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SANDIA NATIONAL LABORATORIES
WASTE ISOLATION PILOT PLANT
TEST PLAN, TP 02-01

Chemical Behavior of Hypochlorite in High Ionic Strength Solutions

Revision 1

(The title of this test plan has been changed. The original title is:
Complexation Behavior of Hypochlorite with Metal Ions)

Task 1.3.5.4.1.2

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1.0 LIST OF ACRONYMS

\mathcal{A}_n	thermodynamic activity
ACS	American Chemical Society
An	actinide
An(III)	actinide in the +III oxidation state
An(IV)	actinide in the +IV oxidation state
An(V)	actinide in the +V oxidation state
An(VI)	actinide in the +VI oxidation state
Ar	argon
B	boron
Br	bromine
C	Coulomb
Ca	calcium
CCA	Compliance Certification Application
Ce	cerium
Cl^\bullet	atomic chlorine free radical
$\text{Cl}_2^{\bullet-}$	molecular chlorine free radical
ClO_3^-	chlorate
Co	cobalt
DBR	Direct Brine Release
DOE CBFO	Department of Energy Carlsbad Field Office
E^0	Standard reduction potential
EDTA	ethylenediaminetetraacetic acid
ERDA-6	Descriptive label applied to a Castile brine composition
F	The faraday constant, (96,485 coulombs/mole)
Fe	iron
GWB	Generic weep brine
H^+	hydrogen ion
H^\bullet	Atomic hydrogen free radical
HCl	hydrochloric acid
HOCl	hypochlorous acid
$\text{HOCl}^\bullet-$	hypochlorous acid, anionic free radical
ICP-OES	Inductively coupled plasma optical emission spectroscopy
J	Joule
K	potassium
Ln	lanthanide
Mn	manganese
NaOH	sodium hydroxide
Nd	neodymium
Ni	nickel
NIST	National Institute of Standards and Technology
OH^\bullet	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
SO ₄ ²⁻	sulfate
T	temperature, in degrees Celsius or kelvins
UV-VIS	ultraviolet-visible (spectroscopy)
WIPP	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-particle	a positron or negatron expelled from a nucleus during a β-decay process
β _{pqr}	stability constant for a metal/ligand complex
γ	activity coefficient (not related to γ-ray)
γ-rays	high-energy photons emanating from a nucleus due to a nuclear decay process
μ	ionic strength

2.0

REVISION HISTORY

This is a revised version, Revision 1, of this test plan. Subsequent revisions will be done in accordance with the Sandia National Laboratories Nuclear Waste Management Program Procedures: NP 20-1 Test Plans, NP 6-1 Document Review Process and NP 6-2 Document Control Process.

3.0

PURPOSE & SCOPE

3.1

Introduction

The position put forth in the Compliance Certification Application (CCA) is that the presence of large amounts of iron, in the form of both waste and waste containers, emplaced within the Waste Isolation Pilot Plant (WIPP) will provide sufficient electrochemically reducing conditions to maintain plutonium as Pu(III) and Pu(IV) (DOE, 1996). The Source Term Test Program (STTP) was initiated at Los Alamos National Laboratory in order to make an examination of the behavior of actinides, particularly Pu, in brines that were in contact with actual waste forms (Villarreal, 1996). During the course of the experimental program, there was evidence of the appearance of Pu(VI) in some of the test containers. It was proposed that the generation and persistence of radiolysis products in brine solutions exposed to α-radiation was responsible for affecting the solution redox conditions, and that Pu(VI) appeared in response to alteration of a reducing state imposed by the presence of metallic iron (Villarreal et al. 2000). The appearance of Pu(VI) has been commented upon by Oversby (2000) and Brush et al. (2001). Generation of hypochlorite (OCl⁻) and hydrogen

peroxide (H_2O_2) as a result of α -particle induced radiolysis of brine was suggested as the probable mechanism for oxidation of Pu, but was not experimentally observed or measured (Villarreal et al. 2000). While it is true that OCl^- is a sufficiently strong oxidant to oxidize Pu to Pu(VI) under basic conditions, H_2O_2 can act as an electron donor, and reduces Pu(VI), also under basic conditions. However, both OCl^- and H_2O_2 are highly reactive and unstable in aqueous solutions. For example, the iron-catalyzed decomposition of H_2O_2 is well known and particularly rapid (Greenwood and Earnshaw, 1989a). In fact, both OCl^- and H_2O_2 may be catalytically decomposed by metal ions that have more than one accessible oxidation state in aqueous solution, such as Fe and Pu. Additionally, OCl^- and H_2O_2 react with each other, so cannot coexist to a great extent within the same solution. Hence, solutions containing OCl^- and H_2O_2 , redox active metals, and radioactive materials may result in a plethora of experimental variables to be monitored and controlled. Due to the multiple interactions that simultaneously take place, any attempt to study the redox behavior of Pu with radiolysis products requires *exceedingly* careful experimental design and control, lest erroneous conclusions be made as a result of either failure to control or monitor critical variables.

There are different, but widely applied approaches to the examination of complex systems, that may be broadly described as the “top-down” and the “bottom-up” approaches. The former is primarily concerned with observation of the total behavior of a system, without regard to the fundamental reasons for the behavior. The limitation inherent in this method is that predictive capability is not developed, no matter how similar the alternative systems are to the studied system. Such a method acknowledges a lack of control of critical experimental variables, and even fails to recognize their identity. The “bottom-up” approach is profitably used when it is necessary to develop a fundamental understanding of a system in order to take into account the relative impacts that variations in experimental variables impart to the overall system behavior. In carrying out the “bottom-up” approach it is necessary to identify, isolate, control and quantify the experimental variables. Neglect of a single one of these four activities constitutes a critical failure of experimental design. Additionally, the “bottom-up” approach may be used to quantify the influence of a variable on system behavior, and evaluate its overall relative importance. The work described in this test plan is patterned after the “bottom-up” approach, in an attempt to determine whether generation of radiolysis products may have a significant impact on the total system performance of the WIPP. Production of OCl^- in NaCl-based brine solutions exposed to α -radiation does occur. The question to be addressed is whether the process can have a significant impact upon the oxidation-states and solubilities of actinides within the WIPP. Examination of the chemical behavior of OCl^- does not require use of any radioactive materials, but can be used to determine the stability and reactivity of OCl^- under WIPP representative conditions.

The Environmental Evaluation Group has expressed concern over the report of the appearance of Pu(VI) in some containers in the STTP project, and has expressed its opinion in a report, EEG-77 (Oversby 2000). In EEG-77 Oversby briefly quotes EEG-68, describing laboratory observations of Pu(V), (Oversby 2000, Neill et al. 1998):

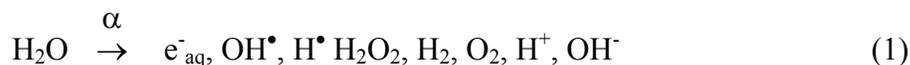
“...Pu(V) is observed as a long-lived transient in many laboratory experiments. Pu(V) may be formed as a result of radiolysis reactions in brine, and while its total abundance in the repository is likely to be low, it might be significant as a transient species in some waste containers.”

In the above statement, Oversby describes the radiolysis effects as possible reasons for appearance of oxidized Pu. It is not possible to produce Pu(V) by direct oxidation of either Pu(III) or Pu(IV) in solution due to the overvoltage required to carry out the oxidation steps. The exact reasons for this behavior will be presented later in this test plan. Presently, it should be borne in mind that the chemical behavior of Pu is rather complex, requiring strict control over experimental variables.

3.2 Radiolysis in Brines

The effect of radioactive decay on aqueous solutions is markedly dependent upon the type and energy of radiation involved. For example, β -particles, with a charge of $\pm 1.602 \times 10^{-19}$ C and a mass of 9.11×10^{-31} kg, have much larger rates of energy transfer to target material than high energy photons, such as γ -rays, which have neither charge nor mass. The α -particles, with charges of $+3.204 \times 10^{-19}$ C and masses of 6.647×10^{-27} kg, exhibit much larger rates of linear energy transfer than β particles, leaving intense tracks of ionized target material, including many atomic and molecular species in highly excited states. 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. Combination processes become increasingly important in the diffusion limited environment surrounding particle tracks of high linear energy transfer species. H_2 and O_2 are two well-known gas generation products due to radiolysis of water and recombination of the hydrogen free radicals, H^\bullet , or the oxygen free radical, O^\bullet , although the mechanisms and products of brine radiolysis may be quite different. The superscript dot indicates a free radical species. Recombination processes may also yield H_2O_2 as a product of the reaction of two hydroxyl radicals. Also significant, but dependent upon the solution composition, are generation of molecular chlorine (Cl_2), hypochlorous acid (HOCl) and OCl^- .

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



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 $\text{HOCl}^{\bullet-}$



The hypochlorous acid anion is also a radical species that equilibrates rapidly with H^+ to give the chlorine radical



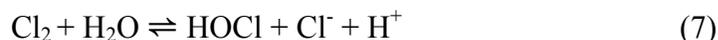
The likelihood of the chlorine radical combining with chloride is greater in solutions with high chloride content:



$\text{Cl}_2^{\bullet-}$ reacts rapidly to produce Cl_3^- , which is more stable than $\text{Cl}_2^{\bullet-}$, (Kim et al. 1987)



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



It has been reported that the production of HOCl and OCl^- depends on the Cl^- concentration (Kim et al. 1987). The dependence of OCl^- concentration 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 $y = 0.0059x - 0.0105$.

