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A Comparison of Brines Relevant to Nuclear Waste Experimentation

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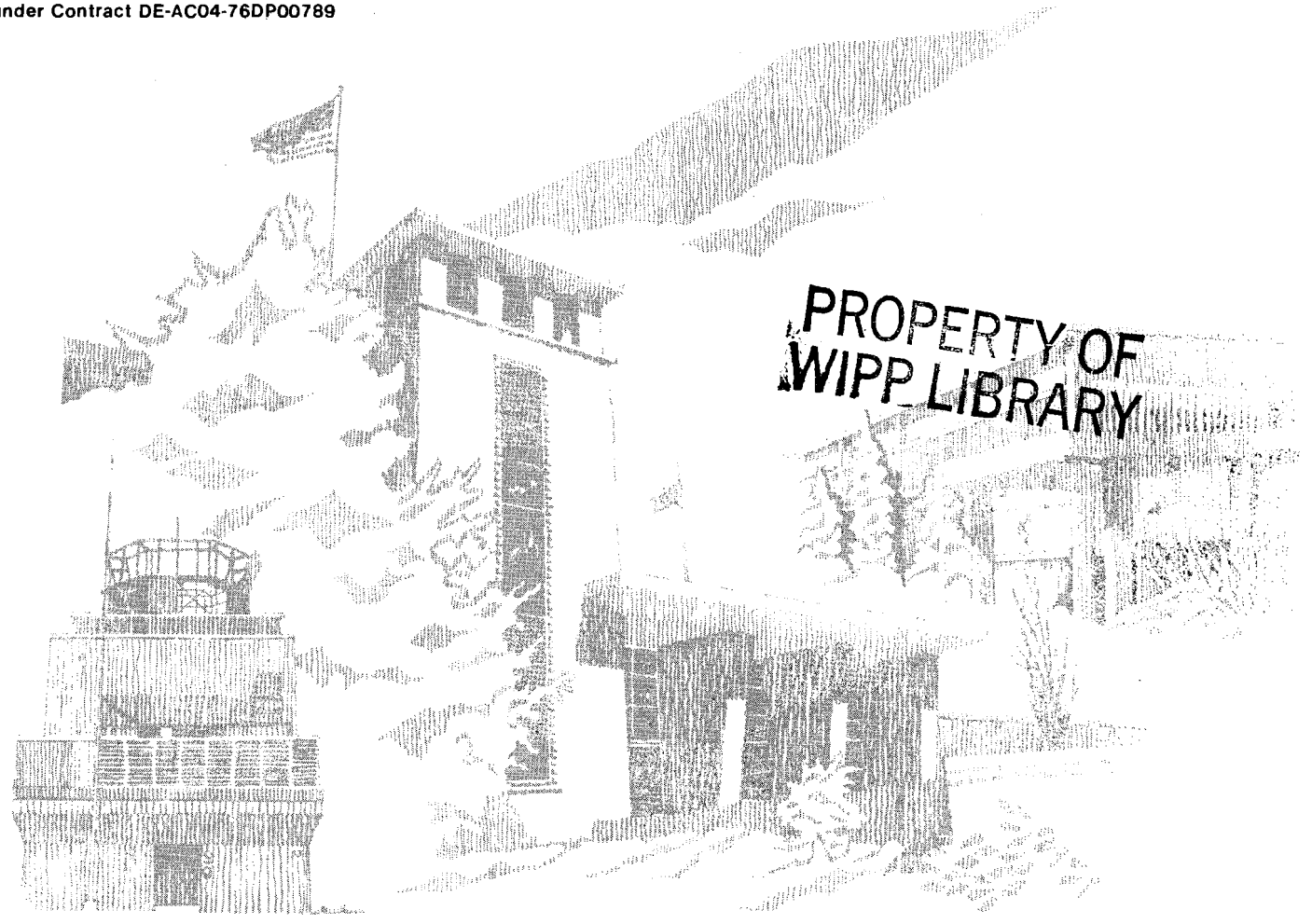

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A COMPARISON OF BRINES RELEVANT TO NUCLEAR WASTE EXPERIMENTATION*

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ABSTRACT

The ionic compositions of 18 brines used in nuclear waste-related laboratory tests or obtained from field tests are described and compared. Also described are the origin of each brine, its predominant use for laboratory testing, and its relevancy for future testing. The brines include Brines A and B (Waste Isolation Pilot Plant (WIPP)/generic), Office of Nuclear Waste Isolation (ONWI) Composite Permian Brine P and Equilibrated Permian P No. 2, Battelle Pacific Northwest Laboratory (PNL)-Sandia High-Level Waste (HLW) package interactions test brines (pretest, intermediate, and posttest samples), WIPP-12 brines (flow and downhole), ERDA-6 brines (flow and downhole), WIPP Inclusions No. 1 and No. 2, Materials Characterization Center (MCC) brine, German quinare Brine Q, U.S. Geological Survey bittern NBT-6a, saturated NaCl (20° and 100°C), and standard seawater.

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A COMPARISON OF BRINES RELEVANT TO NUCLEAR WASTE EXPERIMENTATION

Martin A. Molecke

INTRODUCTION

Many different brine compositions have been proposed or used for the laboratory measurements of wasteform leachability or for corrosion testing of waste package barriers. The purposes of this report are to document the detailed ionic compositions of 18 different brines, to discuss their origins, to compare their similarities or differences and the significance of such differences, and to describe their predominant testing uses. This information is being compiled specifically for use in the area of nuclear waste experimentation, e.g. waste form leachability, waste package materials corrosion or durability testing, interactions testing, etc. An indirect purpose of this report is to stem the proliferation of even more different brines for testing purposes. Also presented are the relevancy of defined brines to actual or expected rocksalt (waste repository) in situ conditions, and recommendations for future test purposes.

The brines listed in this report have particular relevance to high-level waste (HLW) package materials testing programs of the Office of Nuclear Waste Isolation (ONWI), the Waste

Isolation Pilot Plant (WIPP), and the Subseabed Disposal Program. Most of the laboratory testing involving these brines has been conducted at Sandia National Laboratories (SNL) and Battelle Pacific Northwest Laboratory (PNL). However, these brine compositions are of interest and use to many other groups.

COMPOSITIONS

The brines included in this comparison are listed below:

- Brines A and B (also called WIPP Brines A and B)
- ONWI Composite Permian Basin Brine P
- ONWI Equilibrated Permian P No. 2
- PNL-Sandia Waste Package Interactions Test brines
  (pretest, intermediate, and posttest brines)
- WIPP-12 brine (flow and downhole samples)
- ERDA-6 brine (flow and downhole samples)
- WIPP fluid inclusion Brines No. 1 and No. 2
- MCC (Materials Characterization Center) brine
- German quinare Brine Q
- USGS bittern brine NBT-6a
- Saturated NaCl (at 20° and 100°C)
- Standard seawater

Most of these various brines can be classified into two distinct groups, based primarily on high-NaCl or high-Na-Mg-K-Cl content:

1. Brine "B-Like": Brine B, Brine P and P no. 2, PNL-SNL brines (pretest, intermediate, posttest), WIPP-12 (flow and downhole), and ERDA-6 (flow and downhole).

