U.S. DEPARTMENT OF
ENERGY

Prepared for the U.S. Department of Energy
under Contract DE-AC05-76RL01830

PNNL- 20455
53451-RPT15, Rev 0

Mitigation of Hydrogen Gas Generation from the Reaction of Uranium Metal with Water in K Basin Sludge and Sludge Waste Forms

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June 2011

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Summary

Sludge formed and reposing in the K East (KE) and K West (KW) fuel storage basins on the Hanford Site has been a subject of concern since extended storage of metallic fuel from the N Reactor began in the 1980s. Although the last of the fuel was removed from the basins in 2004 and transport of sludge from the KE Basin to the KW Basin was completed in 2007, sludge still remains in the KW Basin stored in engineered containers. Sludge will be recovered from the engineered containers into Sludge Transport and Storage Containers and stored at an interim storage location on the Central Plateau. The stored sludge ultimately will be processed for disposal to the Waste Isolation Pilot Plant (WIPP) as remote-handled transuranic waste. However, before the sludge can go to WIPP, it must be processed and packaged into WIPP-acceptable forms. The presence of uranium metal fuel particles in the sludge poses problems to these operations because uranium metal reacts with water to form flammable hydrogen gas.

Activities surrounding the storage, transport, treatment, and disposition of the K Basin sludge are currently administered under the Sludge Treatment Project (STP) managed by CH2M Hill Plateau Remediation Company (CHPRC) operating under contract to the U.S. Department of Energy. Investigative studies in this report were conducted by Pacific Northwest National Laboratory (PNNL) under contract to CHPRC for the STP.

The reaction of uranium metal with water to form diatomic hydrogen gas (H_2) and uranium dioxide or uraninite (UO_2) proceeds by way of uranium hydride (UH_3). Mechanistic studies show that hydrogen radicals (H) and UH_3 serve as intermediates in the reaction of uranium metal with water to produce H_2 and UO_2. Because H_2 is flammable, its release into the gas phase above K Basin sludge during sludge storage, processing, immobilization, shipment, and disposal is a concern to operational safety.

PNNL conducted literature reviews and laboratory studies to identify methods that could be used to decrease the rate of H_2 gas generation from uranium metal corrosion in water present in sludge (Sinkov et al. 2010). Four means to decrease the H_2 evolution rate were identified for further experimental consideration:

1. decreased temperature
2. reactant isolation (separation of the uranium metal from the water)
3. corrosion inhibition
4. hydrogen scavenging.

The effect of decreased temperature could be inferred based on the known published rates of uranium metal reaction with water (Delegard and Schmidt 2009). Of the remaining three approaches, hydrogen scavenging appeared to be the most promising for laboratory testing, but experimental effort into reactant isolation and corrosion inhibition was also conducted and reported.

Laboratory testing identified nitrate, NO_3^-, and nitrite, NO_2^- (added as their sodium salts) to be the most promising agents to minimize H_2 generation in prospective K Basin sludge operations because of their demonstrated high-attenuation factors, decreasing hydrogen generation rates hundreds- to thousands-times lower than in water alone, and their small effect in decreasing the desired continued uranium metal

corrosion (Sinkov et al. 2010). Of the two, nitrate was determined to be the more desirable because it has higher chemical capacity, lower toxicity—and most importantly—more reliable efficacy and fewer side reactions than nitrite.

With these findings as a background, similar sets of laboratory experimentation were conducted in the present testing to determine if the beneficial effects of nitrate to lower the rate of H_2 generation from the reaction of uranium metal with water in simulated sludge continued for simulated sludge mixed with four different water immobilization agents. Water immobilization agents are added to meet the WIPP waste acceptance criterion that the final packaged sludge, which contains polychlorinated biphenyls, has no free liquids. The tests, conducted under controlled ~60°C, 80°C, and 95°C temperatures, used nearly spherical high-purity uranium metal beads and simulated sludge meant to emulate uranium-rich sludge currently residing in engineered containers KW-210 and KW-220 (also referred to as KW Basin-containerized sludge).

The immobilization agents tested were Portland cement (PC), a commercial blend of PC with sepiolite clay (Aquaset II H), granulated sepiolite clay (Aquaset II G), and sepiolite clay powder (Aquaset II). Solidification agent masses, where applied, were identical to the mass of solids present in the simulated sludge while the solution quantity in each test was 0.9 mL per gram of sludge solids or 0.45 mL per gram of combined sludge solids and immobilization agent. In all cases, except tests with Aquaset II G, the simulated sludge was mixed intimately with the immobilization agent before testing commenced. For Aquaset II G, the granulated clay was added to the top of the settled sludge/solution mixture according to application directions provided by the manufacturer.