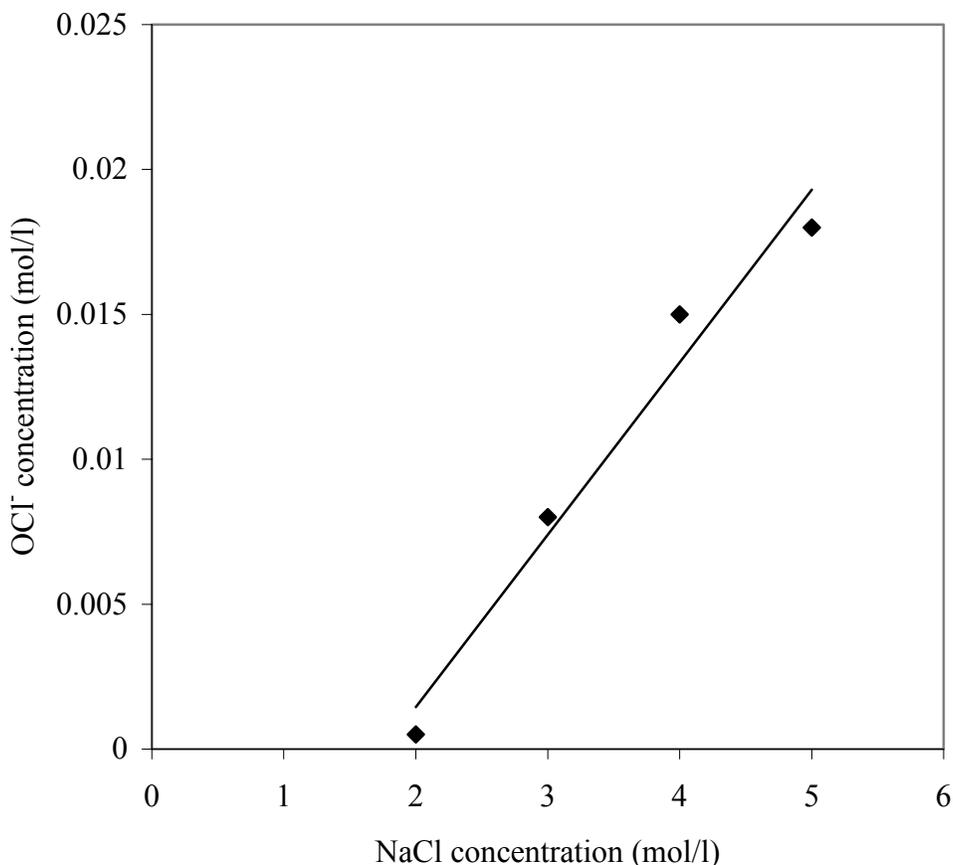


Figure 1. Generation of hypochlorite as a function of aqueous NaCl concentration.

Production of OCl^- is not a significant process for Cl^- concentrations less than ca. 1.8 molar at radioactivity levels of 1 Ci/L. The minimum concentration of Cl^- required for OCl^- hypochlorite 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 ($\mu=1.0$ NaClO_4 , $T=25^\circ\text{C}$), indicating that at pH relevant to WIPP conditions ($\text{pH}\approx 9-10$) the conjugate base (OCl^-) will be the predominant form (Martell et al. 1998). The symbol “ μ ” indicates ionic strength. Decomposition rate constants, determined by measurement of the kinetics of decomposition in high ionic strength solutions, may be used together with kinetic data of radiolytic production to calculate steady state concentrations of hypochlorite under conditions expected to exist within the WIPP. The steady state concentrations may be used to calculate the oxidation/reduction potentials and capacities in brines as a result of radiolytic production of OCl^- .

3.3 Thermodynamic Relationships

Various thermodynamic relationships are discussed in the text of this test plan, therefore, it is appropriate to commence with an introduction to the meanings and use of these relationships. The Gibbs free energy (ΔG) of a system describes whether the reaction under consideration is a thermodynamically favorable process. Reactions that have negative values of ΔG will spontaneously proceed as written, whereas, reactions that have positive values of ΔG will spontaneously proceed in the reverse direction. Oxidation/reduction reactions may be written as half-reactions which have specific values for the associated thermodynamic driving force, sometimes written in terms of electromotive force (e.m.f), usually expressed in volts. The relationship between the ΔG of a reaction and the e.m.f is shown by equation 9:

$$\Delta G = -nFE \quad (9)$$

n is the number of electrons exchanged in the reaction, F is the Faraday constant (96,485 coulombs/mole) and E is the e.m.f., in volts, for the reaction. Equation 9 shows that a reaction that features a positive value for the e.m.f. will have a negative value for ΔG , and will proceed spontaneously as written. Conversely, a reaction with a negative e.m.f. value will proceed in the reverse direction. Oxidation/reduction reactions with negative e.m.f. values may be coupled with other reactions that have positive e.m.f. values, and if the combination of the two reactions yields a positive e.m.f. value, the reaction will proceed. In other words, a strongly favorable half-reaction may supply the thermodynamic driving force necessary to drive another less favorable half-reaction.

The e.m.f. potentials for many reactions may be found in tables of standard reduction potentials, which are tabulated for standard state conditions of 25°C, a partial pressure of one atmosphere for gas phase reactants, such as O_2 , and thermodynamic activity equal to one for all other reactants. However, the reaction potential differs under non-standard state conditions; equation 10 is used in an example:



In equation 10, a moles of reactant A combine with b moles of reactant B to yield c moles of product C and d moles of product D. It should be noted that the reactants, products and coefficients in equation 10 indicate an equilibrium condition. The Nernst equation, which is used to calculate reaction potentials for non-standard state conditions, is illustrated using the reactants and products from equation 10. The concentrations of the reactants and products in equation 11 are not necessarily those at equilibrium, and in fact may be far from equilibrium. For simplicity of expression and mathematical treatment, concentrations rather than activities are used in the present discussion.

$$E = E^0 - \frac{RT}{nF} \ln \frac{[C]^c [D]^d}{[A]^a [B]^b} \quad (11)$$

E^0 is the standard state reaction potential, n is the number of electrons exchanged in the reaction, R is the ideal gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$), T is the temperature in kelvins, and F is the Faraday constant. Equation 11 may be simplified for $T = 298 \text{ K}$, and converting to base 10 logarithms:

$$E = E^0 - \frac{0.059}{n} \log \frac{[C]^c [D]^d}{[A]^a [B]^b} \quad (12)$$

It is apparent that the e.m.f. for a chemical system is greatly dependent on the concentrations of the reactants, which may be affected by other parameters, such as solubility or presence of organic ligands. Complexation by organic ligands has a twofold effect on the redox potential for metals; it changes the concentration of free metal in solution and changes the electron density around the metal ion in a manner that depends on the nature of orbital overlap and the electronic configuration of the metal and ligand. A description of the effects on redox potentials of these two types of effects will be provided in this test plan for Pu and Fe.

The reaction in equation 10 may also be rewritten in terms of the equilibrium constant, K . The ratio in equation 13 should not be confused with the ratio in equation 12. Equations 10 and 13 are for equilibrium conditions, whereas equations 11 and 12 may indicate non-equilibrium concentrations:

$$K = \frac{[C]^c [D]^d}{[A]^a [B]^b} \quad (13)$$

The equilibrium constant is related to the ΔG of the reaction through the following thermodynamic relationship:

$$\Delta G = -RT \ln K \quad (14)$$

A positive value for the equilibrium constant, indicating that the reaction favors the products, yields a negative value for ΔG , consistent with a thermodynamically favorable reaction. The interconnections among the thermodynamic relationships allow determination of parameters, such as the e.m.f. values for redox couples, by numerous and sometimes simpler experimental means. For example, experimental measurements of equilibrium constants are often simpler and more reliable than direct e.m.f. measurements. On the other hand, tables of e.m.f. values are very useful to predict states of thermodynamic equilibrium.

3.4 HOCl/OCl⁻ and H₂O Redox Behavior

HOCl and its conjugate base, OCl⁻, are strong oxidizing reagents, and react vigorously with many materials. The strong thermodynamic driving force for HOCl and OCl⁻ oxidation reactions are clearly indicated by the standard reduction potentials that are listed in Table 1:

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

Reaction	E ⁰ (volts)
$\text{HClO} + \text{H}^+ + \text{e}^- \rightarrow \frac{1}{2} \text{Cl}_2 + \text{H}_2\text{O}$	1.61
$\text{HClO} + \text{H}^+ + 2\text{e}^- \rightarrow \text{Cl}^- + \text{H}_2\text{O}$	1.48
$\text{OCl}^- + \text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{Cl}^- + 2\text{OH}^-$	0.81

Values of 1.61 and 1.48 volts exceed the thermodynamic limit for the stability of water. Both oxidation potentials are sufficiently high that solutions of HOCl in water are not stable, and result in the oxidation of water to O₂. It is useful to consult a Latimer diagram for the standard reduction potentials of water to gain an understanding of the fundamental thermodynamic limitations on the behavior of HOCl and OCl⁻ in an aqueous solution. Simplified versions of Latimer diagrams for water adapted from Greenwood and Earnshaw (1989a) are presented below:

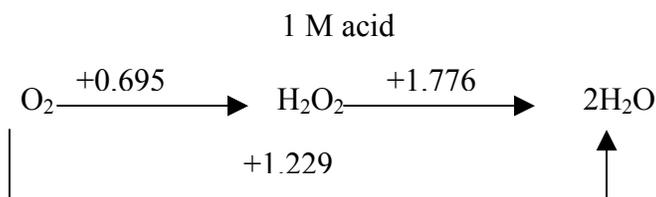


Figure 2. Latimer diagram for oxidation of water.

The data in Figure 2 may be used to prepare a Pourbaix diagram that illustrates the stability fields for water under various pH and redox conditions. The reactions for the standard reductions that are used to generate the Pourbaix diagram are provided in Table 2.