2. Brine "A-Like": Brine A, MCC brine, WIPP fluid inclusion brines No. 1 and No. 2, quinare Brine Q, and USGS NBT-6a.

The ionic compositions for the major cations and anions of each brine are listed in Table 1 (for "B-Like" brines) and in Table 2 (for "A-Like" and other brines). Also listed are the solution pH values, if available. (The pH electrode junction potentials may result in measured pH values in concentrated brines being as much as 1 pH-unit lower than the logarithm of the actual hydrogen ion concentration.) Compositions are specified in concentration units of mg/L (as measured or defined); these values can be easily converted into units of moles/L, Table 3. Stated brine compositions are defined with only two or three significant figures. Higher numbers of significant figures are shown for some analyzed brines. For preparation of synthetic brines for laboratory testing, anything beyond two or occasionally three significant figures should be taken with "a grain of salt." To convert from mg/L

TABLE 1

Brine "B-Like" Brine Composition Comparisons
mg/L

Ion	(WIPP/ Generic) Brine B (±3%)	ONWI Composite Permian P	Equilibrated Permian P no. 2	Pretest PNL-SNL	Brine-Backfill PNL-SNL	Posttest PNL-SNL	Flow WIPP-12	Downhole WIPP-12	Flow ERDA-6	Downhole ERDA-6
Na^+	115,000	123,460	123,000	159,000	155,000	119,000	114,000	140,000	112,000	140,000
K^+	15	39	39	2,550	2,370	5,000	3,100	3,200	3,800	4,800
Mg^{++}	10	134	122	409	463	158	1,700	1,400	450	270
Ca^{++}	900	1,560	1,100	370	695	267	410	380	490	360
Sr^{++}	15	35	35	18	43	34	15	--	18	--
Zn^{++}		7.8	8	< 2.5	--	199	0.5	--	0.6	--
Li^+	20						220	210	240	205
Rb^+	20									
Cs^+	1			--	--	64				
Fe^{+++}	2			< 5	--	55	3.6	6.3	3.6	5.7
Cl^-	175,000	191,380	191,000	190,000	231,000	197,000	160,000	180,000	170,000	180,000
SO_4^{--}	3,500	3,197	1,910	2,086	3,237	16,300	17,000	18,000	16,000	14,000
B(as BO_3^{---})	1,200			16	11	1,280	1,200*	960*	680*	740*
HCO_3^-	700	30	23	7.8	15	0	2,600	2,400	2,600	1,800
Br^-	400	32	24				430	460	880	720
I^-	10									
F^-		1.1	1.0	37	37	0	4.3	--	1.7	--
pH:	6.5	7.055		6.9	6.8	3.8	7.17	7.76	6.42	7.02
Field Eh: (mV)							-211		-152	

*Values reported as B, but assumed to actually be BO_3^{---}
-- = below measureable detection limits

TABLE 2

Brine "A-Like" and Other Brine Composition Comparisons
mg/L

Ion	(WIPP/ Generic) Brine A (±3%)	WIPP Inclusion No.1 (Preliminary)	WIPP Inclusion No.2 (Preliminary)	MCC Brine	Quinare Brine Q (±10%) (55°C)	USGS NBT-6a (±10%)*	OTHER Saturated NaCl (20°C)	OTHER Saturated NaCl (100°C)	Seawater
Na^+	42,000	63,000 ± 5000	32,000 ± 1,100	35,400	6,500	27,000	142,000	154,000	10,651
K^+	30,000	8700 ± 500	6800 ± 200	25,300	29,000	35,000			380
Mg^{++}	35,000	23,000 ± 2000	40,000 ± 1400	29,600	85,000	33,000			1,272
Ca^{++}	600	210 ± 20	150 ± 10			47,000			400
Sr^{++}	5								13
Zn^{++}									
Li^+	20								
Rb^+	20								
Cs^+	1								
Fe^{+++}	2								
Cl^-	190,000	160,000 ± 9,000	160,000 ± 5000	164,000	270,000	250,000	218,000	237,000	18,980
SO_4^{--}	3,500	13,200 ± 2600	13,200 ± 2600		13,000				884
B(as BO_3^{---})	1,200								
HCO_3^-	700								146
Br^-	400								65
I^-	10								0.05
F^-									
pH:	6.5			6.5					8.1

*See note u., Table 4.

TABLE 3

Brine Composition Comparisons, Molarity

Ion	(WIPP/ Generic) Brine B	ONWI Composite Brine P	Equilibrated Permian P no. 2	(WIPP/ Generic) Brine A	MCC Brine	Quinare Brine Q (55°C)	Saturated NaCl (20°C)	Saturated NaCl (100°C)	Seawater
Na^+	5.00	5.37	5.35	1.83	1.54	0.28	6.15	6.69	0.46
K^+	*	*	*	0.77	0.65	0.75			0.01
Mg^{++}	*	0.01	0.01	1.44	1.22	3.49			0.05
Ca^{++}	0.02	0.04	0.03	0.02					0.01
Sr^{++}	*	*	*						*
Zn^{++}		*	*						*
Li^+	*			*					
Rb^+	*			*					
Cs^+	*			*					
Fe^{+++}	*			*					
Cl^-	4.93	5.39	5.38	5.35	4.62	7.68	6.15	6.69	0.53
SO_4^{--}	0.04	0.04	0.02	0.04		0.16			0.01
B(as BO_3^{---})	0.02			0.02					
HCO_3^-	0.01	*	*	0.01					*
Br^-	0.01	*	*	0.01					*
I^-	*			*					*
F^-		*	*						
pH:	6.5	7.055		6.5	6.5				8.1
Specific Gravity:	1.2			1.2	1.17	1.18			

* = less than 0.005 M

to units of ppm, the estimated or approximate solution density (specific gravity) of 1.2 kg/L (for the near-saturated brines, at room temperature) should be utilized.

Two brines, German quinare Brine Q and USGS bittern NBT-6a, were initially specified in terms of salt weight percentages, as listed in Table 4. These two brines were converted into units of mg/L for Table 2.

ORIGINS AND COMPARISONS

Brines A and B were originally defined by Sandia (1) in 1976 for the intended purpose of standardizing future testing. Examples are wasteform leaching and barrier materials corrosion testing, which would be applicable for radioactive wastes emplaced in a salt facility--in particular, the Waste Isolation Pilot Plant (WIPP). At that time, most leachability tests were conducted in deionized or distilled water, not particularly applicable to any proposed repository type, but useful as a reference. The original memorandum defining Brine A and Brine B (1), from M. A. Molecke to distribution, October 8, 1976, is attached as Appendix 1. The analytical work in development of the synthetic compositions for Brine A and Brine B, e.g. brine analyses, techniques, and laboratory formulations, is attached as Appendix 2, a memorandum (2) from R. G. Dosch to M. A. Molecke, Sandia Laboratories, dated October 12, 1976.

TABLE 4

Brine Composition Formulations

Compound	Quinare Brine Q	USGS NBT-6a	
	(wt%)[q]	(wt%)	(moles/L)[u]
NaCl	1.4%	5%	1.16
KCl	4.7%	5%	0.90
$MgCl_2$	26.8%	10%	1.37
$CaCl_2$		10%	1.17
$MgSO_4$	1.4%		
H_2O	65.7%	70%	

[q] Solution density of 1.18 g/mL at 55°C assumed to calculate concentrations in mg/L for Brine Q as shown in Table 2. (1.2 g/mL at room temperature, assumed) x (0.986 g/mL for H_2O at 55°C) = 1.18.

[u] Concentrations shown in Table 2 based on stated molarity; however, the density (specific gravity) of this solution would be 1.32 g/mL, an unusually high value for a brine. If a room temperature density of 1.2 g/mL is assumed as realistic for NBT-6a, the ionic concentrations shown in Table 2 for this brine would be ten percent lower than specified. As such, a 10% uncertainty is assumed for the concentration shown for NBT-6a in Table 2.