The reaction characteristics were monitored by measuring gas volumes and compositions, uranium metal corrosion mass losses, and concentrations of nitrate reduction product (nitrite and ammonia) in the interstitial solutions. The uranium metal corrosion rates were determined and the observed rates compared with the rates forecasted from the STP rate law at individual test temperatures. The ratios of the STP-forecast corrosion rates to the observed rates were calculated to find the uranium metal corrosion rate attenuation factors. In a similar manner, hydrogen quantities were measured and compared with quantities expected based on non-attenuated H_2 generation of the same uranium metal masses at the full anoxic rate forecast at the test temperature by the STP rate law. The ratios of the expected to the observed H_2 productions were calculated to arrive at H_2 attenuation factors.

The uranium metal corrosion rate and H_2 generation data for the present tests were compared and combined with the results of earlier tests performed for the STP (Sinkov et al. 2010) to help determine trends in performance for the solution-only, simulant sludge, and sludge/immobilization agent systems as functions of $NaNO_3$ concentration and test temperature.

Research revealed the uranium metal corrosion rates for six systems of aqueous solution, KW-simulated sludge, and KW-simulated sludge/Aquaset II blends with and without 1 M $NaNO_3$ have reaction activation energies approximating the 16.3 kcal/mole value found in the STP rate law[1] over the studied ~60°C to ~95°C temperature range. Rates in water alone and in simulated sludge were near or slightly below the STP rate while the nitrate-free system of Aquaset II immobilizing agent with simulated

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[1] The STP rate law for uranium metal corrosion in anoxic liquid water is $\log_{10}$ rate, µm/hour = 9.6942 – 3564.8/T where T is absolute temperature in K (Schmidt and Sexton 2009). At this rate, a ¼-in. (6350-µm) diameter uranium metal particle is fully corroded in ~106 years at 20°C and ~96 days at 100°C.

sludge decreased rates by about a factor of 3 below the STP rate. The addition of 1 M $NaNO_3$ to water only decreased the corrosion rate by a factor of ~1.3 below that found for water alone and by a factor of ~2 below the STP rate. Addition of 1 M nitrate to simulated sludge decreased the corrosion rate by a factor of ~5 while addition of 1 M nitrate to sludge/Aquaset II mixtures decreased the corrosion rate by ~2.5 compared with the respective nitrate-free analogues. Overall, mixtures of simulated sludge with Aquaset II and those treated with 1 M $NaNO_3$ showed uranium corrosion rates about a factor of 8 to 10 lower than the STP rate law. The observed parallel adherence to the STP rate law in Arrhenius coordinates for these varied systems allows more confident prediction of process-scale system behavior at lower temperatures.

The uranium metal corrosion rates in 0.5 M to 2 M $NaNO_3$ solution were about a factor of 2 lower than the STP rate in water (i.e., attenuation factor of 2). Addition of 1 M $NaNO_3$ to simulated sludge decreased the uranium metal corrosion rate about a factor of 7 compared with the STP rate, but values between about 4 and 10 were observed. The corrosion rate attenuation observed for UO_2 in 0.5 M $NaNO_3$ in prior testing (Sinkov et al. 2010) was consistent with rate attenuations found for the full KW Basin-containerized sludge simulant under similar conditions. The corrosion rate for simulated sludge immobilized with Aquaset II or II G in 1 M $NaNO_3$ was about a factor of 10 lower than the STP rate. Table S.1 provides a high-level summary of the uranium metal corrosion rate attenuation factors observed at 60°C.

Table S.1. Uranium Metal Corrosion Rate Attenuation Factors at 60°C

Matrix	**Uranium Metal Corrosion Rate Attenuation Factors (Corrosion Rate Predicted by STP/Measured Corrosion Rate)**			
	0 M Nitrate	**0.5 M Nitrate**	**1 M Nitrate**	**2 M Nitrate**
U metal and water	1–1.5	2	2	2
U metal and KW simulant sludge	1.2–2.2	2–8	4–10	17
U metal, KW simulant sludge, and Aquaset II	1.4	12	8.5–11	10

Of most interest to the STP was that nitrate still provided substantial H_2 mitigation for immobilized simulant sludge waste forms containing Aquaset II or Aquaset II G clay. Hydrogen attenuation factors of 1000 or greater were found at 60°C for sludge-clay mixtures at 1 M $NaNO_3$. Results of H_2 mitigation for tests with PC and Aquaset II H (which contains PC) were inconclusive because of suspected failure of these tests to overcome their induction times and fully enter into the anoxic corrosion regime.