Table 2. Oxidation/reduction reactions of water

Reaction	E^0 (volts)
$O_2 + 4H^+ + 4e^- \rightleftharpoons 2H_2O$	+1.229
$O_2 + 2H^+ + 2e^- \rightleftharpoons H_2O_2$	+0.695
$H_2O_2 + 2H^+ + 2e^- \rightleftharpoons 2 H_2O$	+1.776
$H^+ + 1e^- \rightleftharpoons \frac{1}{2} H_2$	0.000

The stability fields, i.e. combinations of redox and pH conditions are presented in Figure 3.

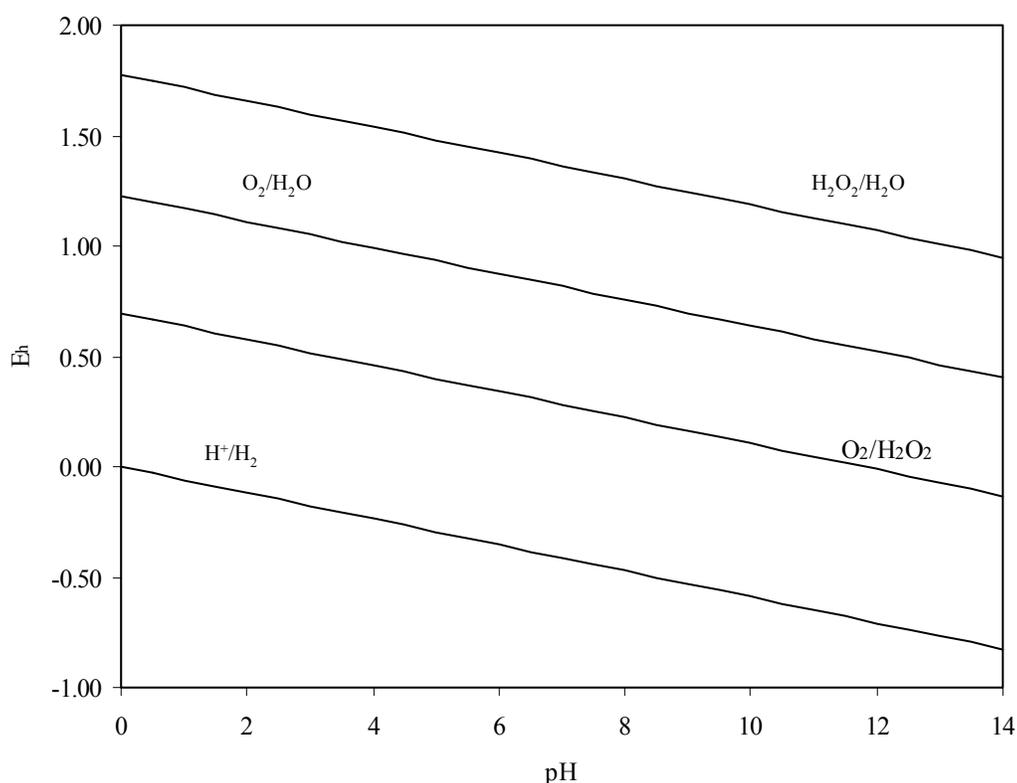


Figure 3. Poubaix diagram illustrating oxidation/reduction stability fields for water.

The line designated by the H_2O_2/H_2O couple indicates the potential at which water is oxidized to H_2O_2 (or H_2O_2 is reduced to water). Water is the more stable species at combinations of half-cell reduction potential (E_h) and pH below the line, although H_2O_2 may still form slowly to satisfy equilibrium conditions. When conditions are sufficiently oxidizing, as occurs above the line, H_2O_2 is the more stable species, and water is spontaneously oxidized to H_2O_2 . The line designated by O_2/H_2O_2 delineates the equilibrium condition at which H_2O_2 is further oxidized to O_2 (or O_2 is reduced to H_2O_2). At pH = 9 the

value for the oxidation of H₂O₂ to O₂ is -0.16 volts, which, although negative, may be coupled with a reaction in which Pu is reduced from Pu(VI) to Pu(V), where the stronger thermodynamic driving force for the reduction of Pu is the dominant force (vide infra). The line designated by the O₂/H₂O couple indicates the overall limit of thermodynamic stability for water, which results from the combination of the reactions for the oxidation of H₂O to H₂O₂ and further oxidation of H₂O₂ to O₂.

Some macromolecular electron transfer catalysts, such as enzymes, can catalyze the synchronous four-electron reduction of O₂. However, the reduction of O₂ in water occurs in successive steps in the absence of such catalysts. The initial two-electron oxidation of water to H₂O₂, with an oxidation potential of -1.776 volts, is very unfavorable thermodynamically, and provides the kinetic barrier to the rapid oxidation of water for solution compositions that have oxidation potentials that lie in the region between the lines established by the reactions for the four electron O₂/H₂O couple, and the two electron H₂O₂/H₂O couple. In other words, an aqueous solution of a strong oxidant may be metastable in water, even if oxidation of water is thermodynamically favorable, due to the high oxidation potential required by the initial oxidation of water to H₂O₂. As a result, it is possible to prepare solutions of OCl⁻ or H₂O₂ that are metastable with respect to oxidation of water.

Under acidic conditions, the reaction for the oxidation of HOCl to Cl₂ and H₂O may be combined with the reaction for the oxidation of water to oxygen, as shown in Table 3.

Table 3. Reaction of hypochlorous acid in water

4HClO + 4H ⁺ + 4e ⁻ → 2Cl ₂ + 4H ₂ O	1.61
2H ₂ O → O ₂ + 4e ⁻ + 4H ⁺	-1.229
4HClO + → 2Cl ₂ + O ₂ + 2H ₂ O	0.381

The positive value for the reaction of HOCl with water indicates that a solution of HOCl in acid is thermodynamically unstable, and that HOCl will spontaneously react with water to produce Cl₂ and O₂. However, the reaction may be kinetically slow due to the large positive overvoltage for the oxidation of water to O₂. Nevertheless, the volatility and relatively low aqueous solubility of both Cl₂ and O₂ may act as an additional driving force for the oxidation of water by HOCl. Like HOCl, OCl⁻ is thermodynamically unstable with respect to oxidation of water, but the reaction is also kinetically hindered due to the overvoltage required for oxidation of water to oxygen. Consequently, it is possible to prepare solutions containing OCl⁻ that are metastable, although such solutions do eventually decompose.

The redox lability of OCl⁻ is well known, and has been discussed by other authors (Greenwood and Earnshaw 1989b, Cotton et al., 1999). Both HOCl and OCl⁻, as strong oxidants, react very readily with numerous materials, such as metallic iron. There have also

been reports of the observation of decomposition of OCl^- in aqueous solutions (Lister 1952, Adam et al. 1992, Church 1994, Wang and Margerum 1994, Adam and Gordon 1999). Decomposition pathways include a reaction of HOCl with OCl^- in addition to reaction with water. Additionally, HOCl and OCl^- may undergo catalyzed decomposition reactions in the presence of redox active metals, such as Fe or Pu. The generation rates of HOCl and OCl^- in NaCl brine exposed to α -radiation have been studied, and generation rate constants may be determined based upon data already existing in the chemical literature. Hence, some statements may be made about the expected persistence of HOCl and OCl^- in aqueous solutions:

- HOCl is thermodynamically unstable in acid and neutral solutions, and OCl^- is unstable in basic solutions
- HOCl and OCl^- in solution spontaneously decompose either by reaction with each other or with water
- HOCl and OCl^- decomposition reactions act as a pathway to limit their uppermost concentrations that may be reached under conditions of continuous generation
- Bounding conditions for upper limits of OCl^- concentrations due to radiolytic generation may be determined from knowledge of production and decomposition rates

3.5

Redox Behavior of Pu

Ultimately, it is the objective of the experimental work described in this test plan to determine whether HOCl or OCl^- generation in irradiated brines can produce conditions sufficiently oxidizing to affect the oxidation state distribution of Pu. It has been previously documented in the chemical literature that OCl^- oxidizes Pu to Pu(VI) (Choppin and Morgenstern, 2000); the question at hand is whether the process can become an important one in the WIPP environment. It is necessary to understand the redox behavior of Pu in order to determine the potential impact that the presence of OCl^- can have on Pu, both as an oxidant, and potentially as a complexing agent. The effect of acidity and complexation may be seen in Latimer diagrams for the reduction potentials of Pu under acidic, neutral, and basic conditions are presented as Figure 4, which is adapted from Weigel et al., (1986). An introductory discussion of Pu redox chemistry is based in part on these Latimer diagrams.