Brine A is a high Na-Mg-K chloride brine representative of brines that have interacted with potassium and magnesium minerals and could potentially intrude into a waste facility in bedded salt, e.g., a brine which might intrude into the WIPP waste horizon by percolation through an overlaying zone containing potash. Brine A is similar in composition to brines found in small fluid inclusions in rocksalt (as will be shown by comparison to WIPP inclusions No. 1 and No. 2). Brine A is based on the analyses of several brine seeps from the Salado region in southeastern New Mexico overlaying the WIPP (vicinity),as supported by the analytical work described in Appendix 2.

Brine B is a near-saturated, predominantly NaCl brine representative of brines potentially intruding into either a domed salt repository or into relatively pure bedded halite. It is based on an analysis of the brine obtained by the following steps: (1) dissolving a portion of rocksalt core in deionized water heated at about 100°C for several hours, (2) equilibrating at room temperature for 72 hours, (3) filtering out insolubles (predominantly clays and a mixture of calcium and iron compounds), and then (4) analyzing (see Appendix 2). The rocksalt core was from hole AEC 8 at the 2725.0 to 2725.5-ft (about 831-m) horizon (depth), less than about 4 mi from the center of the WIPP site. The WIPP horizon for radioactive waste testing and demonstration is at about 2160 ft (659 m). (In 1976, there was a planned second, lower horizon at

about 800 m. The rocksalt at the lower horizon is somewhat purer, with several percent less clay and other impurities than the present mined horizon.)

While Brines A and B were originally defined as WIPP site-specific brines, their widespread laboratory usage (to be described) over the past six or more years has broadened their applicability to essentially generic test brines. This generic nature is reflected in their current definition. As such, they are now termed WIPP/generic Brine A and Brine B.

The ONWI Composite Synthetic Permian Basin "Brine P" is based on a series of brines made by dissolving a blend of ten Permian Basin rocksalt cores (crushed) (specified as G. Friemel Hole No. 1 Core Composite; cores sampled were from the lower San Andreas Unit 4, between the 2440 to 2580-ft, 744 to 786-m, horizon) in distilled water, then analyzing (in a manner similar to the original analysis and definition of Brine B). The analyti- cal work supporting the formulation of synthetic Brine P is documented in Reference 3a,b,c. Brine P is representative of brine from the potential ONWI salt site (and "most probable" salt horizon) in the Permian Basin area of Texas; it is intended to be a site-specific brine.

ONWI Brine P is quite similar in composition to Brine B; the significant differences are slightly higher levels of Na^{+}, Mg^{++}, and Ca^{++}, and slightly lower levels of Br^{-} than Brine B.

These differences are attributed to slightly different concentrations of impurities in the halite cores selected. The nonsoluble (filtered) impurity content of the Permian Basin rocksalt was reported (3) to be 3.35 ± 0.17 wt.%, consisting primarily of anhydrite, quartz minerals (montmorillonite plus several other unidentified clays), and unknown iron compounds. The similar impurity components for the AEC #8 core used to originally prepare WIPP/generic Brine B (2), was 0.96 wt.%.

Upon high-temperature autoclave testing using Permian Basin Brine P (at Battelle PNL), it was found that retrograde solubilities of certain compounds, presumably anhydrite, in the brine caused frequent plugging of the autoclave inlet line (in a flowing test system). This problem has been avoided by formulating a slightly modified brine (4) based on the composition of the supernatant fluid resulting from equilibrating the saturated Brine P at 150°C. The resultant brine, termed Equilibrated Permian Basin Brine P no. 2, has the analyzed ionic composition as shown in Table 1 (4). Brine P no. 2 has slightly lower Ca^{++} and SO_4^{--} concentrations than Brine P (or "P no. 1").

The brines listed in Table 1 as PNL-SNL are the analyzed pretest, intermediate, and posttest brines used in the PNL-SNL HLW Package Interactions Test conducted in 1980-81 (5). Although these brines were specific to only one test, they are included for the primary purpose of indicating changes in brine

compositions forced by high-temperature (250°C) interactions with all potential components of an HLW package system--the glass wasteform, metallic canister (stainless steel 304L) and overpack (TiCode-12), tailored backfill (bentonite clay and silica sand) and the host rocksalt. The "pretest" brine was produced by dissolving bedded rocksalt from the Mississippi Chemical Company potash mine in southeastern New Mexico (from a depth of approximately 1150 ft, in the Salado) in water. This rocksalt was selected because it was available in large blocks (necessary for the PNL-SNL test), was located in the same formation, although 1000 ft higher up and about 15 mi (24 km) away from the WIPP, and was relatively pure halite. The rocksalt used was (6) approximately 88 wt.% halite (NaCl), 4% sylvite (KCl), and 8% polyhalite ($Ca_2K_2Mg(SO_4)_2 \cdot 2H_2O$), with smaller, variable (0 to 10%) amounts of interbedded impurities, e.g., clays and anhydrite ($CaSO_4$). The "brine-backfill" or intermediate brine is the composition after mixing in the bentonite clay and sand backfill material at room temperature; it is an intermediate-phase brine, sampled and analyzed before the hydrothermal portion of the test. It indicates the chemical influence of backfill materials on the initial, pretest brine. The "posttest" brine was analyzed from samples obtained after 95 days of testing (at 250°C), after the autoclave was opened. The "posttest" pH value was measured in a room-temperature, unfiltered liquid sample. Inductively coupled plasma spectroscopy (ICP) and ion chromatography (IC) were used in the brine analyses(5).

The posttest PNL-SNL brine is characterized (5) by increases in K^+, B, Cs^+, Zn^{++}, and SO_4^{--} ions. Ca^{++} and Mg^{++} were moderately depressed. The increased B, Zn^{++}, and Cs^+ (as well as Mo) are due undoubtedly from leaching of the glass (PNL 76-68) present. Increases in K^+ and SO_4^{--} are the result of increased dissolution of rocksalt and impurities at elevated temperatures. The decreases in Ca^{++} and Mg^{++} are the result of calcium sulfate (anhydrite or gypsum) precipitation and Mg reaction with silica and aluminosilicate components of the waste glass and backfill yielding hydrated Mg silicates and Mg aluminosilicates, e.g.:

a.) $3\ MgCl_2 + 4SiO_2 + 4H_2O = Mg_3Si_4O_{10}(OH)_2 + 6H^+ + 6Cl^-$

b.) $0.66\ MgCl_2 + 2Al_4(Si_4O_{10})(OH)_8 + 0.33Ca^{++} =$
$Ca_{.33}(Mg_{.66}Al_{3.34})Si_8O_{20}(OH)_4 \cdot nH_2O$ (smectite)
$+ 4.66\ Al^{+++} + 1.22\ Cl^- + 4OH^-$

Reactions of $MgCl_2$ with silica in solution can also lead to a decrease in solution pH, e.g. equation a., due to the formation of HCl; this is probably the major reason for the experimentally observed pH decrease (5) in the posttest PNL-SNL brine.

A comparison can be made between the PNL-SNL brines, the Permian Basin Brines P and P no. 2, and Brine B. They are all very similar in their major ionic compositions. Their differences in Ca^{++}, K^+, Mg^{++} and SO_4^{--} ions can be simply explained

as minor differences in halite impurities (e.g., anhydrite, polyhalite, or sylvite), and in differences in calcium sulfate precipitation as a function of temperature and various magnesium-silica-aluminosilicate hydrothermal reactions. The need for having two distinct (WIPP/generic and ONWI) but similar (test reactant) brines can be justified only by defining each composition as site-specific. It is expected that any significant compositional differences between these similar brines would be further obscured during tests on waste package materials or interaction tests, as it was in the PNL-Sandia interactions test.

