems/hr at the bottom and top of the assembly.*

D.5 Possible Effects of Gamma Radiations on Corrosion of Canister in Salt

D.5.1 General

One requisite for the occurrence of any radiation-corrosion effect is that liquid brine be present within the emplacement cavity and located at elevations exposed to appreciable gamma-ray intensities. Brine located near and below the bottom of the canister will be exposed to negligible intensities.

*Rems = rads·quality factor. For gamma rays with energies typical of those emanating from SF, the quality factor for absorption of the gammas in water is approximately equal to unity.

Another requisite is that liquid brine be in contact with the canister surface at some area. If there are no wetted areas, the corrosion will probably be vapor-reaction controlled, and radiolytic products would not affect the corrosion rate.

Radiolytic formation of strongly oxidizing species is the most likely avenue through which the radiation would affect corrosion. The strongly oxidizing species most likely to occur around a canister are gaseous O_2 and, in solution, ClO_3^- . Possible amounts and effects of these oxidants are discussed in the following sections.

D.5.2 Oxygen

An estimate can be made of the maximum effects of radiolytic O_2 on corrosion by assuming that all of the O_2 resulting from radiolysis in liquid and gases around the canister takes part in the cathodic corrosion reactions shown in Reactions (B.7) and (B.8) and that the anodic reaction is the formation of Fe_3O_4 ,

The ratio of moles of O_2 consumed to moles of Fe oxidized is 2:3 for these assumed corrosion reactions.*

If we further assume that the canister is backfilled with sand and that corrosion is fairly uniform over the outer surfaces of the canister, we can write

$$dV_o/dt = K_f - 43R , \quad (D.6)$$

where

K_f = net rate of formation of oxygen by radiolysis; proportional to the difference between the rate at which radiolytic O_2 formed in the brine enters the gas phase and the rate at which the O_2 is radiolytically combined with H_2 in the gas space, cm^3/hr ;

*The overall net reaction is $3Fe + 2O_2 \rightarrow Fe_3O_4$.

R = average rate of corrosion of reference canister surface,
mils/year;

43 = volume rate of consumption of O_2 in the cathodic corrosion reactions [see Reactions (B.7) and (B.8)], cm^3 (STP) $\cdot hr^{-1}$.
(mils/year) $^{-1}$ (where mils/year refers to average corrosion rate on the reference canister);

V_o = volume of O_2 in irradiated space around canister, cm^3 (STP).

An explicit expression for K_f , shown in Eq. (D.7), for the reference canister in salt with sand backfill was derived assuming:

1. $G(O_2) = \frac{1}{2}G(H_2) = 1.05$ in liquid brine;
2. $G(H_2O) = 3$ in gas-vapor mixture around canister;
3. Average gamma-ray dose rate around canister = 1.5×10^4 rads/hr and no significant volume of O_2 dissolved in irradiated brine.

Therefore,

$$K_f = 3.6 \times 10^{-4} (W_w - 1.4W_g) \quad (D.7)$$

where

W_w = weight of brine water exposed at average gamma-ray dose rate, g;

W_g = weight of gas exposed at average gamma-ray dose rate, g.

In order to relate W_w and W_g to the reference canister, we define V_g as the volume occupied by gases within the irradiated backfill region around the canister in cubic centimeters. Assuming sand backfill with 40% void spaces, the void volume around a 12-ft length of the reference canister is 8.4×10^4 cm^3 . Then accounting for the volume occupied by liquid brine,

$$V_g = 8.4 \times 10^4 - V_b, \quad (D.8)$$

where V_b is the volume of brine within the backfill in cubic centimeters.

Now the value of W_g for an assumed gas mixture of 70% H_2 , 25% water vapor, and 5% Ar at 77°C and 1 atm is

$$W_g = (2.7 \times 10^{-4})V_g \quad (D.9)$$

Substituting for W_g in Eq. (D.7) from Eq. (D.9) and rearranging,

$$K_f = (3.6 \times 10^{-4})W_w - (1.4 \times 10^{-7})V_g. \quad (D.10)$$

Substituting for V_g in Eq. (D.10) from Eq. (D.8),

$$K_f = (3.6 \times 10^{-4})W_w - (1.1 \times 10^{-2}) + (1.4 \times 10^{-7})V_b. \quad (D.11)$$

Obviously, the V_b term in Eq. (D.11) is negligible relative to the W_w term and can be neglected.

It is notable that Eq. (D.11) shows K_f equal to 0 when W_w equals 30 g. That is, no significant net amount of O_2 is expected to occur unless the amount of water within the irradiated region exceeds about 30 g, a result of the radiolytic reaction between H_2 and O_2 in the gas phase.