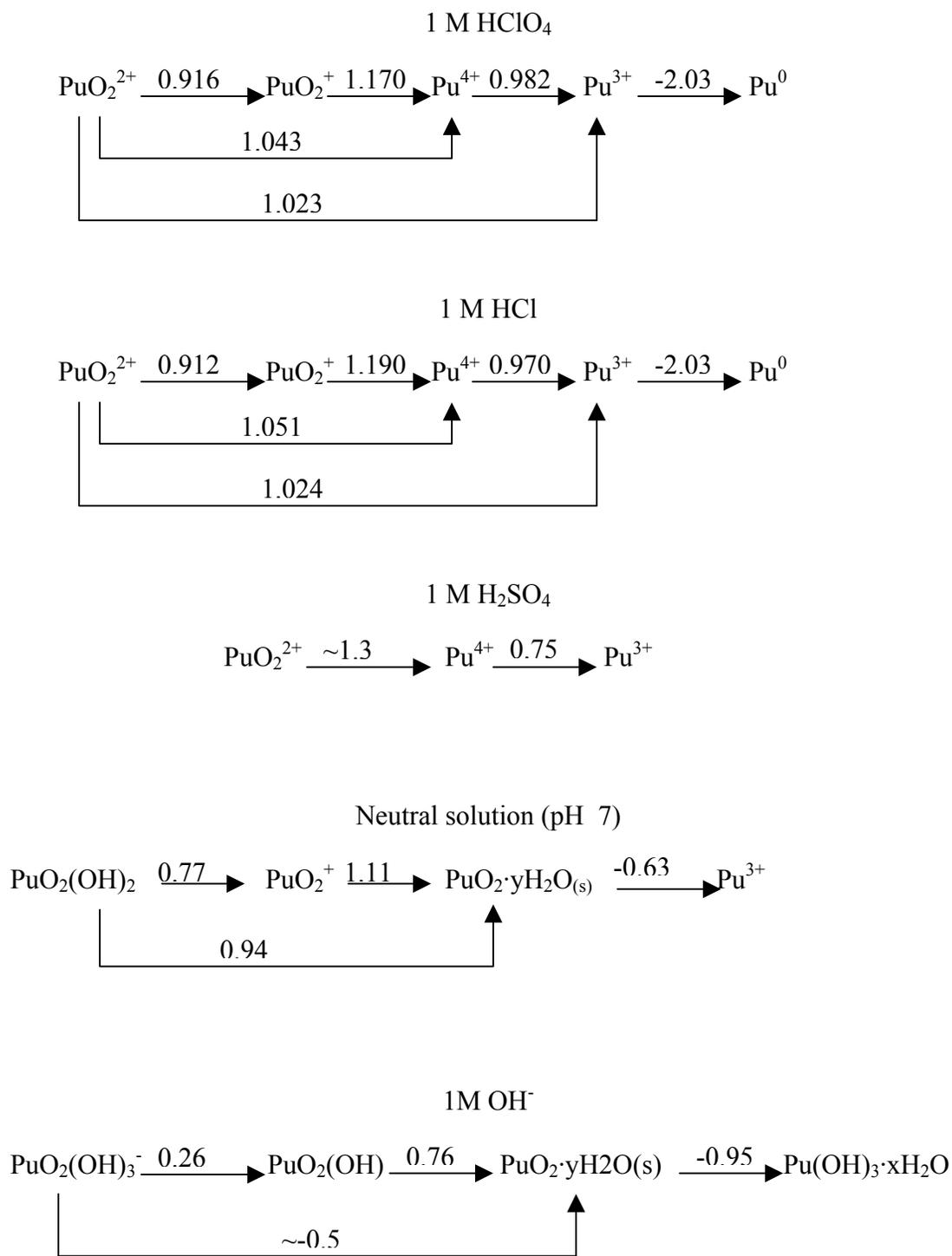
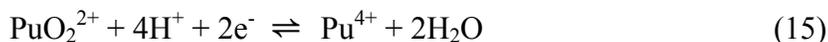
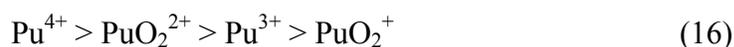


Figure 4. Latimer diagrams for oxidation/reduction behavior of plutonium.

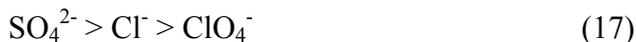
The Latimer diagrams illustrated in Figure 4 are based on total concentrations of Pu at each respective oxidation state, not concentrations of the free metal ion. Since a positive e.m.f. indicates a thermodynamically favored reaction, the voltage values indicated on the Latimer diagrams for Pu shows that Pu³⁺ is strongly favored in acidic solutions. Comparison of the voltage values in HClO₄, HCl, and H₂SO₄ provide an illustration of the way that complexing and non-complexing media can affect the redox potentials. For example, the reaction:



has potentials that are 1.043, 1.051, and ~1.3 volts, in HClO₄, HCl, and H₂SO₄, respectively. The differences among the potentials may be explained by the fact that for a given ligand the order of strength of complexation for the four oxidation states of Pu usually is given by

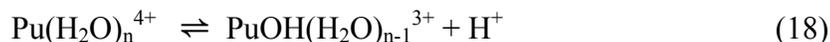


The conjugate bases ClO₄⁻, Cl⁻, and SO₄²⁻ form complexes with a given oxidation state of Pu that have relative stabilities occurring in the same order as the charge densities on the ligands, i.e.



For this series of Lewis bases, complexation with Pu⁴⁺ is stronger than with PuO₂²⁺. As a result, for the reduction of Pu(VI) to Pu(IV), the reaction that takes place in the more complexing medium tends to stabilize Pu(IV) relative to Pu(VI), and with increasing degrees of complexing ability further favoring the oxidation state that forms the strongest complexes, i.e. Pu(IV). Consideration of the relative abilities of SO₄²⁻, Cl⁻ and ClO₄⁻ leads to the prediction that the reduction potential should be the most positive in H₂SO₄, and the least positive in HClO₄, which is confirmed by experimental measurements.

Pu(IV) has a very strong affinity for oxygen, so much so that it is capable of displacing protons from water, even under acidic conditions. In effect, the waters of hydration that are within the inner coordination sphere of Pu(IV) become very acidic. The tendency of coordinated water to lose a proton, referred to as hydrolysis, may be illustrated in the following reaction (with n ≈ 9):



The first hydrolysis of coordinated water becomes an important mechanism at about pH = 1, and is followed by subsequent hydrolysis reactions until, in the neutral pH region, PuO₂ has formed due to the loss of four protons from two water molecules. PuO₂, which is very insoluble, may have additional waters of coordination associated with it, and is sometimes written as PuO₂·yH₂O_(s). It is the insolubility of Pu(IV) oxides, or hydrous

oxides that shifts the reaction equilibria for Pu in neutral and basic solution to favor the Pu(IV) oxidation state. Examination of the Latimer diagram for Pu in neutral solution reveals that the reduction potential for the reduction of Pu(VI) to Pu(IV) is 0.94 volts, which implies that in order to oxidize Pu(IV) to Pu(VI) in near neutral solutions it would be necessary to employ a strong oxidant that has a rather large oxidation potential. However, the situation is further complicated by the fact that the presence of any complexing ligand will have an impact upon the redox couples of Pu. For example, in strongly basic media (pH 14) Pu(VI) has about the same stability as Pu(IV), due to formation of anionic Pu(VI) complexes with hydroxide. It is generally true that for Pu, higher pH favors the higher oxidation states.

There are other aspects of Pu solution chemistry that may be discerned by examination of the Latimer diagrams for Pu. For example, it is apparent that it is not possible to prepare a solution of PuO_2^+ by direct oxidation of an acidic or neutral solution of Pu(III) or Pu(IV). This is due to the fact that the voltage required to oxidize Pu(IV) to Pu(V) is greater than the voltage required to oxidize Pu(IV) to Pu(VI). As a result, application of an oxidizing condition, either chemical or electrical, invariably results in quantitative oxidation of Pu to Pu(VI). In order to obtain Pu(V) in solution, it is necessary to oxidize all Pu to Pu(VI), then gently reduce the Pu(VI) to Pu(V). For that reason, oxidizing solution conditions will usually result in the presence of Pu(VI), but not Pu(V). Additionally, it should be noted that it is not possible to obtain large concentrations of Pu(V) in acidic solutions due to the Pu(V) disproportionation reaction, as illustrated for 1 M solutions of HCl in Table 4:

Table 4. Disproportionation of PuO_2^+

Reaction	E^0
$\text{PuO}_2^+ + 4\text{H}^+ + 1\text{e}^- \rightarrow \text{Pu}^{4+}$	1.190
$\text{PuO}_2^+ \rightarrow \text{PuO}_2^{2+} + 1\text{e}^-$	-0.912
$2 \text{PuO}_2^+ + 4\text{H}^+ \rightarrow \text{Pu}^{4+} + \text{PuO}_2^{2+}$	0.278

However, there are ways to explore Pu(V) chemistry in acidic solutions, such as using classic radiotracer methods with ^{238}Pu . The short half-life of ^{238}Pu (87.7 years) allows the possibility of working with very dilute solutions of Pu, effectively quenching the disproportionation reaction by slowing the reaction kinetics.

As described earlier, Oversby has stated that (Neill 1998, Oversby 2000):

“...Pu(V) is observed as a long-lived transient in many laboratory experiments. Pu(V) may be formed as a result of radiolysis reactions in brine, and while its total abundance in the repository is likely to be low, it might be significant as a transient species in some waste containers.”

Oversby describes the possible reasons for appearance of oxidized Pu due to radiolysis effects. It is impossible to produce Pu(V) by direct oxidation of either Pu(III) or Pu(IV) in solution due to the overvoltage required to carry out the oxidation steps. Pu(VI) is the resultant oxidation state whenever direct oxidations of Pu(III) or Pu(IV) are carried out in solution. Pu(V) may then be produced by gentle reduction of Pu(VI). Observations of Pu(V) in brine solutions that are significantly affected by radiolysis may be due to initial oxidation of Pu(III,IV) to Pu(VI), by OCl^- , followed by reduction of Pu(VI) to Pu(V) by a reducing agent such as H_2O_2 . Further reduction of Pu(V) to Pu(IV), or disproportionation of Pu(V), in basic solutions is kinetically hindered by the inverse fourth power dependence upon the hydrogen ion concentration.

This discussion is intended to introduce the reader to some of the subtleties of Pu solution chemistry, and describe some of the difficulties inherent in experimental work with Pu. It should be apparent that qualitative observations may be of little use when not obtained in conjunction with careful experimental design, vigilant control of numerous experimental variables, and judicious interpretation of data.