The WIPP-12 borehole is located 1 mi north of the existing central shaft of the WIPP facility. In November 1981, WIPP-12 (originally cored in 1978) was reentered and extended from 2776 to 3925 ft (846 to 1196 m), in order to determine the nature and extent of possible deformation in the Castile Formation underlying the Salado. (The WIPP facility horizon is in the Salado Formation, at approximately 659 m) At a depth of about 3012 ft (918 m), pressurized brine flow was encountered, indicating a brine reservoir or pocket in (the fractures in) the Anhydrite III unit of the Castile Formation. The main fluid producing fractures of this zone are probably between 3016 and 3021 ft (919 and 921 m) (7). About 2,478,200 gal, 655,000 L, of brine were allowed to flow from WIPP-12. Flow and downhole samples of this brine were analyzed by D'Appolonia (7) and are

listed in Table 1. A summary table of the WIPP-12 brine analyses (arithmetic means) reported by D'Appolonia is attached (from Reference 7) as Appendix 3. The chemical compositions of both flow and downhole WIPP-12 brines are, not surprisingly, relatively similar to those of both Brine B and Permian Basin Brine P. (Note: the WIPP is in the Delaware Basin, which is a portion of the larger Permian Basin.)

WIPP-12 brine contains a larger concentration of K^+ and Mg^{++} than does Brine B (but much less than Brine A) and a SO_4^{--} concentration that is five times greater than that in either Brine A or B. WIPP-12 brine is not used for any laboratory testing; it is listed for comparative reference.

Another brine(s) that is listed in Table 1 for comparative reference is that from drill hole ERDA-6, approximately 5.3 mi, (8.6 km) north-northeast of the present WIPP site. In the summer of 1975, ERDA-6 was drilled at the southwest corner of the then-proposed WIPP site. A brine pocket was encountered at a depth of about 2711 ft (826 m), in the Anhydrite II unit of the Castile Formation. The WIPP site was subsequently moved approximately 6 mi (10 km) to the southwest to its present location, for location in more level, predictable geologic strata. The brine compositions for flow and downhole samples of ERDA-6 brine listed in Table 1 were obtained from a drill

stem test and brine analyses conducted by D'Appolonia (7) in October 1981. A summary data table of the ERDA-6 brine analyses (arithmetic means) reported by D'Appolonia (from Reference 7) is also attached in Appendix 3. The ERDA-6 brine compositions are very similar to those for WIPP-12 brines; however, the Mg^{++} concentrations in ERDA-6 brines are about a factor of four lower than in WIPP-12.

About ten small samples of the fluid in brine inclusions (in negative crystals, small cubic voids in the rocksalt filled with brine and, frequently, gas bubbles) in WIPP rocksalt have been recently obtained and chemically analyzed (10). The preliminary compositions are listed in Table 2 as WIPP Inclusion No. 1 and Inclusion No. 2. The compositions of these fluids could be classified into two distinct populations (10); WIPP Inclusion No. 1 is the average composition from four separate inclusions. WIPP Inclusion No. 2 is the average from four analyses from two inclusions. The brine samples were about 10 to 100 mg each; they were obtained by drilling into fluid inclusions 2 mm or less in diameter, then removing the liquid with a syringe. The inclusions also contained (10) up to approximately 70 vol.% of gas(es), not analyzed. The rocksalt samples containing these inclusions were obtained from the south drift (tunnel) of the WIPP, at a depth of approximately 2160 ft (659 m). Cations were analyzed (by J. L. Krumhansl, Sandia) by dc plasma emission spectroscopy; sulfate was analyzed (by C. L. Stein, Sandia) by laser Raman

spectroscopy. The sulfate analysis was made on a separate inclusion than those used for the other analyses; it was, however, from the same approximate location in the WIPP. Other anions may be analyzed by ion chromatography (IC). More fluid inclusion samples are being obtained at the WIPP facility and will be analyzed to expand the data base. Due to the uniqueness of these brine inclusion analyses, all results will be formally documented (10).

The preliminary analyses of the compositions of WIPP Inclusions No. 1 and No. 2 yield a very close similarity to the composition of Brine A, with the inclusion compositions for Na^{+} and Mg^{++} bracketing that for Brine A, while the inclusion values for K^{+}, Ca^{++}, and Cl^{-} are somewhat less than in Brine A. This similarity supports the earlier (unquantified) statement of assumption that Brine A is representative to the brine(s) in inclusions.

The Materials Characterization Center has defined a "new standard" brine, MCC brine, to be used for standardized laboratory wasteform leachability tests (8). The MCC brine is based on the composition of Brine A (9); it is approximately 84% as concentrated as Brine A, and is intended to be stable at higher temperatures (e.g., 90°C) without retrograde solubilities causing precipitation of some compounds. The nonmajor

components of Brine A, e.g. Ca^{++}, SO_4^{--}, BO_3^{---}, HCO_3^-, and Br^-, were eliminated entirely, for simplicity. MCC brine was defined solely to establish reproducibility in standardized test procedures. The MCC brine must be regarded as somewhat "artificial" when compared to the other brines described, due to the dilution and ionic simplifications inherent in its formulation.

The Asse and Gorleben rocksalt sites that have been evaluated in Germany for a radwaste experimental facility or potential waste repository consist of halite in close proximity to significant quantities of the mineral carnallite, $KMgCl_3 \cdot 6H_2O$. As such, in the event of eventual brine intrusion, the Germans expect a brine much higher in K^+ and Mg^{++} concentrations than either American Brines A, B, or P. For laboratory testing purposes, the Germans have defined (11) a quinare brine solu- tion, Brine Q, as listed in Tables 2, 3, and 4. This Brine Q composition is specified at 55°C; corrosion testing with it was conducted at 90°C (11). The weight percent formulation for Brine Q in Table 4 was converted into units of mg/L for Table 2, for comparability with the other brines listed. A solution density had to be estimated for this conversion and is described in Table 4. Because of such assumption, an uncertainty of ±10% was assigned to Brine Q. Brine Q has a K^+ composition similar to that of Brine A, but its Mg^{++} concentration is a factor of about 2-1/2 times

higher; Brine Q can therefore be expected to be more corrosive than Brine A, due to Mg^{++}-SiO_2 reactions yielding HCl, i.e., Equation a. described earlier.

The USGS bittern brine specified as NBT-6a and listed in Tables 2 and 4 was originally defined for laboratory testing (approximately 5 years ago), basically as an alternate to WIPP Brine A. It is included for historical purposes only. The ionic composition listed in Table 2 may be 10% high; see the note in Table 4.

The seawater composition listed in Tables 2 and 3 was initially listed in Reference 12, as used for corrosion testing for the subseabed disposal program (at Sandia). It can be simply described as "standard 35 parts-per-thousand" open ocean water.

Information on saturated NaCl brines (reagent grade) at 20° and 100°C, as listed in Tables 2 and 3, was obtained from "The Handbook of Chemistry and Physics." They are specified for reference purposes only. They are, however, similar to the "B-like" brines.

TESTING USAGES

Corrosion Testing

As a result of the early definition (1) of WIPP/generic Brine A and Brine B, the largest amount of experimental work and published results exists that uses these two de facto standard brines. References 12-14 are representative of the corrosion studies on waste package canister and overpack materials conducted with these two corrodants. Most of the brine-corrosion studies have been conducted at either Sandia or PNL. More recently, researchers at Brookhaven National Laboratory, as part of the Nuclear Regulatory Commission waste package materials research program, have begun a significant laboratory program utilizing Brines A and B as corrodants (16).

