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Sandia National Laboratories
Waste Isolation Pilot Plant

Chemical Behavior of Bromine in High Ionic Strength Solutions, Test Plan TP 03-02, Rev. 0

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1 ABBREVIATIONS, ACRONYMS, FORMULAS, AND INITIALISMS

An	actinide
Br	bromine
Br ₂	molecular (or diatomic) bromine
Br ⁻	bromide
Br ₃ ⁻	tribromide anion
BrO ₃ ⁻	bromate
CBFO	(U.S. DOE) Carlsbad Field Office
Cl [•]	atomic chlorine free radical
Cl ₂ ^{•-}	molecular chlorine free radical
D ₂	diatomic deuterium, used as UV light source in UV-vis spectroscopy
DOE	(U.S.) Department of Energy
E ⁰	standard reduction potential
ERDA-6	descriptive label applied to a Castile brine composition
F	the Faraday constant, (96,485 coulombs/mole)
Fe	iron
GWB	Generic Weep Brine (representative of Salado brine composition)
H ⁺	hydronium ion
H [•]	atomic hydrogen free radical
HCl	hydrochloric acid
HOBr	hypobromous acid
HOCl	hypochlorous acid
HOCl ^{•-}	hypochlorous acid, anionic free radical
ICP-OES	inductively coupled plasma-optical emission spectroscopy
NaBr	sodium bromide
NaBrO ₃	sodium bromate
NaOCl	sodium hypochlorite
NaOH	sodium hydroxide
NP	(SNL NWMP) Nuclear Waste Management (QA) Procedure
NWMP	(SNL) Nuclear Waste Management Program
OBr ⁻	hypobromite
OH [•]	hydroxyl free radical
OCl ⁻	hypochlorite
OH ⁻	hydroxide
p _c H	negative logarithm of the hydrogen ion concentration of a solution
pH	negative logarithm of the hydrogen ion thermodynamic activity of a solution
pK _a	negative base 10 logarithm of an acid dissociation constant
R	ideal gas constant, 8.314 J/molK
SNL	Sandia National Laboratories
SOP	(SNL) Standard Operating Procedure
SP	(SNL NWMP) Activity/Project-Specific Procedure

1 ABBREVIATIONS, ACRONYMS, FORMULAS, AND INITIALISMS (cont.)

T	temperature, in degrees Celsius or kelvins
U	uranium
UV-vis	ultraviolet-visible (spectroscopy)
WIPP	(U.S. DOE) Waste Isolation Pilot Plant
ΔG	Gibbs free energy of reaction
α particle	high-energy particle expelled from a nucleus during an α -decay process
β_{pqr}	stability constant for a metal/ligand complex
γ	activity coefficient (not related to γ -ray)
μ	ionic strength

2 REVISION HISTORY

This is the first version of this test plan. Subsequent versions will be prepared in accordance with the following Sandia National Laboratories (SNL) Nuclear Waste Management Program (NWMP) Nuclear Waste Management Quality Assurance Procedures (NPs): NP 6-1, NP 6-2, and NP 20-1 (Subsection 5.2).

3 PURPOSE & SCOPE

3.1 Objectives

The high-energy α particles emitted during the course of radioactive decay of many actinide elements intensely interact with the host matrix, whether solid or solution. In aqueous solutions, such as NaCl and MgCl₂ brines, the energy lost by the α particles is transferred to solute and solvent species, leaving them in highly excited states, followed by reactions with each other or with other solution components. The resulting products, referred to collectively as radiolysis products, include hydrogen peroxide (H₂O₂) and hypochlorite (OCl⁻). Radiolysis products, such as OCl⁻, react with bromide (Br⁻), producing oxidized forms of bromine (Br), such as diatomic bromine (Br₂), hypobromite (OBr⁻), or bromate (BrO₃⁻). The products of the oxidation of Br⁻ depend upon solution conditions, such as pH and Br⁻ concentration. The diatomic molecule, Br₂, exhibits greater mobility than the charged OBr⁻ and BrO₃⁻ species, due to partitioning of Br₂ from the aqueous into the gaseous phase. Formation of a complex of Br₂ with Br⁻ to form Br₃⁻ may act to reduce the partitioning of Br₂ into the vapor phase. The oxidized forms of Br are capable of oxidizing U to U(VI), Np to Np(V) and Pu to Pu(VI). However, both metallic and oxidized iron can react with oxidized Br species through oxidation/reduction processes and transition-metal-facilitated catalytic decomposition. Thus, although α -particle induced brine radiolysis may produce oxidized species of Br, the presence of iron may mitigate the attendant oxidizing capacity by reacting with the radiolysis products. In order to assess the potential impact of oxidized forms of Br on actinide (An) solubility and speciation, it is necessary to investigate reactions of Br in brines. The broadly stated goal of the investigation of the chemical behavior of Br in brines is divided into four categories; discussions of the merits of each category are considered individually.

- Task 1. Determination of conditions influencing generation of the oxidized forms of Br: HOBr, OBr⁻, BrO₃⁻, and Br₂.
- Task 2. Determination of the stability constant of Br₃⁻ in brine.
- Task 3. Determination of the partition coefficient of Br₂ between the aqueous and gaseous phases.
- Task 4. Determination of the effect of iron on production and concentration of Br species.

3.2 Introduction

There are two types of brines that naturally occur in the vicinity of the WIPP: Salado-Formation brine, an intragranular brine that includes >1 M Mg²⁺ and is saturated with

respect to NaCl, and Castile-Fm. brine, a predominantly NaCl-saturated brine. Both brine types contain smaller amounts of K^+ , Ca^{2+} , Br^- , SO_4^{2-} , and $B(OH)_4^-$. Synthetic brines have often been used in experimental work to model the behavior of these Salado and Castile brines. Two different brine compositions, referred to as Brine A and GWB, have been used to mimic the Salado brine, whereas work on Castile brine chemistry has utilized a brine type identified as ERDA-6. The compositions of these brines have been described elsewhere (Brush, 1990, Wall, 2002). The brines, which have ionic strengths ranging from 5 to 7, have a small buffering capacity close to $pH = 8$ due to the presence of borate. The high ionic strengths lead to significant departures from ideality of thermodynamic behavior for both solute and solvent species. For example, ionic solutes exhibit thermodynamic activities that depend upon ionic strength as well as the nature of the solution components; there is a decrease in the thermodynamic activity of solvent water and an increase in the activities of other uncharged species. As a result, there are differences in solute behavior, including differing solubilities and stabilities of metal-ligand complex formation due to the differences in characteristics of each of brine type.

Brines that have high chloride contents generate significant amounts of OCl^- when exposed to α irradiation (Kelm, 1999). The present discussion of production of OCl^- is adapted from Wall (2002). This test plan describes production of OCl^- due to α -particle induced radiolysis of brines, and the potential impacts upon aqueous chemistry of WIPP brines. OCl^- may act as a strong oxidant or complexing agent for metal ions, providing two potential routes for mobilization of actinide ions. However, OCl^- may undergo reactions in solution, leading to decomposition, either through reaction with $HOCl$ or OCl^- , or through decomposition reactions catalyzed by redox active metals. Experimental work on OCl^- behavior in brines has been initiated in SNL's Carlsbad laboratory. These studies have focused on the decomposition rates of $HOCl$ and OCl^- in brines. Reaction rates have been studied in 5 m NaCl solutions to determine the influence of pH and other components, such as iron. The behavior of OCl^- in 5 m NaCl is quite different than in GWB or ERDA-6. Representative WIPP brines, including GWB and ERDA-6, contain millimolar quantities of bromide (Br^-), which can be oxidized by $HOCl$, or OCl^- .

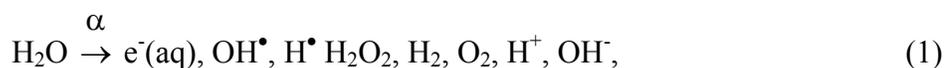
There is immediate oxidation of Br^- upon addition of OCl^- to either GWB or ERDA-6, resulting in a net decrease in OCl^- concentration, accompanied by the formation of oxidized forms of Br. Therefore, from the perspective of $HOCl$ or OCl^- generation, as long as brines contain Br^- , a readily available reaction pathway for the electrochemical reduction of $HOCl$ or OCl^- would exist, effectively limiting the extent to which either $HOCl$ or OCl^- accumulates. However, the issue of the nature of oxidized Br may be of some concern. The products of reaction between OCl^- and Br^- in ERDA-6 and GWB are unknown. Oxidation of Br^- may yield OBr^- , BrO_3^- or Br_2 . The ionic forms, OBr^- and BrO_3^- , although oxidants, would not partition into the gaseous phase, although Br_2 could do so, and would exhibit significantly more mobility than the ionic species. As a result, ionic species produced by α radiolysis would likely be constrained to remain in or near the microenvironments of origin, whereas Br_2 may migrate significantly beyond the region of production.