3.6 Redox Behavior of Fe

The corrosion of iron, present within the waste and as the waste containers, is expected to have a significant impact on the oxidation/reduction conditions within the WIPP. Iron corrosion under anoxic conditions should provide a source of electrochemical reductive capacity, which is expected to maintain Pu in a reduced state, as Pu(III) or Pu(IV). The standard reduction potentials for iron are presented in Table 5.

Table 5. Reduction reactions of iron

Reaction	E^0 (volts)
$\text{Fe}^{2+} + 2e^- \rightarrow \text{Fe}^0$	-0.447
$\text{Fe}^{3+} + 3e^- \rightarrow \text{Fe}^0$	-0.037
$\text{Fe}^{3+} + 1e^- \rightarrow \text{Fe}^{2+}$	0.77

The standard reduction potentials are for standard conditions of activity, and are not pH dependent in the range below which hydrolysis becomes an important feature. It is apparent that the Fe^0 to Fe^{2+} oxidation that occurs during corrosion of iron can provide a thermodynamic driving force of +0.447 volts, which, when coupled with other redox reactions, allows metallic iron to behave as a reducing agent. For example, coupling the oxidation of iron with the reduction of Pu^{4+} to Pu^{3+} in 1 M HCl solution is illustrated in Table 6.

Table 6. Reduction of Pu by metallic Fe

Reaction	Volt-equivalent
$\text{Fe}^0 \rightarrow \text{Fe}^{2+} + 2\text{e}^-$	+0.447
$2\text{Pu}^{4+} + 4\text{e}^- \rightarrow 2\text{Pu}^{3+}$	+1.94
$\text{Fe}^0 + 2\text{Pu}^{4+} \rightarrow \text{Fe}^{2+} + 2\text{Pu}^{3+}$	+2.387

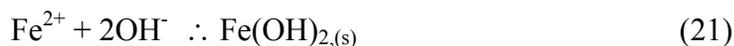
An equilibrium constant for the reduction of Pu^{4+} by iron can be written as

$$K = \frac{[\text{Fe}^{2+}][\text{Pu}^{3+}]^2}{[\text{Pu}^{4+}]^2} \quad (19)$$

Combining equations 9 and 14 and rearranging gives

$$\ln K = nFE/RT \quad (20)$$

When the volt-equivalent is used, $n = 1$, $T = 298$, equation 20 yields a value of 2.4×10^{40} for the equilibrium constant. The large value of the equilibrium constant shows that Pu^{3+} is much more stable than Pu^{4+} in acid solutions containing iron. It is important to note that Fe^{2+} is the stable oxidation state of iron in acid systems, but the situation is quite different in neutral or basic solutions. The redox behavior of iron in neutral solutions is affected by the strong tendency of Fe^{3+} to form insoluble hydrolysis products, which tends to shift the equilibrium position between Fe^{2+} and Fe^{3+} in favor of Fe^{3+} . The reactions for complexation and precipitation of Fe^{2+} and Fe^{3+} by hydroxide may be respectively written as



The solubility product constants, K_{sp} , for iron hydroxide precipitates are written as (Baes and Mesmer, 1986):

$$K_{\text{sp,Fe}(\text{OH})_2} = [\text{Fe}^{2+}][\text{OH}^-]^2 = 10^{-15} \quad (23)$$

$$K_{\text{sp,Fe}(\text{OH})_3} = [\text{Fe}^{3+}][\text{OH}^-]^3 = 10^{-38} \quad (24)$$

The standard reduction potential for the reduction of Fe^{3+} to Fe^{2+} , 0.77 volts, may be used in the Nernst equation, along with the values for the solubility product constants of ferrous and ferric hydroxide precipitates to calculate a value of the reduction potential in

neutral and basic solutions. For example, using the Nernst equation and the K_{sp} values to solve for iron concentrations yields the reduction potential of Fe^{3+} to Fe^{2+} at $pH = 9$:

$$E = E^0 - 0.059 \log \left(\frac{K_{sp,Fe(OH)_2}}{[OH^-]^2} \cdot \frac{K_{sp,Fe(OH)_3}}{[OH^-]^3} \right) \quad (25)$$

$$E = 0.77 - 0.059 \log(10^{18}) \quad (26)$$

$$= -0.292 \text{ volts} \quad (27)$$

The relatively large negative value for the reduction potential of Fe^{3+} to Fe^{2+} indicates that the reaction has a strong tendency to go in the reverse direction, i.e. Fe(III) is the stable oxidation state of iron in basic solutions, and Fe(II) will readily give up an electron in basic solutions. Perusal of the Latimer diagrams for Pu suggests that the dominant oxidation state of Pu in basic solution will probably be Pu(III) or Pu(IV), when coupled with the oxidation of iron from Fe(II) to Fe(III), although it is clear that milder oxidizing conditions can generate Pu(V) and Pu(VI) more easily in basic solutions than in acidic conditions. Additionally, as has been previously noted, complexing solutes will also affect the redox couples, and concomitantly, the redox speciation of Pu. Therefore a complete determination of the redox couples of Pu under WIPP conditions would require carefully designed and controlled experiments. The stability of these respective oxidation states depends upon attainment of a state of thermodynamic equilibrium.

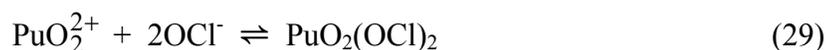
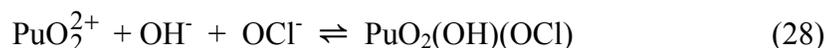
The previous discussion on the redox properties of Pu illustrates the effect that ligands can have on the oxidation state distribution of Pu. In addition to affecting the redox couples, ligands also may affect solubilities, e.g. complexation of actinide ions with organic ligands solubilizes the metal ions, and must be quantified to make meaningful predictions of dissolved actinide concentrations. Well-defined values for complexation constants (commonly called stability constants) as well as solubility product constants are necessary to calculate actinide solubilities

3.7 Complexation Behavior of OCI^-

3.7.1 OCI^- as a Ligand

The complexing ability of OCI^- with actinide ions has not been systematically studied, although Kim has reported formation of OCI^- complexes with PuO_2^{2+} (Pashalidis et al. 1993). Experimentally observed OCI^- concentrations, and a brief summary of likely complexation properties are discussed within this test plan. Previous reports suggest that

OCl⁻ may be present in millimolar concentrations in the immediate vicinity of α -emitting radioactive material.(Kim et al. 1987, Pashalidis et al. 1993) OCl⁻ may affect solution behavior of Pu; as an oxidant it may affect redox speciation, and as a ligand it may affect solubility. Hypochlorite complexes with PuO₂²⁺ are illustrated in equations (28) and (29):



Stability constants for reaction (28) have been reported as $\log \beta_{1-11} = 14.0$ at pH=6.7 and $\log \beta_{1-11} = 14.5$ at pH= 8.4 ($\mu=0.55$ M, T=22° C). The stability constant for reaction (29) is $\log \beta_{102} = 10.3$ ($\mu=0.55$, T=22° C) (Pashalidis, 1993).

The short range of α -particles in solution can cause chemical environments that feature greater concentrations of radiolysis products in the immediate vicinity of radioactive sources than in the bulk solution, i.e. the actinides and ligands will occur together in close proximity. In fact it is likely that dissolution processes in localized heterogeneous microenvironments in a steady-state, non-equilibrium condition will be governed not by average solution concentrations of complexing ligands, but by concentration gradients that increase in magnitude as a function of proximity to the surface of the radiation-emitting solid. Figure 1 demonstrates that significant amounts of hypochlorite may be generated in NaCl solutions, especially brines. It is not necessary for multiple curie levels to be dispersed in brine to generate high local concentrations of hypochlorite because localized solution conditions will be established in the environs of the α -emitting radioactive source.

Figure 4 illustrates the steady state concentration of OCl⁻ generated as a function of radioactivity in 5 molal NaCl solution. The data used to generate the data points in this figure were taken from Kelm et al. (1999). The data points at ca. 6 and 12 Ci/L had not reached their respective steady state concentrations, therefore, there is not enough data to determine the type of function that correctly defines hypochlorite generation. However, the high-radioactivity solutions are not generally representative of conditions expected to persist within the WIPP.

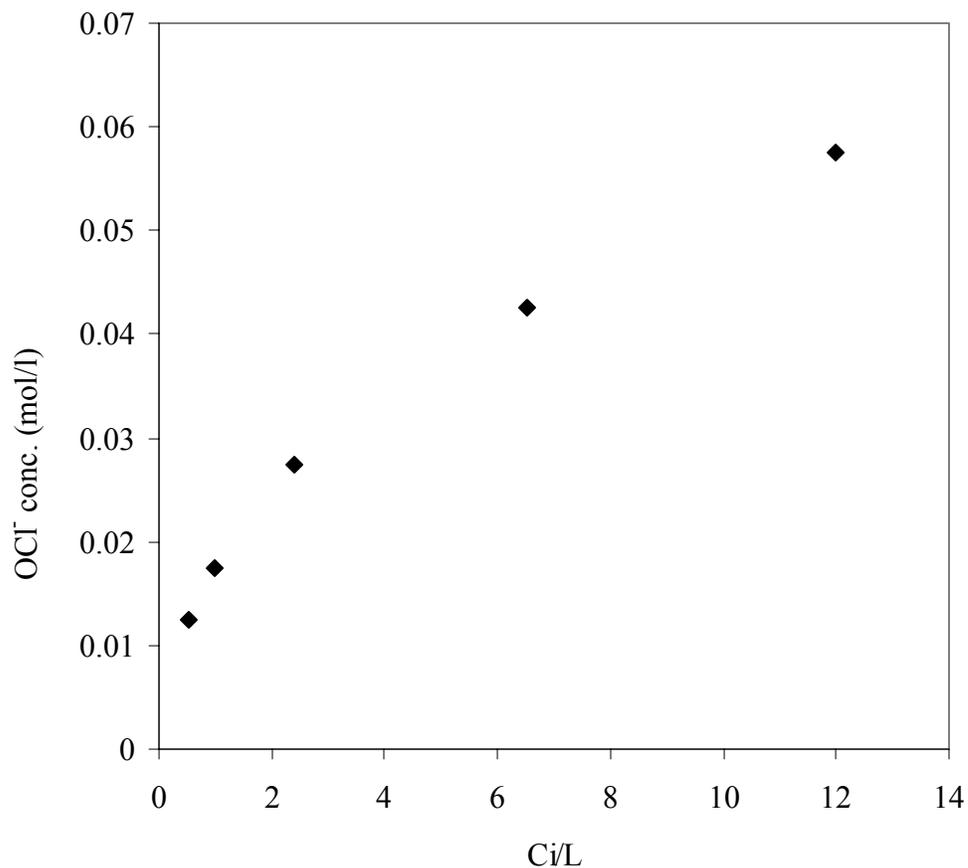


Figure 4. Generation of hypochlorite as a function of radioactivity in 5 mol/L NaCl at pH ca. 12.