Finally, we assume that a steady state exists in which O_2 is consumed in corrosion at a rate equal to the formation rate, and dV_o/dt in Eq. (D.6) equals 0. Then substituting for K_f in Eq. (D.6) from Eq. (D.11) and solving for R at the steady state,

$$R = (8.4 \times 10^{-6})W_w - 2.6 \times 10^{-4}. \quad (D.12)$$

The maximum value for W_w occurs when all the void spaces within the irradiated backfill are filled with brine, at which time W_w equals 8.5×10^4 g. Introducing this value for W_w (max) into Eq. (D.12), we find R equals 0.7 mils/year.

The average corrosion rate in deaerated brine in the absence of radiation is expected to be greater than 0.7 mils/year, and it then seems likely that radiolytic O_2 will have negligible effects on the corrosion of the reference canister emplaced with sand backfill, if the canister surface is wetted uniformly.

A much greater effect of radiolytic O_2 could occur if the canister surface is not wetted uniformly but is wetted on only a relatively small area or areas. As an example, assume that only 1% of the canister surface is wetted and that all of the radiolytic O_2 reaches these areas and reacts cathodically. Then the local corrosion rate could be about

100 times that which would occur if the entire canister surface were wetted uniformly. On the basis of available fragmentary information on corrosion rates in aerated brines at elevated temperatures, I estimated that localized corrosion rates might reach 200 to 300 mils/year on the reference canister emplaced in bedded salt, depending on (1) the fraction of the surface which is wetted by brine, (2) the volume of brine from which radiolytic O_2 reaches the local areas, and (3) the temperature at the wetted areas. The highest rates would occur at the highest temperatures.

It is apparent that emplacement conditions conducive to spot-wetting of the canister should be avoided. In fact, to maximize the period of time for which the canister remains unbreached, complete filling of the backfill with brine would be preferable to fractional filling with wetting on only a small fraction of the canister surface.

Another O_2 -related quantity of interest is that for the amounts of radiolytic O_2 which would accumulate in the backfill when no O_2 is consumed in corrosion. In this case, the radiolytic O_2 will be swept from the disposal cavity into the overlying room along with the H_2 formed in the corrosion of the canister by brine and in the radiolysis of the brine, and with water vapor which will be present within the backfill. The quantitative effects of these processes on the volumes of O_2 around the canister are

$$dV_o/dt = K_f - \frac{(65R + 3K_f)(1.33)V_o}{V_g}, \quad (1.13)$$

where 65 is the volume rate of formation of H_2 from corrosion of the canister in $cm^3(STP) \cdot hr^{-1} \cdot (mils/year)^{-1}$. The factor 1.33 accounts for an assumed partial pressure of water vapor of 0.25 atm. This is equivalent to the vapor pressure of a NaCl-saturated, 4 M $MgCl_2$ solution at $77^\circ C$. The other symbols have the meanings stated for Eqs. (D.6) through (D.8).

As before, we will assume that steady states exist in which the rates of formation of O_2 equal the rates of removal of O_2 . Then Eq. (D.13) is solved for the quantities V_o and V_o/V_g with dV_o/dt equal to 0. After appropriate substitutions from Eqs. (D.7) through (D.10), we have

$$V_o = \frac{30.2W_u - (3.6 \times 10^{-4})W_u V_b - 950}{86R + 0.0015W_u - 0.043} \quad (D.14)$$

$$V_o/V_g = \frac{(3.6 \times 10^{-4})W_u - 0.014}{86R + 0.0015W_u - 0.043} \quad (D.15)$$

Some illustrative values for V_o and V_o/V_g , calculated from Eqs. (D.14) and (D.15) at several different assumed values for W_u and R , are listed below. It was assumed that the numerical value for V_u was equal to that for W_u in each case.

W_u (g)	R (mils/year)	V_o (cm ³ , STP)	V_o/V_g
30	Does not enter	0	0
100	1	25	2.5×10^{-4}
	5	5.0	5.0×10^{-5}
	10	2.5	2.5×10^{-5}
	25	1.0	1.0×10^{-5}
500	1	160	2.0×10^{-3}
	5	33	4.0×10^{-4}
	10	16	2.0×10^{-4}
	25	7.0	1.0×10^{-4}
1,000	1	410	6.0×10^{-3}
	5	83	1.2×10^{-3}
	10	41	6.0×10^{-4}
	25	16	2.5×10^{-4}
10,000	1	3,500	4.7×10^{-2}
	5	780	1.1×10^{-2}
	10	400	5.5×10^{-3}
	25	160	2.2×10^{-3}

Additionally, it can be noted that the brine inflow rate required to maintain a given amount of brine within the backfill varies with the average corrosion rate when the system is free of strong-oxidant corrosion reactions as assumed here. As discussed previously, about 455 g of water per year is required to support an average corrosion rate of 1 mil/year over the surface of the reference canister. Also, water vapor will be swept from the backfill region along with the H_2 formed in the corrosion.