Laboratory studies (12) have shown that Brine A is more corrosive than Brine B for essentially all candidate alloys tested. The dilute brine solution of seawater is intermediate in corrosiveness between these two brines. These differences in corrosiveness are presumably caused by differences in solution pH, indicative of irreversible acid-producing reactions that occur in Brine A and seawater at higher temperatures. (e.g., Equation a., earlier). Other possible reactions in the presence of silicates yield the precipitation of $Mg(OH)_2$ and a Mg-oxysulfate phase, producing HCl. As such, the German

quinare Brine Q, which has the highest Mg^{++} concentration of any defined brine, can be expected to be the most corrosive or lowest pH solution. Not enough comparable German (11) and American data exist to be definitive on this point.

Wasteform Leachability

The variety of brine leachants used for glass, spent fuel, and alternate wasteform leach testing is somewhat more extensive than that for corrosion testing. WIPP/generic Brine B is probably the most widely used brine leachant (17-23). Brine A and seawater leachability studies are extremely limited (20), as are studies with the USGS bittern NBT-6a (24). Few studies using the MCC brine have been published so far (25), but more are expected in the near future using the standardized test procedures defined by the Materials Characterization Center (8). Now that ONWI has defined a site-specific brine, Permian Brine P and Equilibrated Permian P No. 2, more studies using these brines are expected; these will be conducted predominantly at Battelle PNL and Savannah River Laboratory.

Backfill and Other Tests

A limited number of reports on laboratory testing (other than corrosion and leachability) using brines have also been published (5,24,26-33). Most of these reports are for tailored

backfill material, radionuclide sorptiveness measurements (26-28), and hydraulic conductivity (liquid permeability measurements) (29) using Brines A and B. Radionuclide migration or sorption measurements on geologic materials with Brine A or B as the liquid medium have also been reported (31-33).

Brine desiccant capabilities of backfill materials (30) and hydrothermal waste-rock interactions studies (24) using the USGS NBT-6a bittern have been reported. Both of these studies have been concluded; no new groups have, to my knowledge, recommended the use of NBT-6a for future studies.

BRINE RELEVANCY AND RECOMMENDATIONS

Concerns have been raised about which brine or brines may be most appropriate for a particular laboratory test, whether for corrosion, leaching, interaction, or other testing. In several cases, this has led to the definition of a new brine formulation, either to be more site-specific, totally generic, or expedient in the laboratory. To help resolve concerns about the appropriateness or relevancy of any brine, it appears useful to first describe the potential sources or mechanisms for brine intrusion into a rocksalt repository. Three possible sources of liquid come to mind: brine migration from fluid inclusions, intrusion from an aquifer or large brine pocket

near the facility or repository, or water release from the wasteform itself, i.e., TRU wastes.

The most likely source of brine intrusion toward heating-generating HLW is the migration of small fluid inclusions (negative crystals) up the thermal gradient. The mechanisms, fluid inclusion characteristics, experiments, quantities, and consequences of such brine migration are summarized in detail elsewhere (34). Basically, a maximum of 20 L or less of brine could migrate (34) to the vicinity of an individual HLW package in rocksalt within about 1000 years. The preliminary analyses of the brine compositions in several representative fluid inclusions was reported earlier in this report (e.g., WIPP Inclusions No. 1 and No. 2). No data currently exist (34) as to the composition of the migrating brine, or changes therein, after it reaches the vicinity of the waste package. In all experiments to date (34), the brine was vaporized and only the water condensate has been collected. Based on the known initial compositions of these inclusions, and the fact that they must migrate through solid halite, it is a fairly safe assumption that all fluids are saturated (brines). The chemical composition of the brine, assuming it could reach the waste canister and also remain in the liquid state, is expected therefore to be intermediate between (within the range of) the compositions of WIPP Inclusions No. 1 or 2 and WIPP/generic Brine A.

Brine intrusion into the repository from an aquifer flow or movement of a large brine pocket, while much less probable than thermally induced migration of fluid inclusions, could provide a significantly larger volume of fluid for waste package interactions or degradation. Mechanisms for this fluid movement would be (1) along (up or down) a defective borehole seal plug, (2) diffusion or slow flow along a clay seam, fracture paths or impurity bed (e.g. anhydrite or clay), or (3) inadvertent action by man (e.g. drilling). All these pathways are of very low probability. The initial brine composition is expected to be similar to that in (field-sampled) WIPP-12 brines or ERDA-6 brines (Table 1) or, essentially, Brine B or P. By the time these brines percolate through the salt toward the waste package(s), they would most assuredly be saturated. Even if a repository in domed salt were penetrated and saturated with fresh water, the resultant brine would eventually become saturated. It is expected, therefore, that the final brine composition (available for waste package interactions) would be (dependent on the intrusion scenario) quite similar to or bounded by either the initial compositions of Brine A or Brine B, with minor differences dependent on halite impurities.

If any residual water is released from the wasteform itself, e.g. TRU wastes, by means of volatilization, the condensate would collect on the nearby salt. Recall that salt is slightly hygroscopic and would make a fair desiccant. The resultant

saturated composition would be quite similar to that of the host rocksalt dissolved in water, e.g. Brine B or Brine P.

Considering the brine ionic composition range(s) encompassed by the described intrusion mechanisms, it does not appear to be appropriate or prudent to define any more brines. For the thermally induced brine-migration mechanism, Brine A (saturated with excess rocksalt at elevated temperatures) should be regarded as the upper limit or boundary-value composition for testing purposes--based on its relevancy, known high corrosivity (12), and previous widespread usage. For all other scenarios of brine intrusion, a generic NaCl-based brine such as Brine B (saturated with excess rocksalt at elevated temperatures) or Permian Brine P (site-specific) is recommended for laboratory testing purposes. Minor differences in the lesser components of these brines, e.g., K^+, Mg^{++}, Ca^{++}, B, HCO_3^-, Br^-, etc., will probably result in very minor differences in test results, particularly when compared to the significant differences in composition and corrosivity of Brine A. It can be postulated that trace components in the brine(s), i.e., those of less than 1000 ppm, may cause second-order changes in waste package interactions (particularly waste from leachability) due to differences in solution radiolysis effects or catalytic effects. No data currently exist to support this assumption, however. The most appropriate manner to demonstrate differences in reactions caused by differences in

brine trace components would be to conduct in situ, site-specific tests. The use of synthetic Brine B or Brine P for laboratory testing will, however, undoubtedly be based on desires to be site-specific, in anticipation of assumed, future regulatory/licensing procedures.

Significant differences between the geologic characteristics of certain sites could, of course, alter the above discussion of brine relevancy. For instance, the differences between American bedded rocksalt sites and German salt sites (with significant concentrations of carnallite) make the definition of another brine for testing appropriate, i.e., quinare Brine Q. Similar reasoning also applies to testing with seawater for the Subseabed Disposal Program.

Except for seawater, all standard, synthetic brines recommended for testing purposes are essentially saturated except for the MCC brine. This raises some concerns about the (repository) relevancy of this brine. In no brine intrusion scenario yet described (with the possible exception of a salt dome flooding, temporarily) can an unsaturated brine contact the waste package. The MCC brine, based on diluted and simplified Brine A, was specified for ease in testing, e.g., no precipitation during testing at higher temperatures. However, the concerns of brine relevancy due to laboratory expediency should be reassessed. The most appropriate brines for testing (e.g., brines that could

occur or intrude into a salt repository) are saturated brines that are kept that way at elevated test temperatures by contact with excess rocksalt. This is the technique used at Sandia and at Battelle PNL (during static, but not flowing, autoclave tests). The procedure used for formulating Equilibrated Permian Brine P No. 2, i.e., filtering out precipitated solids formed at elevated temperatures, is no doubt expedient for a flowing autoclave system, but also somewhat artificial. In an actual repository, precipitates from the brine solution would form at higher temperatures and remain in contact with the residual brine.