3.7.2 Prediction of $\log \beta$

The actinide ions (An(III,IV,V,VI)), which behave as hard acids due to their relatively low polarizability and high ionization potentials, interact with ligands primarily by electrostatic interaction (Pearson, 1963). As a result, an extended form of the Born equation, which relates electrostatic attraction to the Gibbs free energy of formation, may be used to make an approximate prediction of the magnitude of the stability constant for trivalent actinides or lanthanide analogs when the stability constant for another actinide/ligand pair is known (Choppin and Rizkalla, 1994). The relationship is illustrated by equation 30:

$$\Delta G = \frac{-N_A e^2 Z_1 Z_2}{418.7 D_e d_{12}} - \nu RT 55.5 + \sum \ln f(I) \quad (30)$$

where ΔG is the Gibbs free energy of complex formation, N_A is Avogadro's number, e is the fundamental unit of charge, Z_1 is the charge on the metal ion, Z_2 is the charge on the ligand, D_e is the effective dielectric constant (57 for An^{3+} or Ln^{3+} , 40 for An^{4+} , 65 for AnO_2^+ , 55 for AnO_2^{2+}), d_{12} is the distance between the metal and ligand, ν is the change in number of the reacting species, and $\sum \ln f(I)$ is the activity coefficient term to correct for effect of ionic strength (Choppin and Rizkalla, 1994). The relationship between the Gibbs free energy and the stability constant, β , is:

$$\Delta G = -RT \ln \beta \quad (31)$$

where R is the ideal gas constant, 8.314 J/molK and T is the absolute temperature in kelvins. Substituting equation 31 into equation 30 gives:

$$\ln \beta = \frac{N_A e^2 Z_1 Z_2}{RT 418.7 D_e d_{12}} - \nu RT 55.5 + \sum \ln f(I) \quad (32)$$

Equation 32 may be simplified for when comparing reactions that have the same number of reacting species and are at constant ionic strength:

$$\log \beta = \frac{A Z_1 Z_2}{D_e d_{12}} + B \quad (33)$$

A is a constant that encompasses Avogadro's number, the elementary unit of charge, the ideal gas constant, temperature and the proportionality constant 418.7; B is a constant that includes the change in number of reacting species and ionic strength corrections. Equation 33 indicates that a plot of the logarithm of the stability constants vs. charge on the metal ion for complexes of actinides with a given ligand should be linear when corrected for variations in the effective dielectric constant and the metal-ligand distance. A useful modification of equation 33 is given by equation 34 (Choppin, 1999)

$$\log \beta_n(C) = \log \beta_n(D) \times (Z_C/Z_D) \times (D_D/D_C)(d_{D/C}) \quad (34)$$

C and D are used to

The effective charge on the metal ion for the four common actinide oxidation states may be summarized as (Choppin and Rao, 1984)

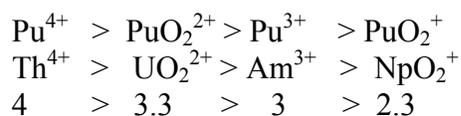


Figure 5. Effective charge on actinide cations.

Plutonium follows the pattern for effective charges on the metal atom as in the corresponding oxidation states of Th^{4+} , UO_2^{2+} , Am^{3+} and NpO_2^+ . The larger effective charge on the AnO_2^{2+} ion relative to the An^{3+} ion often causes the magnitude of the logarithm of the stability constants for $\text{AnO}_2\text{L}^{2-n+}$ complexes to be about 10-30% greater than the respective complexes with An^{3+} when steric effects do not interfere. Therefore, the magnitude of β_{102} for the Am^{3+} (and Nd^{3+}) complexes with OCl^- should be about 8-9 log units, based on the data for the stability constant of OCl^- with PuO_2^{2+} (Pashalidis et al. 1993).

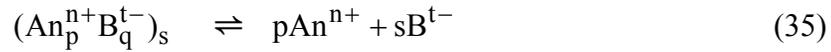
3.7.3 Comparable ligands

A survey of the National Institute of Standards and Technology (NIST) stability constant database reveals a paucity of data for complexes of metals with hypochlorite. Cyanate (OCN^-) may be expected to exhibit similar complexation behavior to hypochlorite since the pseudohalogen cyanide group replaces the chlorine atom. However, since cyanate exhibits linkage isomerism, a comparison would be valid only for coordination through the oxygen atom of the cyanate group. HOCN has $\text{pK}_a = 3.48$ ($\mu=0$ M, $T=25^\circ$ C), making it a weaker conjugate base than OCl^- . Therefore OCN^- complexes formed through the oxygen atom should be weaker than corresponding complexes with OCl^- . Unfortunately, the database for complexation with cyanate is limited to Co^{2+} and Ag^+ , both of which may coordinate through the nitrogen atom of cyanate, and neither of the metal ions are suitable analogs for lanthanides or actinides.

The halate anion ClO_3^- may also be generated as a result of α -radiolysis in chloride brine. Ligands with higher pK_a values form stronger conjugate bases, with attendant greater affinity for metal cations. In general, the stabilities of complexes are proportional to the pK_a values of the protonated form of a ligand. The pK_a value for HClO_3 is -2.7 ($\mu=0.10$ M NaClO_4 , $T=298$ K), making ClO_3^- a rather weak base. Most ligands, with $\text{pK}_a < 2$ (including ClO_3^-) form only outer sphere complexes with actinides, and it has been shown that LnClO_3^{2+} and $\text{UO}_2\text{ClO}_3^+$ conform to this behavioral model (Choppin et al. 1988). In contrast, OCl^- most likely forms inner-sphere complexes with actinides; with the accompanying differences in the nature of the enthalpy and entropy driving forces of the complexation reaction. As a result, halates do not make useful analogs for hypohalite anions.

3.7.4 Effect of Complexing Agents on Actinide Solubility

The effect of ligand complexation upon actinides under WIPP conditions causes an increase of actinide solubility and mobility. Actinide solubility is controlled by the extent of complexation and by the solubility product constant of actinide precipitates, or actinide bearing solids in which actinides are co-precipitated as members in a non-actinide host phase. The dissolution of actinide precipitates may be generally described by the equation:



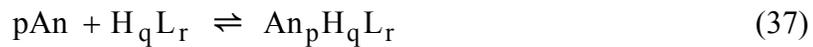
where $np = st$, An represents an actinide cation with overall charge of $n+$, and B is a counter-ion that participates in formation of a precipitate.

The solubility product constant is generally expressed as

$$K_{\text{sp}} = \{\text{An}^{\text{n}+}\}^p \{\text{B}^{\text{t}-}\}^s \quad (36)$$

where the braces indicate thermodynamic activities.

Complexation of the actinide ion in solution will cause further dissolution of the solid phase to compensate for perturbation of the equilibrium expressed in equation (35). Formation of actinide/ligand complexes is described by equation (37), where charges on the metal and ligand are omitted for simplicity:



The thermodynamic stability constant for such a complex is defined as

$$\beta_{\text{pqr}} = \frac{\{\text{An}_p\text{H}_q\text{L}_r\}}{\{\text{An}\}^p \{\text{H}_q\text{L}\}^r} \quad (38)$$

The relationship between the solubility product constant of an actinide bearing solid and the solubilizing effect of complexation is illustrated by substituting equation (38) into equation (36):

$$\frac{K_{\text{sp}}}{\{\text{B}^{\text{t}-}\}^s} = \frac{\{\text{An}_p\text{H}_q\text{L}_r\}}{\beta_{\text{pqr}} \{\text{H}_q\text{L}\}^r} \quad (39)$$

The total solubility of an actinide ion is the sum of the free metal ion concentration and the concentrations of all other soluble species. The sum of concentrations of all soluble species

is described by



where q' and r' are the maximum possible values of q and r , and L is the only ligand in the system. Accordingly, addition of complexing ligands will lead to greater total solubility of metal ions.