The amount of oxidized Br that may be produced is limited by the availability of Br⁻ in the pertinent brines. GWB and ERDA-6 respectively contain 11 and 27 mM concentrations of Br⁻. Relatively speaking, these concentrations are sufficiently large to create oxidizing solution conditions if a substantial fraction of Br were to exist in an oxidized state. Br₂, OBr⁻ and BrO₃⁻ are each sufficiently strong oxidants to cause the oxidation of U to U(VI), Np to Np(V) and Pu to Pu(VI). The higher oxidation states of each of the respective actinides, U, Np, and Pu, are more soluble than the lower oxidation states. Actinide solubility influences transport mechanisms with respect to potential releases only in the event of fluid entry into the repository. Clearly, transport of soluble actinides could not be a feature of any release mechanism in the absence of brine. Therefore, production of oxidants and transport of soluble actinides would provide a credible release mechanism only in the event of an inundation. It is not presently possible to make a quantitative determination regarding the potential for accumulation of oxidized forms of Br under inundated conditions. It is the goal of the work proposed in this test plan to measure the chemical behavior of Br in brines in order to assess the potential impact upon chemical conditions within the repository.

3.3 Production of Hypochlorite

In general, α particles travel 30-70 μm in water (Ganguly et al., 1956). The ionization tracks of α particles in aqueous solutions include numerous hydrogen, oxygen, and hydroxyl free radicals. Ordinarily, free radicals have very short lifetimes in solution due to rapid reaction with solute and solvent molecules. Recombination processes are important in the diffusion-limited environment surrounding particle tracks of high-linear-energy-transfer species, which may yield H₂O₂ as a product of the reaction of two hydroxyl radicals. Also significant, but dependent upon the solution composition, are generation of molecular chlorine (Cl₂), hypochlorous acid (HOCl) and OCl⁻.

In the following discussion, the symbol “→” denotes a thermodynamically irreversible process, while the symbol “⇌” indicates a thermodynamically reversible process. Water radiolysis in the tracks of α particles leads to generation of numerous species, such as:



in which e[·](aq) are aquated electrons, OH[·] represents hydroxyl free radicals, and H[·] represents hydrogen free radicals. Aquated electrons (e[·](aq)) and free radical species are very reactive, rapidly combining with many other dissolved species. Additional reactions take place in the presence of significant concentrations of other solute species, such as Cl⁻. Participation of Cl⁻ in radiolytically initiated reactions leads to generation of additional chemical species due to subsequent oxidation/reduction reactions. For example, the hydroxyl radical can oxidize chloride, yielding the hypochlorous acid anion free radical HOCl^{·-} (Kim et al., 1987)



The hypochlorous-acid free-radical anion equilibrates rapidly with H^+ to give the chlorine free radical:



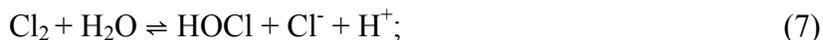
The likelihood of the chlorine radical combining with chloride is greater in solutions with high chloride content:



$Cl_2^{\bullet-}$ reacts rapidly to produce Cl_3^- , which is more stable than $Cl_2^{\bullet-}$,



The Cl_3^- species is in equilibrium with other chlorine species, ultimately producing OCl^- :



It has been reported that the production of HOCl and OCl^- depends on the Cl^- concentration (Kim et al., 1987). The dependence of OCl^- generation on NaCl concentration is illustrated in Figure 1. Data used to generate this figure were taken from Kelm et al. (1999). Each sample contained 1 Ci/L of ^{238}Pu introduced as finely divided precipitate of Pu(VI) hydroxide. The solutions were adjusted to a pH of ~12. No error bars are included because the literature reference includes insufficient data to estimate or evaluate the uncertainty. The equation for the linear best-fit line is $y = 0.0059x - 0.0105$.

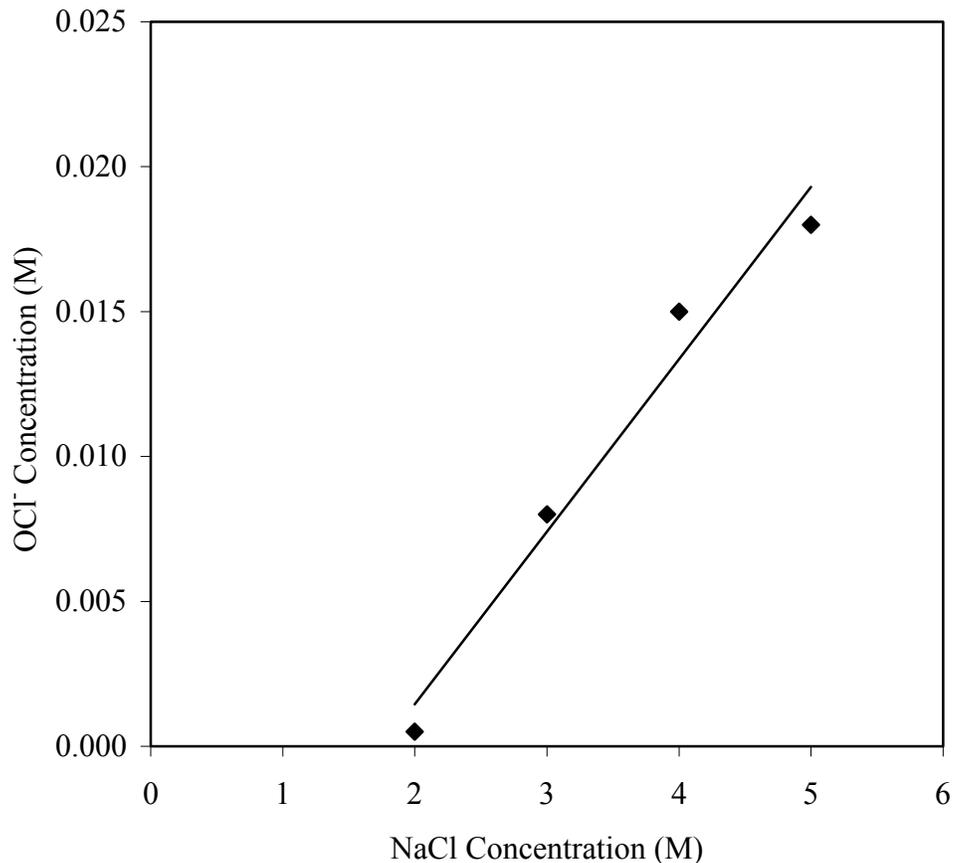


Figure 1. Generation of OCl⁻ as a function of aqueous NaCl concentration.

Production of OCl⁻ is not a significant process for Cl⁻ concentrations less than ca. 1.8 M at radioactivity levels of 1 Ci/L. The minimum concentration of Cl⁻ required for OCl⁻ generation most likely reflects the decreased probability of reactions 4 and 5 taking place. Conversely, the data indicate that the reactions leading to HOCl production in 5 M NaCl solution produce significant quantities of OCl⁻, (nearly 20 mM), in the presence of 1Ci/L of α -emitting radionuclides. The pK_a value of HOCl is 7.43 ($\mu = 1.0$ NaClO₄, T = 25 °C), indicating that at pH relevant to WIPP conditions (pH \approx 9-10) the conjugate base (OCl⁻) will be the predominant form (Martell et al., 1998). The symbol “ μ ” indicates ionic strength.

3.4 Chlorine Species as Oxidants

HOCl, OCl⁻ and Cl₂ are all strong oxidants in aqueous solution. Relevant reactions are given in Table 1.

Table 1. Standard Reduction Potentials for Reactions of HOCl and OCl⁻(a)

Reaction Number	Reaction	E° (V)
1.1	$\text{HOCl} + \text{H}^+ + \text{e}^- \rightleftharpoons \frac{1}{2} \text{Cl}_2 + \text{H}_2\text{O}$	1.61
1.2	$\text{HOCl} + \text{H}^+ + 2\text{e}^- \rightleftharpoons \text{Cl}^- + \text{H}_2\text{O}$	1.48
1.3	$\text{OCl}^- + \text{H}_2\text{O} + 2\text{e}^- \rightleftharpoons \text{Cl}^- + 2\text{OH}^-$	0.81
1.4	$\frac{1}{2} \text{Cl}_2 + \text{e}^- \rightleftharpoons \text{Cl}^-$	1.36

(a) Values are taken from Lide (1995)

Reaction 1.1 in Table 1 shows that under acidic conditions HOCl is strongly oxidizing, and may be reduced to elemental chlorine. Reaction 1.1 also shows that the oxidation of molecular chlorine to hypochlorous acid is strongly disfavored in acidic solutions, suggesting that acidic solutions of HOCl will tend to react to produce Cl₂. Reaction 1.2 suggests that HOCl may also be reduced to chloride, depending upon the pH and the identity of the species being oxidized. Reaction 1.3 illustrates that OCl⁻ is a strongly oxidizing anion in basic solutions, lying outside the thermodynamic stability field of water. Cl₂, also a strong oxidant as illustrated by Reaction 1.4, may be present under solution conditions that favor the existence of Cl₂ over HOCl.