In summary, the following recommendations for laboratory testing using standardized brines are made:

Corrosion Testing: WIPP/generic Brine A (in contact with excess rocksalt at elevated test temperatures) is recommended for realistic overtests (or upper boundary conditions) of the corrosion resistance of candidate waste package barrier materials. Any differences in ionic composition of potential site-specific "Brine A-like" solutions would undoubtedly be overshadowed by other variables of testing--specifically, changes in brine corrosivity caused by effects of gamma irradiation and oxygen concentration (particularily applicable to Fe-base barrier materials).

Wasteform Leachability: A NaCl-based brine, e.g., WIPP/generic Brine B or site-specific Permian Brine P is recommended for laboratory testing to determine the relative leach resistance and leaching mechanisms of various wasteforms. Techniques to keep the brine(s) saturated at higher temperatures are at the option of the experimenter. For testing to determine the durability of the wasteform under repository-relevant conditions (including the presence of gamma radiation and other waste package barriers and their degradation products), there can be no one specific recommendation. The leachant should be in contact with waste package degradation products, e.g., corrosion products (especially iron) and various silicates (from glass dissolution, backfill materials if present, and any clay impurities naturally occurring in the halite). The specific ionic composition of the brine really depends on the postulated intrusion scenario. A saturated Brine "B-like" brine would seem appropriate for most testing. However, Brine A would be more corrosive and yield a more conservative estimate of waste-form durability. The MCC brine is assumed to be slightly less corrosive than Brine A; data do not currently exist to support this assumption. The choice of brine in this case shall be up to the experimenter.

Barrier Material Interaction Testing: Brine A, as in the case of corrosion testing, is recommended although a "B-like" brine may also be adequate. As in the case of leach testing, the

solution should be in contact with appropriate degradation (and brine radiolysis) products. The formulation of another site-specific brine for use in such a complex system as interaction testing seems quite inappropriate, in view of the changes in the composition of the PNL-SNL brines (Table 1) during the course of the test.

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APPENDIX 1

Sandia Laboratories

Albuquerque, New Mexico
Livermore, California

Date: October 8, 1976

To: Distribution

Martin D. Molecke

From: M. A. Molecke - 1141

Subject: Revised Representative Brines/Solutions for WIPP Experimentation

This memo is intended to provide specifications for the ionic content and chemical formulations for three solutions/brines for experimental purposes. These solutions are representative of waters which can potentially intrude into the Waste Isolation Pilot Plant. Brine transport of radionuclides from the radioactive waste stored in a salt mine into the geosphere and biosphere are of major concern. Experiments in progress or planned (at Sandia plus other laboratories) to quantify and evaluate such transport plus related aspects of brine intrusion include: radionuclide distribution coefficient measurements, waste matrix leaching, radionuclide mobility and interactions, and corrosion aspects. The various laboratory groups supporting the WIPP project should utilize the specified brines/solutions for both uniformity and intercomparison purposes.

The ionic compositions of the representative brines/solutions "A", "B", and "C" are given in Table I, attached, in units of mg/liter of solution. To facilitate preparation of these solutions, the required chemical compounds, also in units of mg added per liter of solution, are presented in Table II. All ions added have been balanced in terms of milliequivalents/liter for both cations and anions. If substitutions are made for various compounds in preparation, rebalancing calculations will be necessary. Following preparation, the pH of the solutions should be adjusted, as specified, with small additions of either dilute HCl or NaOH, as required. The specified pH values of solutions "A", "B", and "C" are representative of the "as measured" pH's of the naturally occurring solutions on which they are based.

Solutions "A" and "B" are near-saturated brines. Solution "A" is based on the analyses of several brines from the Salado region overlying the planned WIPP facility/horizon. This is a potash bearing region and consequently is enriched in both potassium and magnesium ions, relative to sodium chloride. Solution "A" is intended to be representative of brine which could intrude into the waste horizon via flow or percolation from above.

Solution "B" is based on the analysis of the brine obtained by dissolving a portion of rock salt core in de-ionized water. The salt core was from AEC #8 at approximately the same horizon (2725 ft.) as the intermediate-level waste and high-level waste experiment horizon of the WIPP facility. Since the AEC #8 hole is less than four miles from the center of the WIPP facility, no significant differences in the salt content are expected. This analyzed brine has an approximately 98% NaCl content and a total undissolved content (not included in analysis) of less than 1%. Solution "B" is representative of the brine resulting from a conceivable catastrophic scenario at the WIPP mine (flooding, service water line rupture, etc.) whereby water pours in, dissolves the salt, becomes saturated, then begins to attack the waste.

Solution "C" is representative of groundwater pumped from one of the aquifers in the Rustler formation. This potable water was sampled near the WIPP location. The solution "C" composition is based on two separate analyses; it consists primarily of a dilute solution of calcium and magnesium sulfates. Being representative of the WIPP hydrological and geographical locale, solution "C" was deemed more suitable for experimental tests and intercomparisons than was de-ionized water. Once tracers and geological specimens are added to de-ionized water, it no longer simulates de-ionized water. The higher ionic strength of solution "C" solves this problem.

This memo supercedes my memo entitled "Representative Simulated Brines for WIPP Experimentation," dated August 11, 1976. The brines specified there were based on commercial brine analyses which were erroneously high for several ions. This resulted in greater than saturated solutions. Brines/solutions "A", "B", and "C" have been tested in-house for solubility.

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October 8, 1976

TABLE I

REVISED REPRESENTATIVE BRINES/SOLUTIONS

FOR

WIPP EXPERIMENTATION

Ion	Solution "A" (mg/liter) (± 3%)	Solution "B" (mg/liter) (± 3%)	Solution "C" (mg/liter) (± 3%)
Na^+	42,000	115,000	100
K^+	30,000	15	5
Mg^{++}	35,000	10	200
Ca^{++}	600	900	600
Fe^{+++}	2	2	1
Sr^{++}	5	15	15
Li^+	20	-	-
Rb^+	20	1	1
Cs^+	1	1	1
Cl^-	190,000	175,000	200
SO_4^{--}	3,500	3,500	1,750
B (BO_3^{---})	1,200	10	-
HCO_3^-	700	10	100
NO_3^-	-	-	20
Br^-	400	400	-
I^-	10	10	-
pH (adjusted)	6.5	6.5	7.5
specific gravity	1.2	1.2	1.0

October 8, 1976

TABLE II

RECOMMENDED CHEMICAL COMPOUNDS FOR PREPARING REPRESENTATIVE BRINES/SOLUTIONS FOR WIPP EXPERIMENTATION

Compound	Solution "A" (mg/liter)	Solution "B" (mg/liter)	Solution "C" (mg/liter)
NaCl	100.10g	287.00g	-
Na_2SO_4	6.20g	6.20g	170
$Na_2B_4O_7 \cdot 10H_2O$	1.95g	16	-
$NaHCO_3$	960	14	-
NaBr	520	520	-
$NaNO_3$	-	-	27
KCl	57.20g	29	9.5
KI	13	13	-
$MgCl_2$	137.00g	40	-
$MgSO_4$	-	-	990
$CaCl_2 \cdot 2H_2O$	2.20g	3.30g	380
$CaSO_4 \cdot 2H_2O$	-	-	2.13g
$FeCl_3$	6	6	3
$SrCl_2 \cdot 2H_2O$	11	33	33
LiCl	125	-	-
Rb_2SO_4	30	1.6	1.6
CsCl	1.3	1.3	1.3
pH (adjusted)	6.5	6.5	7.5
Total Dissolved Solids	306.3g/liter	297.2g/liter	3.72g/liter

APPENDIX 2

Sandia Laboratories

Albuquerque, New Mexico
Livermore, California

date: October 12, 1976

to: M. A. Molecke - 1141

R. G. Dosch

from: R. G. Dosch - 5824

subject: Analytical Work in Development of Synthetic Brine Compositions

Ref 1: Memo from M. A. Molecke, dated August 11, 1976, subject: "Representative Simulated Brines for WIPP Experimentation"

The need for standard synthetic brines for use in inter-laboratory studies supporting the WIPP project in the general area of interactions of brine and brine-radionuclide solutions with various waste forms, containers, and surrounding rock strata is obvious. The initial attempt at defining compositions(1) based on commercial laboratory analyses of various brines from the Carlsbad area was unsatisfactory as neither of the compositions could be satisfactorily duplicated in the laboratory.