3.8 Extraction Method for Determination of Stability Constants

Liquid/liquid extraction is a well-developed method and has been extensively used in support of the WIPP actinide science program to determine the stability constants of actinide metal ions and other metal cations with numerous different ligands (Chen et al. 1999, Bronikowski et al. 1999, Choppin and Pokrovsky 1997, Bronikowski et al. 1998, Borkowski et al. 1999, Borkowski et al. 1996, Borkowski et al. 2000). The distribution of a metal ion between two immiscible phases in the presence of an organophilic extractant is described by a distribution coefficient:

$$D = \frac{\sum [\text{M}_{\text{org}}]}{\sum [\text{M}_{\text{aq}}]} \quad (41)$$

where $\sum [\text{M}_{\text{org}}]$ is the sum of the concentrations of all metal species in the organic phase and $\sum [\text{M}_{\text{aq}}]$ is the sum of the concentrations of all metal species in the aqueous phase. An aquophilic complexing agent may exert a competitive influence on the metal distribution that is described by equation 42:

$$\frac{D_0}{D} - 1 = \sum_1^n \beta'_{10n} [\text{L}]^n \quad (42)$$

where D_0 is the distribution coefficient in the absence of the complexing ligand, β'_{10n} are the successive apparent stability constants, and $[\text{L}]$ is the ligand concentration. The apparent stability constant is related to the true stability constant as expressed by equation 43:

$$\beta'_{101} = \beta_{101} / (1 + \sum_1^n \beta_n^{\text{OH}^-} ([\text{OH}^-])^n + \sum_1^n \beta_n^{\text{B}^-} ([\text{B}^-])^n) \quad (43)$$

where $\beta_n^{\text{OH}^-}$ is the n^{th} hydrolysis constant, $\beta_n^{\text{B}^-}$ is the n^{th} stability constant of the metal with the buffer, $[\text{OH}^-]$ is the hydroxide concentration and $[\text{B}^-]$ is the free buffer concentration.

In solvent extraction determination of stability constants, it is necessary that the complexing ligand and the metal/ligand complex are much more soluble in the aqueous phase than in the organic phase. This condition is often fulfilled when the metal ligand complex is charged, solvated with water molecules, or has ligands that exhibit aquophilicity through hydrogen bonding. Metal/hypochlorite complexes are expected to satisfy these conditions.

3.9 Use of Analogs

The trivalent lanthanide Nd(III) will be used for stability constant determinations due to its redox stability and to its similarity in charge density to Am(III) and Pu(III). The use of lanthanide cations as analogs for the trivalent actinides is a widely accepted practice, and has been documented elsewhere (Choppin, 1999). Initial determination of the stability constant of OCl^- with Nd is expected to be advantageous because the +3 oxidation state is the only stable oxidation state of Nd. Lack of other accessible oxidation states obviates the necessity of oxidation state control of the metal ion and ensures that it is not possible for the metal ion to cause catalytic decomposition of OCl^- . Moreover, Nd is not a radioactive material, does not present notable toxicity hazards, and may be conveniently handled in experimental work as an ordinary chemical component.

3.10 Brine Compositions

Compositions of WIPP Brine A and ERDA-6 and GWB are given in Table 7. The ionic strengths were calculated from data in Table IV with the equation

$$\mu = 1/2 \sum c_i z^2 \quad (44)$$

where μ represents the ionic strength, c_i is the concentration of component “i”, and z is the charge on the ion. In this case, ionic strength is given in concentration units, rather than activities. The higher ionic strength of Brine A is predominantly due to the higher Mg^{2+} content.

Table 7. Chemical Components of WIPP Brines

Ion or Chemical Property	Brine A (a)	ERDA-6 (a)	GWB (b)
B ³⁺ (mM)	63	20	156
Br ⁻ (mM)	11	10	27
Ca ²⁺ (mM)	12	20	14
Cl ⁻ (mM)	4800	5350	5610
K ⁺ (mM)	97	770	467
Mg ²⁺ (mM)	19	1440	1020
Na ⁺ (mM)	4870	1830	3570
SO ₄ ²⁻	170	40	178
ionic strength (M)	5.57	7.07	6.0

(a) data from Table SOTERM-1, DOE (1996)

(b) data taken from Zhang et al. (1999)

Other metals, such as Fe, Co, Ni, and Mn, will be present in the WIPP as a result of corrosion of waste containers. Steel, composed primarily of iron, with smaller amounts (usually less than 1%) of other components such as Co, Ni and Mn, will provide masses of Fe that far exceed the amounts of the other transition metals. As a result, it is expected that the primary transition metal component in the WIPP environment that can affect the stability of OCl⁻ will be Fe. It is not anticipated that transition metals other than Fe will exhibit a greater influence than that of Fe.

3.11 Objectives

The objectives of the studies proposed in this test plan are to:

- Determine the rate of decomposition of OCl⁻ in WIPP-representative brines, including the influence of waste components, such as iron, on decomposition.
- Determine and measure solution conditions that have an impact on complex formation of metal ions with OCl⁻
- Determine the stability constants for complex formation of OCl⁻ with metal ions

Intended use of the data:

Actinide solubility affects the magnitude of the contribution of the direct brine release to the generation of a Complementary Cumulative Distribution Function (CCDF), which is used as an EPA mandated evaluation of regulatory compliance.

The results of this study will be used to:

- Determine OCl^- decomposition rates in order to calculate whether OCl^- generation will be sufficient to affect oxidation/reduction conditions within the repository
- Determine whether complexation by radiolysis products, such as OCl^- , will contribute to increased actinide solubility in the WIPP.

Additionally, of equal importance is a demonstration that processes that are deemed to be significant to repository behavior are quantitatively understood.

4.0 EXPERIMENTAL PROCESS DESCRIPTION

4.1 Sample and Data Control

4.1.1 Critical Variables to be Measured and Controlled

Variables that must be controlled in the types of experiments described within this test plan include:

- pH
- temperature
- sample volume
- sample composition

The decomposition of HOCl or OCl^- may have an effect on the pH of the host solution. Reactions of HOCl and OCl^- , which may affect solution pH values, are listed in Table 1. HOCl is a weak acid, with a $\text{pK}_a \approx 7.5$ in low ionic strength solutions, and will probably exhibit an increase of 0.5 to 1 pK unit in high ionic strength solution. There will be some buffering of pH by the acid/base pair of HOCl/OCl^- , although the self-buffering capability will depend upon decomposition pathways and kinetics, which must be experimentally determined. Initially, an attempt will be made to use the self-buffering capacity of the HOCl/OCl^- pair because it is also unknown whether other buffers, such as boric acid/borate will react with either HOCl or OCl^- . The kinetics of decomposition with and without added buffer may be compared to determine whether there is an effect. The representative WIPP brines, ERDA-6, GWB, and WIPP Brine A all contain boric acid/borate, which makes an initial determination of kinetics in a non-boron bearing brine an important first step in the overall examination of the behavior of HOCl and OCl^- in WIPP brines. Solution pH will be controlled by adding small amounts of non-interfering acid or base, such as HCl or NaOH solution. Solution pcH (pcH is the negative logarithm of the hydrogen ion concentration) will be measured with a standard, calibrated pH meter equipped with a combination glass electrode. Any adjustments to solution pH at the beginning or during the course of the experimental work will be recorded in the scientific notebook, along with the measured pH values.

The solution temperatures will be controlled during titrations by performing the

experiments in sample vessels immersed in a constant temperature water bath. Refer to the section describing measuring and test equipment for a description of temperature control apparatus.

Sample volumes will be measured with standardized volumetric glassware and calibrated Class A pipets, or calibrated autopipets. Refer to the section describing measuring and test equipment for a description of calibration and control of volumetric glassware and pipets.

Sample composition will be determined by solution preparation using standard laboratory techniques with calibrated equipment. Concentration of HOCl and OCl⁻ in the decomposition kinetics experiments will be determined by UV-Vis spectroscopy. Concentrations of Nd will be determined by complexometric titration and analysis by atomic emission spectroscopy.

Deviations from these standards, such as allowing sample temperature to equilibrate with ambient temperature rather than remaining under controlled conditions, will be noted in the laboratory notebook, along with descriptions of the acceptability of such deviations and the impact upon the experiment.

4.1.2 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 with regard to screening as a feature, event, or process that may affect the long-term performance of the WIPP.

4.1.3 Procedures to be Used/Developed

It is not necessary to develop new procedures to accomplish the tasks described in this test plan. 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 atmosphere, 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.

4.1.4 Known Sources of Error and Uncertainty

Sources of error include:

- pH measurement
- volume measurement
- weighing error
- impure reagents
- data transcription error

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. Volume and weighing measurement error will be minimized by calibration of all volumetric and weighing equipment with accompanying documentation in the laboratory notebooks. All reagents will be A.C.S. reagent grade or better. If necessary, reagents will be purified by standard, documented procedures. Data transcription error will be minimized, and can be traced by attaching hardcopies of instrumental data output within the laboratory notebook.

4.1.5 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.

4.1.6 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 Sandia National Laboratories records center along with other QA records.

4.1.7 Sample Handling and Control Requirements

Standard procedures for sample identification, handling, storage, shipping, archiving and

disposition have been described in Sandia National Laboratories Nuclear Waste Management Program Procedure NP 13-1. Sample handling will be performed under the guidance of NP 13-1.

Samples will be labeled with unique identification numbers, date, and will be referenced within 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 the laboratory of Sandia National Laboratories, Carlsbad. No special precautions are planned to secure the samples.

4.1.8 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 the Sandia National Laboratories Carlsbad laboratory. Hazardous waste generation is not anticipated at the time of this writing.

4.1.9 Data Acquisition System

Calibrations and calibration checks will be performed on instruments in the manner described in the Measuring and Test Equipment section. 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 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.

4.1.10 Commercial Software, Not Modified

The commercial 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 spreadsheet software for performing routine calculations.

The IPC-OES is operated by the system software supplied by the instrument manufacturer.

The Cary-300 UV-Vis spectrophotometer is operated by the system software supplied by the instrument manufacturer.