3.5 Hydrolysis of Chlorine

The hydrolysis constant of chlorine in water may be calculated by adding reactions 1.1 and 1.4 from Table 1:

	<u>E° (V)</u>
$\frac{1}{2} \text{Cl}_2 + \text{H}_2\text{O} \rightleftharpoons \text{HOCl} + \text{H}^+ + \text{e}^-$	- 1.61
$\frac{1}{2} \text{Cl}_2 + \text{e}^- \rightleftharpoons \text{Cl}^-$	1.36
$\text{Cl}_2 + \text{H}_2\text{O} \rightleftharpoons \text{HOCl} + \text{H}^+ + \text{Cl}^-$	- 0.25

The thermodynamic equilibrium constant (or hydrolysis constant) for reaction of Cl₂ with water is defined as

$$K = \frac{a_{\text{HOCl}} a_{\text{H}^+} a_{\text{Cl}^-}}{a_{\text{H}_2\text{O}} a_{\text{Cl}_2}} \quad (9)$$

The subscripted terms in equation 9 indicate the thermodynamic activities for the respective species. The activities of each species may be expressed as products of the concentrations and the respective activity coefficients:

$$K = \frac{[\text{HOCl}] \gamma_{\text{HOCl}} [\text{H}^+] \gamma_{\text{H}^+} [\text{Cl}^-] \gamma_{\text{Cl}^-}}{a_{\text{H}_2\text{O}} [\text{Cl}_2] \gamma_{\text{Cl}_2}} \quad (10)$$

The activity of water is ≈ 0.7 in NaCl brines, which, as a first approximation, is the value used in this example. The equilibrium constant can be calculated by combining the thermodynamic relationships

$$\Delta G = -nFE \quad (11)$$

and

$$\Delta G = -RT \ln K \quad (12)$$

ΔG is the Gibbs free energy of reaction, n is the number of electrons exchanged, F is the Faraday constant, E is the cell potential, in volts, for the reaction, R is the ideal gas constant, T is the temperature in kelvins, and $\ln K$ is the Napierian logarithm of the equilibrium constant. Combining equations 10 and 11, and solving for $\ln K$ gives

$$\ln K = \frac{EF}{RT} \quad (13)$$

Solving for the hydrolysis of chlorine in water at $T = 298$ yields

$$\ln K = \frac{(-0.25\text{V})(96500\text{coulombs/mol})}{(8.314\text{J/molK})(298\text{K})} = -9.737 \quad (14)$$

Raising e to the power -9.737 yields the equilibrium constant K :

$$e^{-9.737} = 5.91 \times 10^{-5} \quad (15)$$

The hydrolysis constant may be used to calculate the approximate ratio of HOCl to Cl₂ as a function of pH by rearranging equation 9 and using a Cl⁻ concentration of 5 m NaCl:

$$\frac{K_{a_{H_2O}} \gamma_{Cl_2}}{[H^+] \gamma_{H^+} [Cl^-] \gamma_{Cl^-} \gamma_{HOCl}} = \frac{[HOCl]}{[Cl_2]} \quad (16)$$

The values of the activity coefficients for each species depend upon ionic strength and solution composition. The activity coefficients for HOCl and OCl⁻ in brines are unavailable; therefore, for the sake of this example, are assumed to be unity, along with the corresponding values for Cl₂, H⁺, Cl⁻ and H₂O. The plot in Figure 2 illustrates the relative concentrations of HOCl and Cl₂, as a function of pH. The equation for the straight line is $y = x - 4.93$, which suggests that Cl₂ is the predominant species at pH values less than 4.93, while HOCl becomes the dominant species at $4.93 < \text{pH} < \approx 8$; above $\text{pH} \approx 8$ hypochlorous acid deprotonates to form OCl⁻. Hypochlorite solutions that are acidified to pH values less than ca. 4.9 should react in the presence of Cl⁻, releasing chlorine gas.

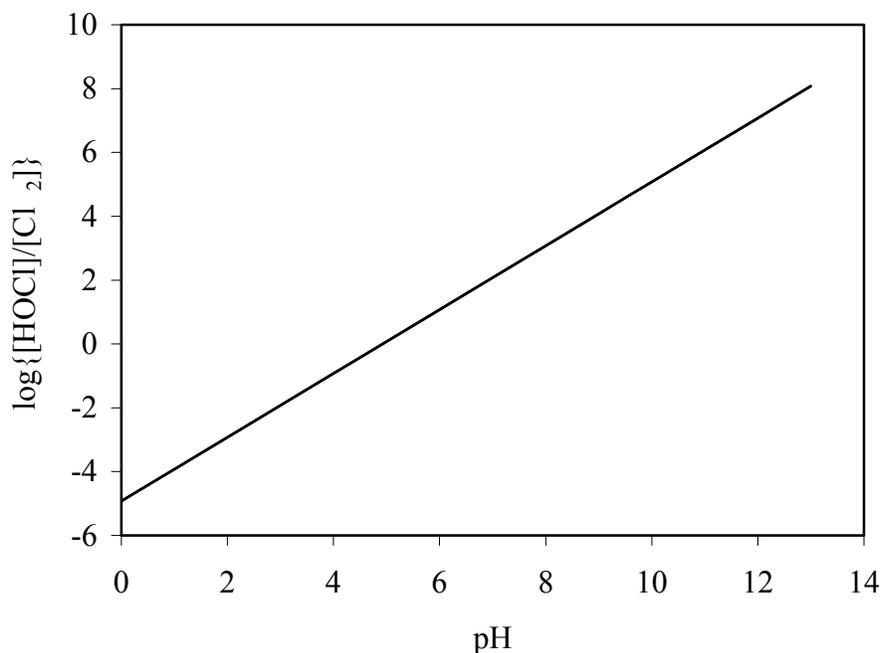


Figure 2. Plot of $\log \{[HOCl]/[Cl_2]\}$ as a function of pH.

3.6 Bromine Behavior

Bromine, (Greek *bromos*, stench) a dark brown mobile liquid, was first isolated by A.J. Balard in 1826. Commercial recovery of Br₂ in the United States is carried out on brines found in Arkansas and Michigan which respectively contain 4000-5000 ppm and ca. 2000 ppm Br⁻. The Br⁻ anion is oxidized to Br₂ by contact with Cl₂, and subsequently separated by partitioning of Br₂ into a stream of air or steam, from which it may be condensed as liquid Br₂. Some properties of Cl and Br are summarized in Table 2.

Table 2. Properties of Cl₂ and Br₂

Property	Cl ₂	Br ₂
Melting point (°C)	-101	-7.25
Boiling point (°C)	-34.0	59.5
Density (liquid, g/ml)	1.66 (-70 °C)	3.187 (0 °C)
Density (gas, g/l at 20 °C)	3.214	7.59

It should be noted that while Cl₂ is a gas at room temperature, Br₂ is a liquid, but has a substantial vapor pressure, resulting in partitioning into the vapor phase. Br₂ is a vigorous oxidant, and may react with many substances. Some reactions featuring Br are presented in Table 3.

Table 3. Aqueous Reactions of Bromine

Reaction Number	Reaction	E° (V)
3.1	$\text{OBr}^- + \text{H}_2\text{O} + 2\text{e}^- \rightleftharpoons \text{Br}^- + 2\text{OH}^-$	0.76
3.2	$\text{H}^+ + \text{HOBr} + \text{e}^- \rightleftharpoons \frac{1}{2} \text{Br}_2 + \text{H}_2\text{O}$	1.59
3.3	$\text{BrO}_3^- + 3\text{H}_2\text{O} + 6\text{e}^- \rightleftharpoons \text{Br}^- + 6\text{OH}^-$	0.61
3.4	$\text{BrO}_3^- + 6\text{H}^+ + 5\text{e}^- \rightleftharpoons \frac{1}{2} \text{Br}_2 + 3\text{H}_2\text{O}$	1.52
3.5	$\frac{1}{2} \text{Br}_2(\text{g}) + \text{e}^- \rightleftharpoons \text{Br}^-$	1.07

Reaction 3.1 shows that OBr^- is a strong oxidant in basic solution; comparison with Reaction 1.3 in Table 1 indicates that Br^- may be oxidized to OBr^- by OCl^- . Reaction 3.2 demonstrates that HOBr is strongly oxidizing in acidic solutions, and may yield diatomic bromine upon reduction of HOBr . Reactions 3.3 and 3.4 show that BrO_3^- is a strong oxidant under acidic and basic conditions. Reaction 3.5 illustrates that Br_2 is a strong oxidant in solution, and that the standard reduction potential for this reaction does not depend upon the pH of the solution. As ionic solutes, both OBr^- and BrO_3^- could exhibit mobility by diffusion through the solution, but its presence would be limited to the liquid phase. Conversely, Br_2 , which possesses a substantial vapor pressure at room temperature, could readily partition into the gaseous phase, in which it would have the means to migrate more rapidly and over greater distances than is possible for liquid phase components.

Both OBr^- and HOBr form metastable solutions in water, and may undergo thermodynamically irreversible decomposition reactions. HOBr can disproportionate into BrO_3^- and Br^- , whereas OBr^- can decompose to yield oxygen and Br^- . Two examples of thermodynamically irreversible reactions are illustrated in Table 4.