As a result, a considerable amount of time was spent in analyzing various brine samples in an attempt to provide another baseline for establishment of synthetic brine compositions. Brines analyzed included the original(1) standard brine compositions "A" and "B" (after insolubles were removed), samples of natural brines labeled as "ERDA 6-9/14/75 - 1500 hours" and "Duval Nash Draw Mine, Drill hole drip, 1090' level - SE Main - 1st Right Breakthrough 25, Eddy, N. Mex. - 12/10/75 at 1320', and a solution prepared by dissolving a part of an AEC 8 core sample from the 2725.0 - 2725.5 horizon.

The primary purpose in analyzing brines(1) "A" and "B" was to determine what remained in solution for use in modifying their compositions. The results are given in Tables 1 and 2, respectively, along with the nominal composition and the general analytical technique employed. Where two methods of analyses were used in determining a single species, both results are included for comparison. As in all analyses reported herein, the atomic absorption (AA) work was done by G. Noles, 5824, the EDTA and volumetric analyses by S. L. Erickson, 5821, and the remainder by R. G. Dosch, 5824.

Both brines "A" and "B" were heated at 100°C for several hours and allowed to equilibrate at room temperature for 72 hours prior to filtration. It appears that the large amount of insoluble in brine "A" consisted in-part of all major constituents. The small amount of insoluble observed in brine "B" was apparently a mixture of calcium and iron compounds. Two brine solutions, "A'" and "B'", were prepared using the compositions dictated by the analyses of brines "A" and "B". The only

Table 1. Analyses of Standard Brine "A"

Species	Nominal Comp (mg/l)	Method	Result (mg/l)
Na	56,980	AA	47,000
K	52,000	AA	47,000
Mg	38,000	AA and EDTA	34,600 35,700
Ca	1,300	AA and EDTA	1,050 950
Fe	50	AA	3.1
Sr	20	AA	12.6
Li	20	AA	30(1)
Rb	20	AA	22.5
Cs	10	AA	9.6
Cl	242,700	Spec Ion Elec	224,000
$SO_4^{=}$	7,000	Grav	6,690
B	171	Vol	210
HCO_3^{-}	700	Vol	1,090
Br	400	--	--
I	10	--	--

(1) Li was observed as an impurity in one or more of the chemicals used in preparing brine.

Table 2. Analyses of Standard Brine "B"

Species	Nominal Comp (mg/l)	Method	Result (mg/l)
Na	115,000	AA	117,700
K	5,000	AA	4,700
Mg	1,000	AA and	980
		EDTA	1,030
Ca	800	AA and	420
		EDTA	480
Fe	50	AA	2.6
Sr	20	AA	10.4
Li	20	AA	29(1)
Rb	20	AA	20.5
Cs	10	AA	10
Cl	178,200	Spec Ion Elec	174,700
$SO_4^=$	10,000	Grav	9,760
B	110	Vol	138
HCO_3^-	700	Vol	95
Br	400	--	--
I	10	--	--

(1) Li was observed as an impurity in one or more of the chemicals used in preparing brine.

solids observed prior to filtration appeared to be trace amounts of an Fe precipitate, and no solids crystallized out in a two-week period after filtration, when the solutions were discarded.

Table 3 lists the results of analyses of the natural brine samples described earlier, abbreviated as "ERDA 6" and "Duval Nash". Comparison of these results with results from commercial laboratories for the same brines or brines from the same source show reasonably good agreement except for the sodium content, where values calculated by the commercial labs were considerably higher (a factor of 2 in the Duval Nash brine) than our experimental results.

Table 3. Analyses of Natural Brine Samples

Species	Analytical Method	Results (mg/l) Duval Nash	ERDA 6
Na	AA	27,500	112,000
K	AA	30,000	5,100
Mg	AA and	48,000	540
	EDTA	55,400	560
Ca	AA and	715	83
	EDTA	640	130
Fe	AA	3.2	5.3
Sr	AA	1.2	6.6
Li	AA	64	336
Rb	AA	28	9.4
Cs	AA	ND < 1(1)	ND < 1(1)
Cl	Spec Ion Elec	236,500	186,100
$SO_4^=$	Grav	3,650	16,000
B	Vol	1,050	790
HCO_3^-	Vol	1,090	1,310

1) ND - Not Detected

The final brine analyzed was prepared from a portion of an AEC #8 core sample from the 2725.0 - 2725.5 horizon. A 634.9 g sample (sawed off of the core sample with a band saw) was dissolved in water to give a final volume of 2193 milliliters. The water insoluble material which was filtered off and air-dried, weighed 6.1 gram or 0.96% of the original sample. The brine was analyzed using the same analytical methods shown in Tables 1-3 and the results are given in Table 4.

Table 4. Analysis of Brine Prepared from ERDA #8 Core Sample(1), 2725.0-2725.5 Horizon

Species	Results (mg/l)
Na	112,170±1550(2)
K	11
Mg	5.5
Ca	925
Fe	2.5
Sr	13
Li	ND < 1
Rb	ND < 2
Cs	ND < 1
Cl	170,900±140(2)
$SO_4^=$	2450±5(3)
B	ND < 10
HCO_3^-	ND

1) 634.9 g sample dissolved in total volume of 2193 ml.

2) Average of three determinations.

3) Average of two determinations.

The final synthetic brine compositions "A" and "B", based in part on the analyses herein, which you supplied on 9/30/76, have been prepared. The final solutions prior to filtration exhibited a slight turbidity, which qualitatively appeared to be the result of hydrolysis of some of the iron. No solids have crystallized from the solutions in the 72 hour period since they were prepared.

The preparation used for latest composition brines "A" and "B" are given in Tables 5 and 6. The compositions and chemicals used are based completely on your latest calculations, however, several material substitutions were necessary due to current in-house availability. The only one which changes the composition is the use of RbCl in place of Rb_2SO_4. However, both the resulting decrease in sulfate concentration and the increase in chloride are negligible in terms of the concentrations of those species already present from other sources.

Synthetic brine solutions of the compositions given in Tables 5 and 6 will be used in repeating the ^{137}Cs and ^{85}Sr distribution coefficient measurements and in subsequent measurements with other fission products and actinides.

RGD:5824:cgc

Distribution

1141 L. R. Hill
1141 S. J. Lambert
5821 S. L. Erickson
5824 G. T. Noles
5824 R. W. Lynch
5820 R. L. Schwoebel

Table 5. Solution "A" Preparation - Final Composition

Two Liter Batch Preparation -

1. Addition of Components -

Compounds	Weight (g)	Steps
NaCl	200.2	Dissolve in H_2O. Total Volume ~ 1900 ml.
Na_2SO_4	12.40	
$Na_2B_4O_7 \cdot 10H_2O$	3.90	
$NaHCO_3$	1.92	
NaBr	1.04	
KCl	114.4	
$MgCl_2 \cdot 6H_2O$	584.2	
$CaCl_2$(Anhydr.)	3.32	
CsCl		Added 5 ml aliquot of one liter of solution containing: 0.52 g CsCl
RbCl		10.87 g RbCl
LiCl		50.0 g LiCl
$SrCl_2 \cdot 6H_2O$		6.0 g $SrCl_2 \cdot 6H_2O$
KI		5.2 g KI
$FeCl_3$		Added 5 ml aliquot of 250 ml of solution containing 1.25 g $FeCl_3 \cdot 6H_2O$. dilute to 2000 ml.