For the system assumed in the illustration discussed above, the partial pressure of water vapor is 0.25 atm, and the amount of water vapor swept out equals about 160 g/year per mil/year rate of average corrosion. Then the total rates of water inflow required to maintain a given amount of brine within the backfill are about 0.62, 3.1, 6.2, and 15.4 kg/year for strong-oxidant-free corrosion rates of 1, 5, 10, and 25 mils/year respectively.

The results of the estimates developed and discussed in this section indicate that small volumes of radiolytic O_2 might accumulate in the backfill, but it is unlikely that the amount will exceed a few percent of the total volume of gases within the backfill.

D.5.3 ClO_3^-

Chlorate is a strong oxidant which might be formed in place of O_2 in the radiolytic decomposition of any brine water that accumulates within the irradiated portion of the backfill. The ClO_3^- would remain in solution and could contribute to the corrosion of a carbon steel surface in contact with the solution. However, the effects of the ClO_3^- on the corrosion rate could not exceed those which would occur with radiolytic O_2 produced locally in place of ClO_3^- . Then, since no diffusion of ClO_3^- through the gas-vapor phase would take place, the maximum expected effect of the radiolytic ClO_3^- would not exceed the maximum effect expected for the radiolytic O_2 under the condition that the canister surface is uniformly wetted with brine (i.e., <1 mil/year).

Appendix E. DERIVATION OF DIFFUSION-TRANSPORT EQUATION

H. C. Claiborne

The assumption is made that the physical process can be approximated by a slab with an initial zero concentration that has an instantaneous source impressed on one end with an insulated boundary. The opposite end is maintained at zero concentration. The equation for diffusion in the domain $0 \leq x \leq a$ is

$$D \frac{\partial^2 C}{\partial x^2} + S_0 \delta(x', t = 0) = \frac{\partial C}{\partial t}, \quad (\text{E.1})$$

where

D = diffusion coefficient, cm^2/sec ;

C = concentration, g or moles/ cm^3 ;

x = distance into slab, cm;

t = time, sec;

S_0 = source strength, g or moles/ cm^2 ;

$\delta(x', t = 0)$ = a delta function representing the presence of an instantaneous source located at x' .

The solution of Eq. (E.1) for a general set of boundary conditions is given in ref. 94. By selection $h_1 = 0$ and $k_1 = 1$ at $x = 0$, and $h_2 = 1$ and $k_2 = 0$ for use in the general boundary condition equation given in the reference, the required boundary conditions for this model obtains; namely,

$$\frac{\partial C}{\partial x} = 0 \text{ at } x = 0,$$

and

$$C = 0 \text{ at } x = a.$$

For these boundary conditions the eigenvalue equation is $\tan \alpha a = 0$, and the roots are

$$\alpha_n = \frac{(2n - 1)\pi}{2a}. \quad (\text{E.2})$$

By substituting into the general solution equation⁹⁴ the above constants and eigenvalues [Eq. (E.2)], the solution for our problem is

$$C = \frac{2S_0}{a} \sum_{n=1}^{\infty} \cos \frac{(2n-1)\pi x}{2a} \exp \left[-\frac{D(2n-1)^2 \pi^2 t}{4a^2} \right]. \quad (\text{E.3})$$

The current out of the slab is

$$J = -D \frac{\partial C}{\partial x} \text{ (at } x = a \text{)}. \quad (\text{E.4})$$

Differentiating Eq. (E.3) and substituting the result into Eq. (E.4) we have for $x = 0$,

$$J = \frac{\pi D S_0}{a^2} \sum_{n=1}^{\infty} (-1)^{n+1} (2n-1) \exp \left[-\frac{D(2n-1)^2 \pi^2 t}{4a^2} \right]. \quad (\text{E.5})$$

The cumulative leakage as a function of time is

$$Q = \int_0^t J dt. \quad (\text{E.6})$$

Combining Eqs. (E.5) and (E.6) and performing the integration, we have

$$Q = S_0 \left[1 - \frac{4}{\pi} \sum_{n=1}^{\infty} \frac{(-1)^{n+1}}{(2n-1)} \exp \left(-\frac{D(2n-1)^2 \pi^2 t}{4a^2} \right) \right], \quad (\text{E.7})$$

since

$$\sum_{n=1}^{\infty} \frac{(-1)^{n+1}}{2n-1} = \frac{\pi}{4}.$$

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