Table 4. Thermodynamically Irreversible Reactions of Bromine

Reaction Number	Reaction
4.1	$3\text{HOBr} \rightarrow \text{BrO}_3^- + 2\text{Br}^- + 3\text{H}^+$
4.2	$2\text{OBr}^- \rightarrow \text{O}_2 + 2\text{Br}^-$

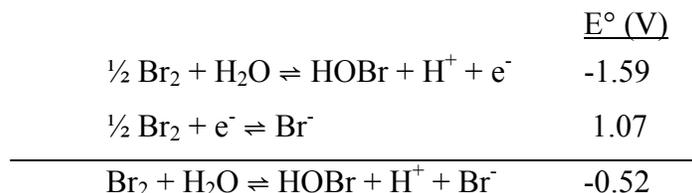
Br_2 can also react with chloride to form a bromine-dichloride anion, which may release bromide to give bromine chloride (Wang et al. 1994). BrCl , a red-brown gas at room temperature, dissociates to give Br_2 and Cl_2 . The formation of Br_3^- is well documented, with a formation constant of $\sim 10^2$ although it is unlikely that Br_3^- can form to a significant extent in ERDA-6 or GWB due to the relatively low concentration of Br^- (Pink, 1970). Hypobromous acid is a weak acid, with a pKa of 8.7 to 9.2, which suggests that it may either appear as the acid HOBr or conjugate base OBr^- in WIPP brines. Reactions of Br with Cl, and the dissociation reaction of HOBr are illustrated in equations 17 through 19. The equilibrium constant for reaction 18 is $\log K \approx 2$.



The reaction pathways that will dominate within the repository are unknown at this time. For example, Br^- may be oxidized to OBr^- , which may become protonated to HOBr, depending upon solution pH.

3.7 Hydrolysis of Bromine

The hydrolysis of Br in aqueous solutions can be expressed by adding equations 3.2 and 3.5 from Table 3:



The equilibrium constant for the hydrolysis reaction may be calculated applying the formats of equations 12 and 14:

$$\ln K = \frac{(-0.52\text{V})(96500\text{coulombs/mol})}{(8.314\text{J/molK})(298\text{K})} = -20.25; \quad (20)$$

$$K = e^{-20.25} = -1.6 \times 10^{-9}. \quad (21)$$

The hydrolysis constant may be used to calculate the ratio of HOBr to Br_2 as a function of pH:

$$\frac{K\gamma_{\text{Br}_2}}{[\text{H}^+]\gamma_{\text{H}^+}[\text{Br}^-]\gamma_{\text{Br}^-}\gamma_{\text{HOBr}}} = \frac{[\text{HOBr}]}{[\text{Br}_2]}. \quad (22)$$

A plot of the ratio of HOBr to Br_2 in ERDA-6 is illustrated in Figure 3. The function was calculated using a Br^- concentration of 0.011 m and a hydrolysis constant of 9.6×10^{-9} at zero ionic strength (Pink, 1970). The values for the activity coefficients of WIPP brines are not known, so were not taken into account in the calculation of the relationship illustrated in Figure 3, therefore the ratio must be regarded as an approximation. The equation that describes the line in Figure 3 is $y = x - 6.26$, which indicates that at pH values less than ca. 6.26 HOBr tends to react to form Br_2 . Conditions that favor formation of Br_2 include the higher ionic activity coefficient of the H^+ ion in brines, which is not taken into account in Equation 21, and the partitioning of Br_2 out of the aqueous phase into the vapor phase.

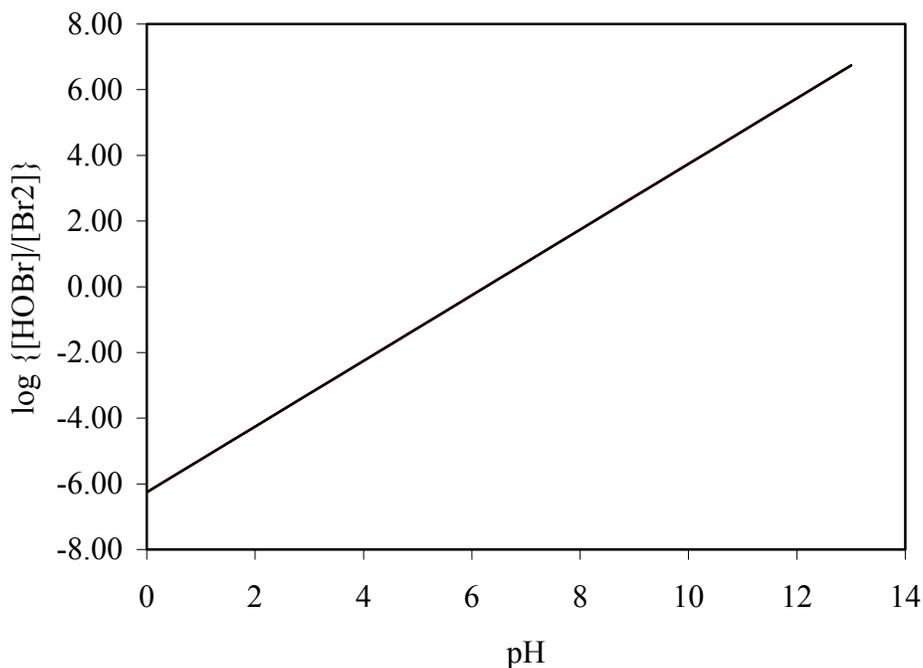


Figure 3. Plot of $[\text{HOBr}]/[\text{Br}_2]$ as a function of pH.

3.8 Bromine Absorbance Spectra

Some reference spectra of Br species are illustrated in Figure 4 (Betts and MacKenzie 1951, Pink 1970).

The spectra of Br_2 , Br_3^- , HOBr and BrO_3^- allow the absorption bands to be used as a means of both identification and quantification. HOCl and OCl^- have absorbance maxima at 242 nm and 292 nm, respectively. The concentration of a chromophore (light-absorbing species) in solution is related to the spectral absorbance by the Beer-Lambert Law:

$$A = \epsilon_n c l. \quad (23)$$

A is the absorbance, ϵ_n is the molar absorptivity (sometimes called molar extinction coefficient) at wavelength n , c is the concentration of the absorbing species, and l is the path length of the sample. As a result, when the sample size and molar absorptivities are known the UV-vis spectra may be used to monitor the concentrations of the species in solution.

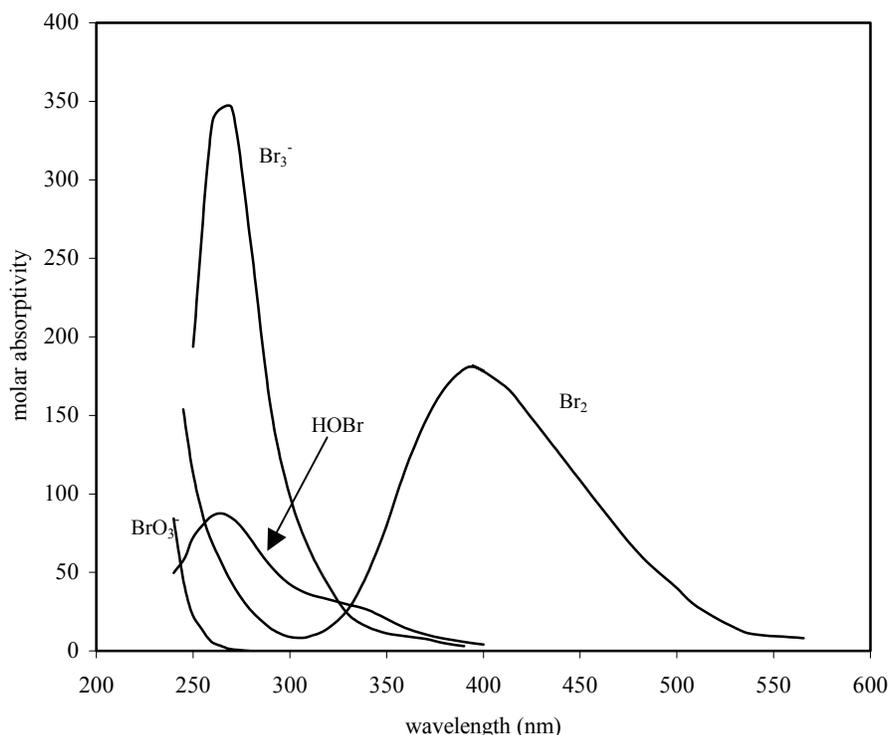


Figure 4. Sample spectra of Br species in water.

The UV absorbance maximum of Br_2 at ~ 390 nm, is due to excitation of an electron from the highest occupied molecular orbital (π_g) to the lowest unoccupied molecular orbital (σ_u). The symbols π_g and σ_u refer to the symmetry of the orbitals; both are antibonding orbitals. An interaction between a halogen molecule and another solution component, either solute or solvent, that tends to lower the energy of the π_g orbital or raise the energy of the σ_u orbital causes an increase in the difference in energy between the orbitals, with a concomitant increase in the energy required to promote an electron from the lower energy to the higher energy orbital, which would cause the absorbance peak to shift toward the higher energy blue region of the electromagnetic spectrum. Conversely, an interaction tending to increase the energy of the π_g orbital or decrease the energy of the σ_u orbital leads to lesser separation in the orbital energies, thus demanding less energy input to cause an electronic transition between the respective levels, resulting in a shift toward the lower energy red region of the electromagnetic spectrum. The possible transitions are illustrated in Figure 5, which shows the relative molecular orbital energies for diatomic halogens.