2. pH Adjustment -

   The pH of the complete solution was 6.57. No adjustment was made.

3. Filtration - Solution was filtered through a medium glass frit filter.

Table 6. Solution "B" Preparation - Final Composition

Two Liter Batch Preparation -

1. Addition of Components -

Compounds	Weight (g)	Steps
NaCl	576	Dissolve in H_2O to give a total volume of ~ 1900 ml.
Na_2SO_4	12.4	
NaBr	1.04	
$CaCl_2$ (Anhydr.)	4.98	

CsCl RbCl $SrCl_2 \cdot 6H_2O$ KI $MgCl_2 \cdot 6H_2O$ KCl	Added 5 ml aliquot of one liter of solution containing: 0.52 g CsCl 0.58 g RbCl 18.1 g $SrCl_2 \cdot 6H_2O$ 5.2 g KI 34.1 g $MgCl_2 \cdot 6H_2O$ 11.6 g KCl
$NaHCO_3$ $Na_2B_4O_7 \cdot 10H_2O$	Added 5 ml aliquot of 250 ml of solution containing: 1.40 g $NaHCO_3$ 1.60 g $Na_2B_4O_7 \cdot 10H_2O$
$FeCl_3 \cdot 6H_2O$	Added 5 ml aliquot of 250 ml of solution containing 1.25 g of $FeCl_3 \cdot 6H_2O$. dilute to 2000 ml.

2. pH Adjustment -

   The pH of the complete solution was 7.20. Adjusted to pH = 6.53 with HCl.

3. Filtration - Solution was filtered through a medium glass frit filter.

APPENDIX 3

TABLE 4

SUMMARY OF ANALYSES OF BRINE FROM WIPP-12 WELL

USING ARITHMETIC MEANS[1]

PARAMETERS	UNITS	FLOW SAMPLES[2]	DOWNHOLE SAMPLES	
SAMPLE TYPE:				
LABORATORY:		D'APPOLONIA	CORE LABORATORY	D'APPOLONIA
LOCATION:		WIPP-12	WIPP-12	WIPP-12
FIELD DETERMINATIONS:				
Temperature (Downhole)[3]	°Celsius	26.6	—	—
pH	Standard Units	6.81	--	--
Eh	Millivolts	-211	—	—
Specific Gravity	—	1.219	--	--
Specific Conductance	umhos/cm @ 25°C	526,100	—	—
Bicarbonate	mg/l	2840	--	--
Chloride	mg/l	191,100	—	—
Sulfate	mg/l	20,400	--	--
Total Hardness	mg/l as $CaCO_3$	6310	—	—
Total Iron	mg/l	0.15	--	--
Hydrogen Sulfide	mg/l	555	—	—
LABORATORY DETERMINATIONS:				
pH	Standard Units	7.17	7.3	7.76
Specific Gravity	—	—	1.2184	--
Specific Conductance	umhos/cm at 25°C	490,000	—	--
Total Dissolved Solids	mg/l	320,000	342,000	--
Total Suspended Solids	mg/l	58	—	3265
Total Hardness	mg/l as $CaCO_3$	—	5280	--
CATIONS:				
Barium	mg/l	0.32	—	—
Calcium	mg/l	410	310	380
Lithium	mg/l	220	—	210
Magnesium	mg/l	1700	1246	1400
Potassium	mg/l	3100	3074	3200
Sodium	mg/l	114,000	119,800	140,000
Strontium	mg/l	15	--	--
ANIONS:				
Bicarbonate	mg/l	2600	2270	2400
Bromide	mg/l	430	—	460
Chloride	mg/l	160,000	188,150	180,000
Fluoride	mg/l	4.3	--	--
Sulfate	mg/l	17,000	20,100	18,000
NUTRIENTS:				
Ammonia (as N)	mg/l	430	—	--
Nitrate (as N)	mg/l	500	--	--
Phosphate (as P)	mg/l	<0.13	—	—
OTHER ELEMENTS:				
Aluminum	mg/l	2.8	--	--
Boron (as B)	mg/l	1200	--	960
Copper	mg/l	0.64	--	--
Iron	mg/l	3.6	25	6.3
Manganese	mg/l	0.29	—	--
Zinc	mg/l	0.48	--	--

NOTES:

(1) Samples containing contamination by drilling fluids excluded in calculation of the means.

(2) Mean value based on data collected during Flow Test 1, Activity WIPP-12.7 only.

(3) Downhole temperature was measured at approximately 3005 feet below the surface.

"--" = Not Determined

TABLE 5

SUMMARY OF ANALYSES OF BRINE FROM ERDA-6 WELL
USING ARITHMETIC MEANS[1]

PARAMETERS	UNITS	FLOW SAMPLES	DOWNHOLE SAMPLES	
SAMPLE TYPE:				
LABORATORY:		D'APPOLONIA	CORE LABORATORY	D'APPOLONIA[2]
LOCATION:		ERDA-6	ERDA-6	ERDA-6
FIELD DETERMINATIONS:				
Temperature (Downhole)[3]	°C	26.7	-	-
pH	Standard Units	6.17	-	-
Eh	Millivolts	+152	-	-
Specific Gravity	—	1.216	-	-
Specific Conductance	umhos/cm @ 25°C	473,100	-	-
Bicarbonate	mg/l	2,580	-	-
Chloride	mg/l	188,800	-	-
Sulfate	mg/l	19,100	-	-
Total Hardness	mg/l as $CaCO_3$	2,640	-	-
Total Iron	mg/l	0.22	-	-
Hydrogen Sulfide	mg/l	380	-	-
LABORATORY DETERMINATIONS:				
pH	Standard Units	6.42	6.7	7.02
Specific Gravity	-	-	1.2116	-
Specific Conductance	umhos/cm @ 25°C	490,000	-	-
Total Solids				
Dissolved	mg/l	330,000	355,700	-
Suspended	mg/l	87	-	5,970
Cations				
Barium	mg/l	0.76	-	-
Calcium	mg/l	490	402	360
Lithium	mg/l	240	-	205
Magnesium	mg/l	450	239	270
Potassium	mg/l	3,800	3,670	4,800
Sodium	mg/l	112,000	119,500	140,000
Strontium	mg/l	18	-	-
Anions				
Bicarbonate	mg/l	2,600	1,990	1,800
Bromide	mg/l	880	-	720
Chloride	mg/l	170,000	196,300	180,000
Fluoride	mg/l	1.7	-	-
Sulfate	mg/l	16,000	19,980	14,000
Nutrients				
Ammonia (as N)	mg/l	870	-	-
Nitrate (as N)	mg/l	620	-	-
Phosphate (as P)	mg/l	0.37	-	-
Other Elements				
Aluminum	mg/l	2.4	-	-
Boron (as B)	mg/l	680	-	740
Copper	mg/l	0.49	-	-
Iron	mg/l	3.6	162	5.7
Manganese	mg/l	6.9	-	-
Zinc	mg/l	0.55	-	-

NOTES:

(1) Samples containing contamination by drilling fluids excluded in calculation of the means.

(2) Changes in pH and Eh indicate oxidation during transportation or storage by Core Laboratory. Samples also contained large quantities of solids.

(3) Downhole temperature of 26.7°C was measured at 2462 feet below the surface. A temperature of 21.9°C was measured at 405 feet below the surface.

"-" = No analyses performed.

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