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

4.1.11 Other Software

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

4.1.12 Methods of justification, evaluation, approval, and documentation of any deviations from test standards

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

4.1.13 Experimental Controls

Each experimental determination of decomposition rate constants will be repeated in order to reduce likelihood of inadvertent introduction of indeterminate errors. The use of blank spikes, matrix spikes, internal or surrogate standards are not necessary or compatible with the experimental methods used in the kinetics experiments proposed in this test plan.

Each experimental determination of the metal/ligand stability constant will be performed at least three times, with no less than two nominally identical samples used to determine values for each data point. Known quantities of reagents will be introduced into each sample, so mass balances may be calculated from the amount recovered from each phase, making internal and surrogate standard spikes generally unnecessary. It should be noted that experimental procedures may be altered such that spikes are included in experimental procedures if it is necessary to account for variations in instrumental response.

4.1.14 Control and Characterization of Test Media

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

4.1.15 Data Identification and Use

Data that is 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
- 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 within the laboratory notebook.

4.1.16 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 within a data binder specifically designated for the purpose. Data that is stored separately from the laboratory notebook, e.g. in a designated three ring binder, will be appropriately referenced and described with respect to location, within the laboratory notebook.

4.1.17 Identification, Segregation, Disposal of Erroneous Data

Data that is suspected to be 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.

4.2 Reagents and Procedures

4.2.1 Measuring and Test Equipment

Measuring and test equipment, including but not limited to, the Sandia National Laboratories Carlsbad laboratory ICP-OES, balance, pipets, pH meter, UV-VIS spectrophotometer will be used in accordance with the Sandia National Laboratories Nuclear Waste Management Program Procedure NP 12-1, Control of Measuring and Test Equipment.

The ICP-OES is an inductively coupled plasma atomic emission spectrometer. Liquid samples are introduced into the instrument through an autosampler. 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. The spectrometer is calibrated by using the measurement of instrument response to plot a calibration curve 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. No use of internal standards is anticipated. Use of surrogate standards, blank spikes, matrix spikes, or other methods of batch control will be documented in the scientific notebook.

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 pipets, or autopipets equipped with disposable tips. Calibration of all pipets 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. Density conversion factors for water as a function of temperature will be taken from the Handbook of Chemistry and Physics, published by CRC Press, or another reliable, documented source. Atmospheric buoyancy corrections for calibration of volumetric glassware are not required.

Instrument response of potentiometric pH measurement instrumentation 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 atmosphere conditions will be maintained during titrations, if necessary, by immersion of the titration vessel in a thermostated 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 N₂. Temperature and atmosphere control and conditions will be recorded in the scientific notebook.

The UV-VIS spectrophotometer is a Cary 300 Ultraviolet-Visible Spectrophotometer, equipped with D₂ and tungsten filament lamps. The instrument performs an internal wavelength calibration upon start-up, using emission lines generated by the D₂ 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.

4.2.2 Reagents

Deionized water will be used to prepare all aqueous solutions. All aqueous and organic solutions will be filtered through 0.20 or 0.45 mm pore size membrane filters, as necessary.

High purity OCl^- will be synthesized by one of several methods documented in peer-reviewed literature, or obtained from documented commercial sources. Possible methods include bubbling Cl_2 gas through carbonate free 0.6 M aqueous NaOH or passing Cl_2 gas through an HgO slurry with subsequent reduced pressure distillation into aqueous NaOH (Adam and Gordon, 1999). Concentration of OCl^- may be determined spectrophotometrically ($\epsilon = 350 \text{ M}^{-1} \text{ cm}^{-1}$ at 292 nm), by potentiometric titration, or by other appropriate, documented methods (Vogel 1989, Adam and Gordon 1999).

4.2.3 Metal Solutions

Lanthanide solutions will be standardized by published procedures, such as complexometric titration with volumetric standard EDTA solution and xylenol orange indicator (Vogel, 1989).

4.2.4 Electrolyte Solution Compositions

The proposed work will be conducted in solutions of four different general composition types:

1. NaCl at 5 molal ionic strength
2. Modified WIPP Brine A
3. Modified WIPP ERDA-6
4. Modified GWB

Brine A, ERDA-6 and GWB are saturated solutions, so loss of small amounts of water, (e.g. by evaporation), causes precipitation, and possible formation of lanthanide-bearing solids, either as co-precipitates, or as adsorbates onto the crystal surfaces of solids. Using a diluted form of the brine in order to remain below saturation most easily mitigates the potential for manifestation of such an uncontrolled variable. Consequently, modified forms of Brine A, ERDA-6, and GWB will be prepared that are diluted by 5% on the molar scale. It is possible that preparation of pH standards will require further modification of the brine compositions. All brine compositions will be documented in the laboratory notebooks, along with explanations for use of a particular brine composition.

4.2.5 Experimental Procedures

4.2.5.1 General Conditions

Sample preparation and analysis procedures, (weighing, pipetting, etc.) are parts of standard laboratory analytical procedures. Instrumental analyses, such as ICP-AES and UV-Vis spectroscopy will be performed in accordance with written procedures that have been supplied by the instrument manufacturer, or other documented procedures that have been demonstrated to be appropriate. Atmospheric components, such as N₂, O₂, Ar and CO₂ have not been reported to affect the decomposition of HOCl/OCl⁻, and there is no current evidence that such control is necessary, therefore, controlled atmospheric conditions for complexation and decomposition experiments will not be used. Calibration of pH measurement instrumentation will be performed under inert (N₂) 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.

4.2.5.2 Decomposition Kinetics

Samples of HOCl and/or OCl⁻ will be prepared under various conditions of concentration, pH, brine composition, and added components. A general description of sample preparation will be given here, but complete, detailed, and documented descriptions of sample preparation will be provided in the laboratory notebooks.

Samples of HOCl/OCl⁻ will be prepared by diluting a stock solution, (either synthesized or obtained from a commercial source) into solutions of various pH and brine compositions. Samples of specific composition will be large enough (e.g. 250 ml) for repeated sampling and analysis by UV-Vis examination of the HOCl/OCl⁻ absorbance peaks. Approximately 5-10 ml aliquots will be removed for each analysis, allowing as many as 25 to 50 analyses per sample. Upon preparation, a spectrum of each sample will be obtained. The intensities of the absorbance maxima associated with the electronic transitions attributable to HOCl and OCl⁻ may be used to determine the respective concentrations of each moiety. The UV-Vis spectra of the samples will be repeatedly obtained over measured time intervals in order to determine the change in concentration of HOCl and OCl⁻ as a function of time. The time dependence of the change in concentration may be used to derive rate constants that quantitatively describe the kinetic behavior of the decomposition pathways, and their dependence on pH and solution composition.

There have not been reports of the dependence of the decomposition of HOCl or OCl⁻ on exposure to light, therefore, some samples will be stored in the dark, and others exposed to room light in order to establish whether exposure to light affects the systems. The appropriate number and type of samples held in the dark and exposed to light will be experimentally determined.

HOCl and OCl⁻ concentrations will be varied to measure the rate dependence on the concentration of these components. The pcH dependence of decomposition rates will also be determined by preparing samples adjusted to different initial pcH conditions, and measuring change in HOCl/OCl⁻ concentration as a function of time and acidity in order to develop a predictive model that would be useful under a variety of pcH conditions. It is unknown at this time whether brine components, such as SO₄²⁻ or B₄O₇³⁻ will affect decomposition behavior, therefore, initial measurements will be made in solutions, both with and without SO₄²⁻ or B₄O₇³⁻.

The effect of brine composition on kinetics of decomposition of HOCl/OCl⁻ will be determined by measuring the changes in concentration over time in a variety of solution matrices. Redox active transition metals, such as iron, may affect decomposition rates, therefore samples will be prepared that include iron, added in metallic and oxidized form (e.g. FeSO₄).

4.2.5.3 Stability Constant Determination

The theory of the method has been described in Section 3.8. A general description of the experimental process is supplied here, but it will be necessary to experimentally determine specific parameters, such as appropriate reagent concentrations. In a typical experiment, a series of glass liquid scintillation vials (or other appropriate sample vessels), (≈20 ml) will be filled with 5 ml of the aqueous phase and 5 ml of the organic phase. The aqueous phases will contain varying concentrations of the complexing ligand. Other variables, such as pH, ionic strength, temperature, extractant concentration and volumes of the phases, will be monitored. The vials will be mechanically shaken long enough to ensure equilibration of complex formation and interphase transfer reactions. The length of equilibration time must be experimentally determined, but it usually ranges between 15 minutes and several hours. After equilibrium has been reached, the sample containers may be centrifuged to assist in phase separation, then an aliquot removed from each phase for measurement of distribution ratios of the metal ion. Metal ion concentrations in the sample aliquots may be measured by a variety of techniques, such as UV-VIS spectroscopy, or ICP-OES. ICP-OES or another documented technique will be employed to measure phase distribution of Nd, and other metals that will be systematically added to the solutions, such as Fe, Co, and Ni. UV-VIS spectroscopy will be used to determine whether decomposition of solution components occurs during the course of the experiment.

5.0 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 NWMP procedure NP 2-1, "Qualification and Training."

5.2 Standard Procedures

The following NWMP Procedures and Project Specific Procedures are applicable:

SOP-C001: “Standard Operating Procedure for Activities in the SNL/Carlsbad Laboratory Facility.”

SP 13-1 “Chain of Custody

NP 6-1 “Document Review Process”

NP 13-1 “Sample Control”

NP 12-1 “Control of Measuring and Test Equipment”

NP 20-1 “Scientific Notebooks”

NP 2-1 “Qualification and Training

NP 17-1 “Records

6.0 HEALTH & SAFETY

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

7.0 PERMITTING/LICENSING

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

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