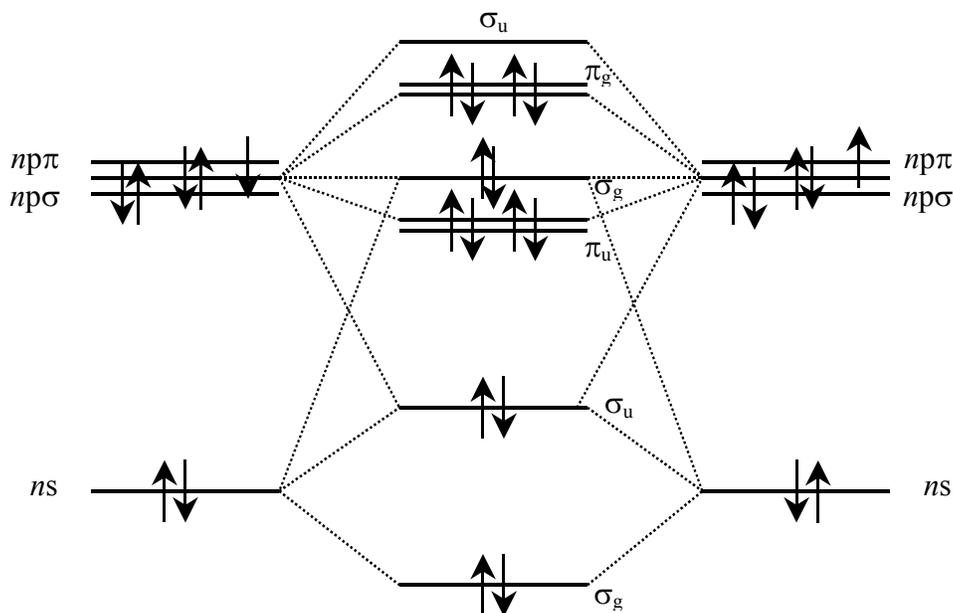


Figure 5. Molecular orbital diagram for diatomic halogen molecules

The ns and np levels correspond to the principle quantum number of the contributions by the linear combination of atomic orbitals, which are $n = 3$ and $n = 4$ for Cl and Br, respectively. It is unknown what type of interactions may occur between Br_2 species and other brine components; as a result, it will be necessary to experimentally determine the spectra of Br_2 , OBr^- , $HOBr$, BrO_3^- and Br_3^- to establish a spectral reference library.

3.9 Interactions of Oxidized Bromine Species with U, Np, Pu

Br_2 , OBr^- , and BrO_3^- will oxidize Pu to Pu(VI), U to U(VI), and Np to Np(V). Figure 6 illustrates the Latimer diagrams for redox reactions of U, Np, and Pu.

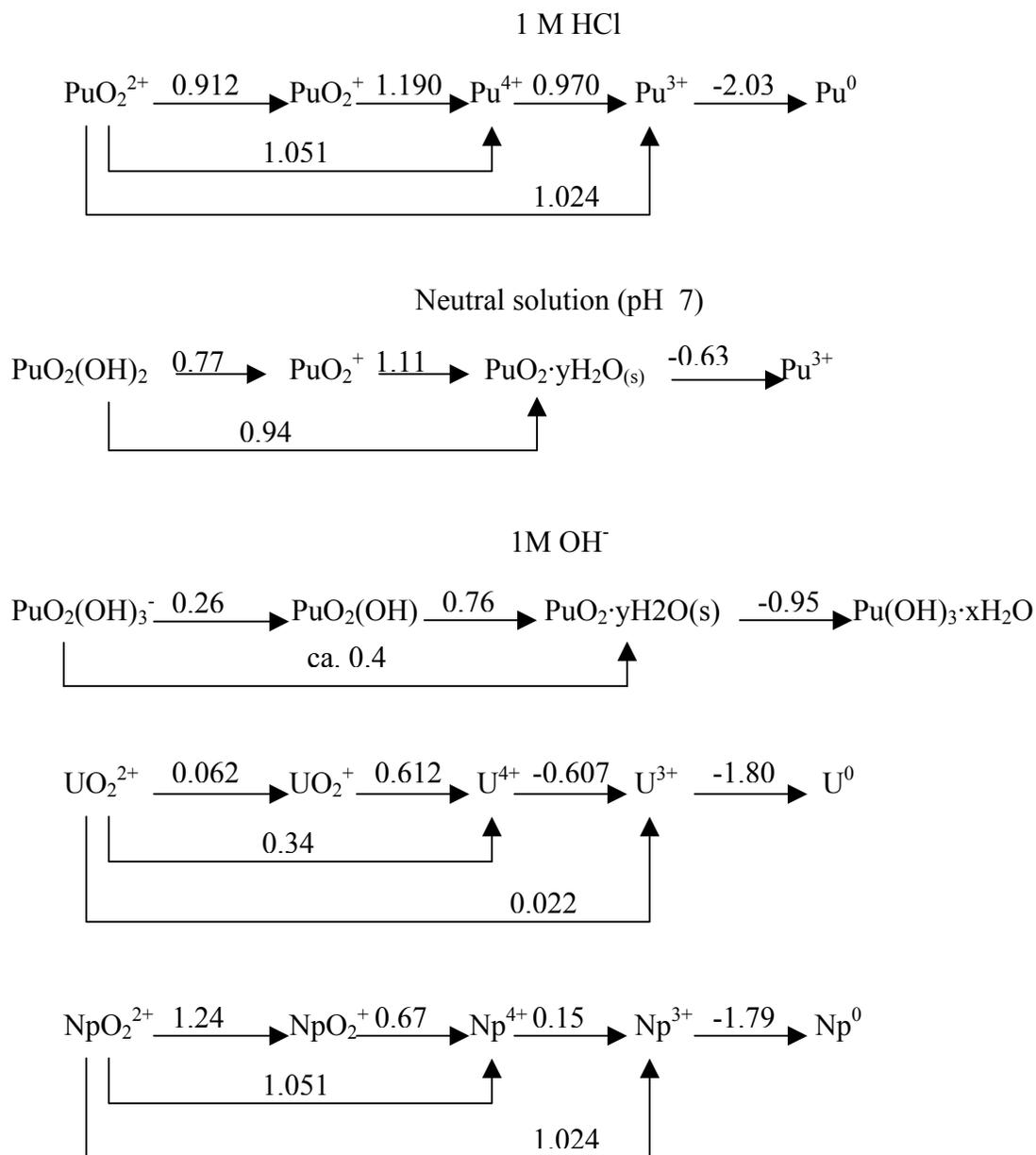


Figure 6. Latimer diagrams for oxidation/reduction behavior of U, Np, and Pu.

Pu data in Figure 6 are adapted from Cleveland (1979); U and Np data are adapted from Katz et al. (1986).

Comparison of the standard reduction potentials of Br species in Table 3 with the potentials for Pu suggests that Br₂, HOBr, OBr⁻ and BrO₃⁻ may all oxidize Pu to Pu(VI) under a wide range of pH. Br₂ is even capable of oxidizing Pu to Pu(VI) under acidic conditions, at which Pu(III) is the most stable. Use of BrO₃⁻ as a holding oxidant to prepare and store Pu(VI) solutions is also a widely practiced procedure. Diatomic bromine can oxidize Pu to Pu(VI), and U to U(VI), but does not oxidize Np beyond Np(V). In fact, it is the capability to oxidize U and Pu to their VI oxidation states that makes Br₂ a useful oxidant to separate either U or Pu from Np. For example, addition of Br₂ to a slightly acidic (pH ≈ 2) solution of Np and Pu will result in the Pu being oxidized to Pu(VI), leaving the Np as Np(V). The two may be easily separated by extraction of PuO₂²⁺ with a solution of di-2-ethylhexylphosphoric acid in heptane.

3.10 Reactions of Cl and Br Species

Solutions of HOCl and OCl⁻ are sufficiently reactive that they will oxidize Br⁻ to HOBr, OBr⁻ or BrO₃⁻ when added to a solution containing Br⁻. The identity and concentrations of the products, i.e., the preferred reaction pathway, depend upon conditions such as reactant concentrations. The significantly different mobility of the ionic (OBr⁻ and BrO₃⁻) vs. molecular (Br₂) species makes it quite important to determine the identity of the products of Br⁻ oxidation in WIPP brines, based upon quantitative, experimental data. The objectives outlined in subsections 3.10.1 through 3.10.4 are described in terms of the previous discussion on the behavior of chlorine and bromine, and how the behaviors may influence other materials such as iron or the actinide elements.

3.10.1 Conditions Influencing Generation of Oxidized Forms of Bromine

It is unknown what form the oxidized species of Br may take in WIPP brines. For example, the reaction of HOBr with Br⁻ and H⁺ may give Br₂ as a product at neutral to basic pH conditions, depending upon activity coefficients of the reactants and products. The impact of high ionic strength on the hydrolysis equilibrium of Br₂ is unknown. It is necessary to experimentally determine which species predominate under conditions similar to those expected to persist in the repository environment.

3.10.2 Determination of the Stability Constant of Br₃⁻ in Brine

Br₂ in aqueous solution combines with Br⁻ to form Br₃⁻. The Br₃⁻ anion would tend to reduce the partitioning of Br₂ from the aqueous phase into the vapor phase due to the nonvolatility of the charged species. A sufficiently stable Br₃⁻ anion may serve to reduce the mobility of Br₂ by formation of the ionic species. It is not known whether the presence of Br⁻ in WIPP brines will lead to the formation of Br₃⁻, with concomitant reduction of transfer of Br₂ to the vapor phase; therefore, it is necessary to determine whether formation of complexes of Br₂ can cause retention of Br₂ in the aqueous phase.