The effectiveness of nitrate in attenuating H_2 generation increased as nitrate concentration increased to about 1 M $NaNO_3$. For uranium corroding in aqueous solution, the H_2 attenuation factor continued to increase to at least 2 M $NaNO_3$ while no attenuation factor increase in simulated sludge or simulated sludge plus Aquaset II or II G was found above 1 M $NaNO_3$. In 1 M $NaNO_3$, H_2 attenuation factors were consistently ~1000 or higher for aqueous solution and simulated sludge at all tested temperatures (~60°C, 80°C, and 95°C) and for simulated sludge plus Aquaset II or II G at ~60°C. Some lessening of H_2 attenuation was observed at ~80°C and ~95°C for simulated sludge and Aquaset II. However, even at these higher temperatures, H_2 attenuation factors around 100 to 200 at 1 M $NaNO_3$ were observed. A high-level summary of the hydrogen generation attenuation factors for 0 to 2 M $NaNO_3$ in matrices at 60°C, 80°C, and 95°C is in Table S.2.

Table S.2. Hydrogen Generation Attenuation Factors

Matrix	**Hydrogen Generation Attenuation Factors (H_2 Predicted by STP/H_2 Measured)**			
	0 M Nitrate	**0.5 M Nitrate**	**1 M Nitrate**	**2 M Nitrate**
U metal and water, 60°C	1–10	30–150	1000–8000	70000
U metal and KW simulant sludge, 60°C	1.5–8	24–1800	3000–12000	2000
U metal, KW simulant sludge, and Aquaset II, 60°C	35	1800	900–17000	2500
U metal, KW simulant sludge, and Aquaset II, 80°C and 95°C	5–30	–	90–260	–

Even after 8 weeks at 60°C in the full uranium metal – simulant sludge – Aquaset II matrix, nitrate consumption was undetectable. This was because with 1 M sodium nitrate and with a sludge simulant containing 3.6 wt% uranium metal on a dry basis, nitrate is present in almost twelve-fold stoichiometric excess. At these tested levels, with uranium metal concentrations well above those observed in actual sludge and with readily attainable nitrate loadings in the immobilized waste form, nitrate is expected to retain efficacy even if all the uranium metal is reacted to extinction (i.e., nitrate concentration would decrease only marginally from 1 M to ~0.9 M).

As shown in prior testing and confirmed in present experiments, the hydrogen-scavenging reaction of nitrate forms dissolved ammonia and hydroxide ion (OH^-) and raises interstitial solution pH. However, even before the nitrate can react, the sodium from the added sodium nitrate exchanges onto metaschoepite and displaces hydrogen ion, H^+, lowering the solution pH.

Because of the sodium-metaschoepite reaction, the initial pH for systems containing simulant sludge and its constituent metaschoepite decreases with increasing $NaNO_3$ concentration. The initial simulant sludge pH ranges widely from about 6.5 to 9.2 in the absence of any immobilization agent and without nitrate but decreases to ~5.0 at 0.5 M $NaNO_3$ and becomes ~4.2 at 1 to 2 M $NaNO_3$. Even after heating to ~60°C to 95°C, the simulant sludge containing $NaNO_3$ solution remains at pH ~5. However, the pH of sludge immobilized and heated with Aquaset II powder or with the granular Aquaset II G is only slightly affected by nitrate concentration and decreases moderately from about 8.5 to 7.4 as nitrate concentration increases from 0 to 0.5, 1, and 2 M. Solution associated with simulant sludge treated with PC and then heated has pH ~12.6 and is hardly affected by nitrate concentration. Instead, its pH is dominated by the buffering provided by the calcium hydroxide intrinsic to the PC.

Besides ammonia and hydroxide, nitrate reduction produces dissolved nitrite and nitrogen and nitrous oxide gases. Gas analyses also showed extensive but relatively constant oxygen consumption and limited nitrogen gas consumption, which was evident in nitrate-free tests.

Satisfactory material balances were found for most tests. The chemical balance, calculated as the number of oxidized chemical equivalents divided by the number of reduced chemical equivalents, should be unity. The observed chemical balance ratios varied widely around 1 (average 0.91 ± 0.58 at 1 σ) but indicate the major reactions are accounted.

As a result of these studies, valuable additional information was obtained on the ability of nitrate to attenuate H_2 gas generation from solution, simulant sludge, and simulant sludge with immobilization agents. Details on characteristics of the associated reactions were also obtained. Present testing confirms prior work that indicates nitrate is an effective agent to attenuate H_2 generation from the corrosion of uranium metal in water and simulated K Basin sludge to show it is also effective in potential candidate solidified K Basin waste forms for WIPP disposal.

Further investigative studies should be conducted to confirm performance observed to date in simulant sludge and sludge/immobilization agent systems extend to lower temperatures, to genuine sludge, and in radiation fields to determine not only the ability of nitrate to attenuate radiolytic H_2 production, but also to determine if significant nitrate depletion occurs by radiolysis.