3.10.3 Determination of the Partition Coefficient of Br₂

Br₂ exhibits a solubility of 33.6 g/l in water at 25 °C. Increases in ionic strength usually cause increased activity coefficients of uncharged atomic and molecular species, which generally leads to decreases in solubility in aqueous solutions, often described as the “salting-out effect.” The effect of WIPP brine compositions on aqueous Br₂ solubility is not known. Increased solubility would have a demobilizing influence on Br₂, while decreased solubility would cause the movement of greater amounts of Br₂ into the gaseous phase. Therefore, it is necessary to investigate the dependence on solution composition of the partitioning of diatomic bromine between the aqueous and gaseous phases.

3.10.4 Effect of Fe on Production and Concentration of Br Species

The presence of Fe may have a significant impact upon the steady-state aqueous-phase concentrations of oxidized Br species. Metallic Fe, and Fe(II) will be available as reductants in the repository, and may react with oxidized Br species, yielding Br⁻. The goal of this task is to examine the effect of the presence of Fe on the stability and concentration of the oxidized Br species: Br₂, HOBr, OBr⁻, and BrO₃⁻.

4 EXPERIMENTAL PROCESS DESCRIPTION

The experimental process description includes further definition and explanation of the tasks to be performed, which will serve as a narrative depiction of a proposed experimental matrix. The objectives of this study will be addressed by defining and carrying out a series of tasks that will provide the data to assess issues of bromine behavior in brines. Descriptions of measuring and test equipment, experimental procedures and materials follow the descriptions of the tasks.

This test plan is not intended to provide a complete description of the details of proposed experiments or in the manner of their implementation. Procedures that will be used during the course of this experimental program are standard laboratory analytical procedures, such as titration and UV-vis spectrophotometry. It is not anticipated that it will be necessary to develop new or unusual experimental methods to carry out the work described within this test plan. All procedures that are employed during the course of this work will be described in detail in the laboratory notebooks in such a way that an independent reader may understand and duplicate the work. It will be necessary to evaluate the results of experiments in order to assess appropriate methods for further experimental procedures; therefore, it is impracticable to attempt to define or employ standardized procedures for much of the work.

Sources of experimental error and evaluation of the impact of error are discussed in Subsection 4.10, Known Sources of Error and Uncertainty.

4.1 Task 1. Determination of Conditions Influencing Generation of Oxidized Br

There are several factors that may affect the identities and concentrations of the reaction products, including:

- ionic strength and chloride concentration,
- temperature, and
- pH.

Sets of standard UV-vis spectra for each chromophore will be obtained by dissolving known amounts of each analyte in each solution matrix and measuring the spectra. The absorbance at each wavelength for a series of samples of known composition will be plotted as a function of concentration to obtain the molar absorption coefficients.

The products of reaction between HOCl/OCl⁻ and Br⁻ will be investigated by adding each component to salt solutions of different compositions. The solution matrices will include various concentrations of NaCl from 0.1 to 5 m. Other samples will be prepared in representative WIPP brines, such as ERDA-6 and GWB, and at various dilutions of the WIPP brines. The reaction of oxychlorine species and oxidation of Br⁻ will be followed by monitoring the change in the UV-vis absorbance spectra of each species. Some reactions may be slow enough to follow the change in concentrations over time by measuring the changing intensity of the UV-vis absorbance. For example, OCl⁻ decomposes slowly in aqueous solutions, and the rate may be easily measured by monitoring the change over time of the intensity of the UV absorbance at 292 nm. HOBr and OBr⁻ are also thermodynamically unstable in water, and will decompose over time, although the reaction rates in brine of oxidized Br species are not currently known. If the formation and decomposition of HOBr and OBr⁻ are sufficiently slow, i.e., on a time scale of minutes to days, the reaction will be monitored and the rate constants determined. For the purposes of this work, reactions will be considered to take place instantaneously if the rates are too rapid to be followed by UV-vis spectroscopy.

The temperature of the solutions will be monitored and controlled. A set of experiments will be initially performed to determine the magnitude of temperature dependence of the bromine hydrolysis reaction and the deprotonation reaction of hypobromous acid. These reactions will be carried out in a titration vessel of a Mettler DL 25 automatic titrator. The vessel will be immersed in a thermostatted water bath to maintain a controlled-temperature environment. Subsequent experiments will be carried out under controlled-temperature conditions (e.g., in a constant-temperature water bath) if it is determined that temperature is a critical variable that must be controlled.

Variations in pH affect the redox potentials for the oxidation and reduction of Cl and Br species, possibly exerting an influence on the reaction pathway and products. Therefore, a series of solutions of OCl⁻ and Br⁻ with pH values between 5 and 10 will be examined. The experiment

will be repeated at each of the ionic strengths used in the set of variable-ionic-strength experiments described above.

Each of the activities described in this section involves combining the appropriate reagents under a variety of conditions, with ensuing analysis of the reaction products. Each test will be carried out at least in triplicate in order to evaluate experimental reproducibility and uncertainty. It is anticipated that, in order to adequately capture an acceptable range of parameter possibilities, it will be necessary to prepare and analyze more than 100 samples, varying in size from 5 to 250 mL. The appropriate number and compositions of the samples will be determined on an ongoing basis according to the judgment of the principal investigator; sample preparation, analysis and justification will be documented in the laboratory scientific notebooks.

4.2 Task 2. Determination of the Stability Constant of Br_3^- in Brine

The stability constant of Br_3^- may be determined by simultaneously measuring the concentrations of Br_2 and Br_3^- in a solution containing a known amount of Br^- . The concentrations of Br_2 and Br_3^- may be determined by measuring the intensity of the UV-vis absorbance peaks of the two species. The Br_2 will be introduced to the solution by dissolution of Br_2 vapor, obtained from a stock sample of $\text{Br}_2(l)$.

This task will be carried out with a series of sample batches to study the dependence of partition coefficients on various independent variables. The impact of each variable (solution composition, pH, temperature, etc.) will be examined through analysis of triplicate samples for a particular set of parameter values, each of which will be systematically varied while holding the values of the remaining parameters constant. Thus, it is likely that this activity will involve the generation of at least dozens, and possibly as many as several hundred samples. The sample sizes are expected to be on the order of 5 to 10 mL per sample, which makes labeling, storage, handling and testing a routine and simple matter.

4.3 Task 3. Determination of the Partition Coefficient of Br_2 between Phases

Br_2 , which exhibits considerable solubility in water, may be less soluble in brines due to the salting-out effect. The partition coefficient between the aqueous and gaseous phase will be determined by preparing aqueous samples of Br_2 in sealed containers, allowing the sample to come to equilibrium, then withdrawing aliquots of each phase for analysis. The aqueous samples will be analyzed by UV-vis spectroscopy for Br_2 concentration, as well as for the presence and concentrations of other hydrolysis products and oxidized Br species. Samples of the gas phase will be analyzed either by passing the gaseous aliquot through a solution of sodium hydroxide (NaOH), in order to form OBr^- , followed by UV-vis determination of the OBr^- concentration or by GC/MS analysis of the gas sample.

Analogous to Task 2 described in Section 4.2, this task requires generation of numerous batches of small samples.

4.4 Task 4. Determination of the Effect of Fe on Oxidized Br Species

Redox active transition metals, such as Fe and Cu are also likely to react with OBr^- . The change in concentration of the reacting Br species will be determined by following the change in the UV-vis absorbance spectra of the reactants and products. The experiments will be performed in brine solutions with different amounts of Br_2 , HOBr/OBr^- or BrO_3^- . The experiments will be repeated at a variety of pH values from 5 to 10 to ascertain the hydrogen-ion-concentration effects.

Aliquots of oxidized Br species (Br_2 , HOBr , OBr^- and BrO_3^-) will be added to brine solutions (5m NaCl, ERDA-6, GWB) along with metallic iron or ferrous chloride salts. A multi-variable test matrix in no less than four-dimensional space will be established to specifically include as independent variables the following parameters:

- identity and concentration of oxidized Br species;
- solution composition (i.e., brine type, including salt composition and concentration);
- additional solution components, such as Fe; and
- pH.

Additional independent variables may be added if it is determined during the course of the experimental work that parameterization of additional independent variables is a necessary factor to adequately characterize the system behavior.

It has been previously determined that the decomposition rates of OCl^- may be measured over the course of 3 to 4 weeks. It is likely that decomposition reactions of OBr^- would proceed at a more rapid pace than OCl^- due to the greater reactivity of OBr^- relative to OCl^- . Oxidation/reduction reactions between Fe and oxidized Br species are likely to proceed at a rapid rate, reaching completion within seconds to minutes. Consequently, an experimental matrix may be devised to elucidate the effect of variation of parameter values, such as solution composition and pH, and execution of such a matrix would entail generation of at least several dozen samples.

4.5 Measuring and Test Equipment

Measuring and test equipment, include the following instruments and types of apparatus:

- Perkin Elmer Optima 3300DV inductively coupled plasma optical emission spectrometer,
- Mettler DL 25 automatic titrator with Mettler Toledo DG111-SC pH electrode,
- Cary 300 Conc UV-vis spectrophotometer,

- Mettler Toledo Delta Range AT261 analytical balance,
- Sartorius Basic balance,
- RC6 Lauda temperature controller,
- Ertco-Eutechnics digital thermometer model 4400,
- Varian 3900 gas chromatograph and Varian 2100T mass spectrometer, and
- JEOL JSM 5900LV scanning electron microscope.

All measuring and test equipment will be used in accordance with NP 12-1 (Subsection 5.2).

The ICP-OES is an inductively coupled plasma atomic-emission spectrometer. Liquid samples are introduced into the instrument through an auto sampler. The samples are aspirated into a plasma ionization chamber, which destroys the sample matrix, atomizes, and ionizes the component atoms. Photons of discrete energies are emitted upon transition from the quantized excited to ground electronic states for each component element, which allows quantification by wavelength-dispersive analysis of the intensities of the light given off during the de-excitation process. External-standard calibration is done by measuring instrument response as a function of analyte concentration for a series of samples containing standardized amounts of the analyte of interest. Under ordinary circumstances the instrument has a dynamic range of several orders of magnitude, and features linear response to sample concentration. Second (parabolic) or higher order response in analytical instruments often indicates detector saturation, matrix interference, or other concentration-dependent instrumental responses. Evaluation and documentation of calibration, and calibration data will be recorded in the scientific notebook. Use of internal standards, surrogate standards, blank spikes, matrix spikes, or other methods of batch control will be documented in the scientific notebook.

The Mettler DL 25 automatic titrator is equipped with a combination glass electrode for potentiometric measurement of hydrogen-ion activity. The titrator can be programmed to measure the pH and to make controlled additions of a titrant from an automatic buret to a sample vessel. The temperature of the titration vessel is controlled by immersion in a thermostatted water bath. N₂ gas is introduced to the interior of the vessel to maintain an inert atmosphere. Data output from the instrument is fed directly to a laser printer, which provides tables of raw data. The data may be transferred to Microsoft Excel (or a comparable spreadsheet program) for further analysis.

Analytical balances will be calibrated before use on a daily basis, at a minimum. Certified, traceable calibration-standard weights will be used as calibration standards, continuing calibration-check standards, or both.

Solution volumes will be measured either with Class A glass pipettes, or autopipettes

equipped with disposable tips. Calibration of all pipettes will be confirmed before use by measuring the volume of water dispensed, which will be determined by mass, as indicated by a calibrated analytical balance.

Instrument response of the pH-measurement system will be checked by calibration against traceable, standard buffer solutions, or by titration of standardized acid and base solutions. Identity of the calibration solutions will be recorded in the scientific notebook. Constant-temperature and constant-atmosphere conditions will be maintained during titrations, if necessary, by immersion of the titration vessel in a thermostatted water bath, the temperature of which will be monitored with a thermometer that will be calibrated against a certified, traceable standard thermometer. If necessary, inert atmosphere will be maintained by purging the titration vessel with N_2 . Temperature and atmosphere control and conditions will be recorded in the scientific notebook.

The UV-vis spectrophotometer is a Cary 300, equipped with D_2 and tungsten-filament lamps. The instrument performs an internal wavelength calibration upon start up, using emission lines generated by the D_2 lamp. The 100%-transmittance calibration is performed by placing a cuvette containing the solvent without the chromophore, and scanning the instrument through the analytical wavelengths. The 0%-transmittance calibration is performed by blocking the sample path with an opaque object, such as black painted sheet metal, and scanning the instrument through the same wavelength region as used in the 100%-transmittance measurement. The instrument responses are assigned to the respective 0- and 100%-transmittance measurements at each wavelength.

4.6 Reagents

Deionized water will be used to prepare all aqueous solutions. All solutions will be filtered to remove insoluble matter.

$NaOCl$ will be obtained from documented commercial sources such as Fisher Chemical Co. The concentration of OCl^- may be determined spectrophotometrically or by potentiometric titration (Vogel, 1989; Adam and Gordon, 1999).

Br_2 will be obtained from documented commercial sources such as Fisher Chemical Co. or prepared by oxidation of Br^- by OCl^- . Oxidation of Br^- may be done as follows: A cold, saturated solution of $NaBr$ in water, acidified to $pH = 1$, will be transferred to a separatory funnel, which is cooled in an ice bath. A second separatory funnel will be used to slowly add a cold solution of $NaOCl$ to the $NaBr$ solution. The OCl^- oxidizes Br^- to Br_2 under acidic conditions. In a cold solution, the Br_2 condenses in the bottom of the funnel, from which it may be removed as the liquid Br_2 . The liquid Br_2 may be conveniently stored in a sealed glass bottle. Supplies of Br_2 will be generated as needed. Aqueous solutions of Br_2 will be prepared by transferring aliquots of gaseous Br_2 from the stock storage container to a syringe and bubbling the Br_2 gas through water or brine. The concentration of Br_2 and other Br species will be determined by UV-vis spectrophotometry.

All other reagents, such as salts used to prepare brine solutions, will be obtained from commercial sources. The quality of the reagents will be appropriate for the intended use. The name of the commercial vendor and lot number for the material will be recorded in the scientific notebook.

4.7 Experimental Procedures

4.7.1 General Procedures

Sample preparation and analysis procedures, (weighing, pipetting, etc.) are standard laboratory analytical procedures. Instrumental analyses, such as UV-vis spectroscopy, will be performed in accordance with written procedures supplied by the instrument manufacturer. Any deviations will be described and justified in the scientific notebook.

Calibration of pH measurement instrumentation will be performed under inert (N_2) atmosphere with temperature control. Design of experimental apparatus and method of control of parameters (temperature, atmosphere, etc.) will be fully described in the laboratory notebooks. Temperatures of samples will be monitored and recorded.

4.7.2 Preparation of Brines

Brine solutions will be prepared according the method given in the SNL NWMP Technical Operating Procedure (TOP)-544 (Subsection 5.2).

4.7.3 Determination of Reaction Products and Stoichiometry

Solutions containing known amounts of NaOCl and will be combined with standardized Br^- solutions. Product identities and yields will be monitored by measuring the change in the UV-vis absorbance spectra.

4.7.4 Development of Baseline Spectra of Each Species in Brines

Known quantities of $NaBrO_3$ will be dissolved in water, ERDA-6, GWB, and Brine A. The UV spectra will be obtained, and used to determine molar absorptivity coefficients for use in quantitative analysis of samples that contain unknown amounts of BrO_3^- .

4.7.5 Determination of Reaction Rate of Br^- with OCl^-

The rate of change in the amounts of products resulting from the oxidation of Br^- by OCl^- will be monitored by measuring the rate of change of the concentrations of the products over time, using UV-vis spectroscopy. The kinetics of the oxidation reactions in brine are not known,

so it is not possible to state whether this analytical method is suitable to follow the progress of the reaction. If the reaction is too fast to follow by this method, no further work will be done to determine the rate constants.

4.7.6 Acid Dissociation Constant of Hypobromous Acid

The acid dissociation constant of hypobromous acid will be determined by spectrophotometric titration and/or potentiometric titration.

In a spectrophotometric titration, a series of samples containing the same total Br concentration will be adjusted to different pcH values, and the UV-vis spectra obtained. The values of the molar absorptivities can be used to calculate the concentrations of HOBr and OBr⁻ at each step in the titration. The concentration values may be entered into the Henderson-Hasselbalch equation, and used along with the pcH values to determine the acid dissociation constant.

4.8 Coordination with Organizations Providing Inputs or Using the Results

There are no other organizations providing inputs in terms of data, experimental design, sample analysis, data compilation or interpretation of results. No coordination activities for inputs are planned at the time of the writing of this test plan.

The outcome of the experimental work described herein is unknown at the time of the writing of this test plan, although it may be anticipated that the data will be used to further evaluate the long-term effects of radiolytic generation of oxidants. The results of the experimental work will be provided to the DOE CBFO for further evaluation.

4.9 Procedures to Be Used/Developed

The procedures that will be used are part of commonly practiced standard laboratory techniques such as titrations and spectrophotometry. The procedures that will be employed are generally described in the section describing reagents and procedures, although specific procedures as applied to a particular experiment will be completely documented in the scientific notebook.

No prerequisites or special controls are specified at the time of the writing of this test plan. No unusual procedures to control specific environmental conditions, such as storage under controlled atmospheres, are necessary. Controls over other relevant conditions will be recorded in the laboratory notebooks. No unusual processes are anticipated to be employed. The skills developed during the course of work in an analytical or inorganic chemistry laboratory are anticipated to be sufficient to successfully perform the work.

4.10 Known Sources of Error and Uncertainty

Sources of error include:

- pH measurement,
- volume measurement,
- weighing error,
- impure reagents, and
- temperature.

Errors of pH measurement will be minimized by calibration of measuring equipment with standard buffer solutions and by titration with standardized acid and base solutions. Standard procedures for instrumental pH measurement are widely practiced and published in peer-reviewed literature. Procedures will be described in the laboratory notebook and relevant procedural references provided. Typical magnitudes of uncertainties in pH measurements are 0.01 to 0.02 log units. Uncertainties in pH are generally introduced by the inherent uncertainty in the pH of calibration standards, instrumental drift, and variations in electrode response due to variations in solution composition. These sources of error can be very difficult to control, therefore assessments must be made on an ongoing basis with respect to balancing the efforts required to minimize sources of uncertainty with the cost in terms of time required to implement extraordinary measures to minimize uncertainties. Uncertainties of 0.01 to 0.02 log units on the pH scale are considered acceptable, and will have minimal impact upon the quality of the results.

Errors in volume and mass measurements have the potential to exert considerable impact upon the quality of the results. Uncertainties in volume measurements will be controlled by use of Class A volumetric glassware that will be calibrated by measuring a standard volume of water with a calibrated laboratory balance. Volumetric glassware must exhibit less than 0.5% error in order to be considered acceptable for use. Mass measurements will be made with standard laboratory analytical balances that have been calibrated and checked against traceable standard weights. Calibration of all volumetric and weighing equipment will be documented in the appropriate scientific notebooks.

All reagents will be certified ACS reagent grade or better. If necessary, reagents will be purified by standard, documented procedures. The reagent grade, source, and if applicable, purification methods will be documented in the laboratory notebooks.

Temperature as a variable may have a significant impact upon the results of kinetics experiments, and a smaller but measurable effect on pH measurements. Kinetics trials will be conducted at a variety of temperatures to assess the importance of this variable. If necessary, the samples will be stored under controlled-temperature conditions, such as within a thermostatted oven or water bath. Assessment of temperature as a variable, and temperature monitoring and

control procedures will be fully documented within the laboratory notebooks. A thermometer that will have been subjected to a calibration check against a traceable standard thermometer will be employed to monitor the titration apparatus during the course of pH measurements. The temperature of the titration apparatus will be controlled with a thermostatted circulator that is capable of temperature control to within 0.1 °C.

4.11 Data Processing and Mathematical Models

Data processing may be done by hand calculation with the aid of an electronic calculator, or with a standard spreadsheet program, such as Microsoft Excel. Data processing more complicated than simple algebraic manipulations are not anticipated at the time of the writing of this test plan. Requirements for documentation of routine calculations are described in the NP 9-1 (Subsection 5.2). Routine calculations will be verified and documented in the laboratory notebooks, in accordance with the procedural requirements described in NP 9-1.

4.12 Documents to be Maintained as QA Records

Scientific notebooks and hardcopies of instrumental output will be maintained as QA records. Instrument output in electronic format will be preserved on a computer disk or other suitable media, and will be submitted to the SNL Records Center along with other QA records.

4.13 Sample Handling and Control Requirements

Standard procedures for sample identification, handling, storage, shipping, archiving and disposition have been described in NP 13-1. Sample handling will be performed in accordance NP 13-1.

Samples will be labeled with unique identification numbers, the date, and will be referenced in the laboratory notebook. Solutions, such as standardized stock metal solutions, will be handled and stored in accordance with documented procedures.

Samples will be stored within the working area of the chemistry and geochemistry research area at SNL's Carlsbad laboratory. No special precautions are planned to secure the samples.

4.14 Sample Disposal

Aqueous solutions of HOCl and OCl⁻ in brines are non-hazardous, and may be disposed of directly into the sewer, without any special precautions. Organic solutions will be disposed of in accordance with standard operating procedures in place at SNL's Carlsbad laboratory. Hazardous waste generation is not anticipated at the time of this writing.

4.15 Data Acquisition System

Calibrations and calibration checks will be performed on instruments in the manner described in Subsection 4.5. Analytical instruments and laboratory equipment will be considered to be exhibiting acceptable performance when the following criteria are met:

- Calibrations for the ICP-OES instrument will be considered successful if the initial calibration data exhibit linearity within tolerances established by the instrument manufacturer.
- Initial or continuing calibration of analytical balances will be considered as indicating fitness for use when the instrument indicates that all standard calibration check weights conform within 0.1% of the nominal value.
- Volumetric equipment must exhibit less than 1% relative standard deviation error in order to be considered acceptable for use.
- Calibration of pH-measuring apparatus will be considered acceptable if the data exhibit linearity, and the instrument response is greater than 90% efficient (i.e., >53.1 mV/pH unit).
- Wavelength and percent-transmittance calibration of the Cary-300 UV-vis spectrophotometer will be performed upon instrument start up, at least one time per day that the instrument is used.

4.16 Commercial Software, Not Modified

The commercial, off-the-shelf software that will be used in the work described in this test plan includes the software that is used to operate the analytical instruments, and Microsoft Excel for performing routine calculations. The software will be used in accordance with NP 19-1 (Subsection 5.2). The commercial, off-the-shelf software will be used as originally written by the software supplier, without changes to the original source code.

Routine spreadsheet calculations will be performed with Microsoft® Excel 2000 run on a Dell Precision 620 desktop PC, or equivalent. Use of any other spreadsheet programs will be described and documented in the scientific notebook.

4.17 Other Software

No software other than commercial, off-the-shelf software, not modified, will be used in this work.

4.18 Justification, and Documentation of Deviations from Test Standards

Significant departures from procedures documented in the open scientific literature will require revision of this test plan.

4.19 Experimental Controls

Each experimental determination of decomposition rate constants, acid dissociation constants, and any other experiment yielding thermodynamic or kinetic values, will be repeated in order to reduce likelihood of inadvertent introduction of indeterminate errors. In order to evaluate reproducibility and develop statistical estimates of uncertainty, each experiment will be replicated with a minimum of duplicate samples and duplicate analyses as is normally expected within the scientific community as a part of sound experimental practice. If it is deemed necessary to use blank spikes, matrix spikes, internal or surrogate standards, the relevant procedures will be documented in the scientific laboratory notebook.

4.20 Control and Characterization of Test Media

Test media and samples will be characterized by the analytical methods described elsewhere in this test plan.

4.21 Data Identification and Use

Data amenable to written recording will be inscribed by hand in appropriate laboratory notebooks. Such information includes, but is not limited to:

- reagent and solution preparation and purification procedures and results;
- sample preparation procedures;
- sample composition and conditions (e.g., pH, reagent volume, reagent concentration, temperature);
- sample handling; and
- sample-analysis procedures and results.

Instrumental data output, such as tabulated values and parameters, will be stored in a data binder, and appropriate reference to the data location will be made in the laboratory notebook.

4.22 Data Transfer and Reduction Controls

Typical data transfer is from instrumental output to laboratory notebook and from laboratory notebook to a spreadsheet program. Printed copies of spreadsheets with full explanations of spreadsheet calculations will be permanently attached to the laboratory notebook or in a data binder specifically designated for the purpose. Data stored separately from the laboratory notebook, e.g., in a designated three-ring binder, will be appropriately referenced in the laboratory notebook.

4.23 Identification, Segregation, Disposal of Erroneous Data

Data suspected of being erroneous will be tested by comparison to replicate samples or replicate experiments. Statistical justification for rejection of erroneous data will be provided within the laboratory notebook.

5 TRAINING AND OTHER STANDARD PROCEDURES

5.1 Training

All personnel participating in the work described in this test plan will be trained and qualified for the assigned tasks. This requirement will be implemented in accordance with NP 2-1 (Subsection 5.2).

5.2 NPs, SOPs, and SPs

The following NPs, SNL Standard Operating Procedures (SOP), and SNL NWMP Activity/Project-Specific Procedures (SPs), and TOPs are applicable. Note that the versions listed below may not be the current versions. Always check the SNL NWMP web site (www.nwmp.sandia.gov/onlinedocuments/) to find the current version of these or other NPs, SOPs, or SPs.)

- NP 2-1, “Qualification and Training;”
- NP 4-1, “Procurement;”
- NP 6-1, “Document Review Process;”
- NP 6-2, “Document Control Process;”
- NP 9-1, “Analyses;”

- NP 12-1, “Control of Measuring and Test Equipment;”
- NP 13-1, “Sample Control;”
- NP 17-1, “Records;”
- NP 19-1, “Software Requirements;”
- NP 20-1, “Test Plans;”
- SOP-C001, “Standard Operating Procedure for Activities in the SNL/Carlsbad Laboratory Facility;”
- SP 1-1, “QA Grading;” and
- SP 13-1, “Chain of Custody;”
- TOP 544, “Preparing Synthetic Brines for Chemical Retardation and Transport Experiments.”

5.3 Procurement Procedures

Procurement of materials or services will be done in accordance with NP 4-1 (Subsection 5.2). Procurement of capital equipment is not expected.

6 HEALTH AND SAFETY

Elemental bromine exhibits considerable volatility and due to its activity as an oxidant, exhibits corrosivity and reactivity that make it hazardous if inhaled. Accordingly, work that has the potential to release significant amounts of gaseous bromine will be performed in a fume hood with adequate ventilation in order to preclude inhalation of hazardous vapors. The principal investigator of this project has considerable experience working with hazardous materials, including experience in experimental work in glove boxes and fume hoods. All experimental work will be performed in a manner that minimizes risk and does not adversely affect worker health or safety. Working within a fume hood is not at all unusual in a laboratory environment and is generally considered to be a part of routine good laboratory practice when handling materials that may generate hazardous vapors. There are no unusual health and safety requirements for the work described in this test plan. The health and safety requirements relevant to the tasks for work in this test plan are described in SOP-C001 (Subsection 5.2).

7 PERMITTING AND LICENSING

There are no special licenses or permitting requirements for the work described in this test plan.

8 REFERENCES

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