Levels of hydrogen mitigation afforded by nitrate addition appear to be sufficient to meet the hydrogen generation limits for shipment of various sludge waste streams based on recently measured uranium metal concentrations in engineered sludge and at assumed waste form loadings. However, the acceptability of the application of nitrate addition as a hydrogen mitigation strategy for shipment to and disposal at WIPP must be determined. The presence of nitrate within the final sludge waste form is not expected to be a concern to WIPP officials as nitrate exists in wastes already disposed to WIPP from the Rocky Flats Site and the Hanford Site. However, application of the nitrate addition strategy that includes taking credit for the active chemical reactions surrounding uranium metal corrosion requires consideration of potential modifications to underpinning shipping documentation and waste acceptance criteria.

Depending on the implementation strategy, management of the excess nitrate solution and the impact, if any, of lower pH caused by reaction of sodium ion with metaschoepite also must be evaluated. Future testing should be tailored to target particular waste streams (e.g., settler tank, and container sludge; orphan materials in sludge processing; and decommissioning and decontamination rubble) to meet specific functional design criteria within the particular points of operational insertion (e.g., storage, treatment, or shipping).

Acknowledgments

Numerous and essential gas analyses were performed by Stan Bos and Pam Berry. Cristian Iovin analyzed the test solutions for nitrate and nitrite concentration using ion chromatography. Doinita Neiner analyzed uranium solids by X-ray diffractometry and interpreted the scans. Jen Braley technically reviewed the document and provided helpful suggestions.

Acronyms and Abbreviations

ALE	Hanford Arid Lands Ecology Reserve
ASTM	ASTM International (formerly American Society for Testing and Materials)
CHPRC	CH2M Hill Plateau Remediation Company
DI	deionized water
DOE	U.S. Department of Energy
FGE	fissile gram equivalent
IC	ion chromatography
OIER	organic ion exchange resin
KE	K East
KOP	Knock-Out Pot
KW	K West
PC	Portland cement
PCBs	polychlorinated biphenyls
PNNL	Pacific Northwest National Laboratory
RH-TRAMPAC	Remote-Handled Transuranic Waste Authorized Methods for Payload Control
RH-TRU	remote-handled transuranic waste
SNF	spent nuclear fuel
STP	Sludge Treatment Project
STSC	Sludge Transport and Storage Container
WIPP	Waste Isolation Pilot Plant
XRD	X-ray diffractometry

Contents

Figures

Tables

1.0 Introduction

Sludge formed and reposing in the K East (KE) and K West (KW) fuel storage basins at the Hanford Site has been a subject of concern since extended storage of metallic fuel from the N Reactor began in the 1980s. Although the last of the spent nuclear fuel (SNF) was removed from the basins in 2004, sludge still remains in the KW Basin stored in engineered containers. Transport of the KE Basin sludge from the KE Basin to the KW Basin was completed in 2007 and the KE Basin itself demolished in 2009.

Under the Sludge Treatment Project (STP), K Basin sludge disposition will be managed in two phases. The first phase is to retrieve the sludge that currently is held at ~10°C to 18°C in engineered containers in the KW Basin pool. The six engineered containers are ~12 ft long, 5 ft wide, and 13 ft tall, and each contains between 1 and 8.1 m^3 of sludge for about 27 m^3 of total sludge (Dhaliwal and Johnson 2011). The retrieved sludge will be hydraulically loaded into sludge transport and storage containers (STSCs) and transported to interim storage in the Central Plateau before being treated and packaged for disposal (Honeyman and Rourk 2009). In the second phase of the STP, sludge will be retrieved from interim storage and treated and packaged in preparation for eventual shipment to the Waste Isolation Pilot Plant (WIPP) in New Mexico as remote-handled transuranic waste (RH-TRU). However, before the treated sludge can be shipped, it must be processed and packaged into forms acceptable to WIPP. The presence of uranium metal fuel particles in the sludge poses problems to these operations because uranium metal reacts with water to form flammable hydrogen gas.

1.1 Background

Besides uranium metal, the K Basin sludge contains uranium metal corrosion products (largely uraninite, UO_2, and metaschoepite, $UO_3 \cdot 2H_2O$); aluminum and iron hydroxides [e.g., gibbsite, $Al(OH)_3$, and ferrihydrite, $Fe_2O_3 \cdot 1.8H_2O$] from K Basin metallic structural material corrosion; inorganic and organic ion-exchange media lost inadvertently to the basins (Norton Zeolon 900 mordenite granules and mixed bed cation-anion organic ion-exchange resin [OIER], Purolite NRW37); in-blown Hanford Site soil; and Optimer 7194 Plus flocculating agent, an acrylamide co-polymer that was added during KE Basin sludge containerization to aid in settling. Other components known to be in sludge include Zircaloy cladding bits, Grafoil (a largely graphite gasket material produced as a tape about ¾-in. wide), paint chips, plastic debris (e.g., plastic bags and sheeting), hydraulic oil, trace polychlorinated biphenyls (PCBs), and biological matter (insects, grass, twigs).

There are three primary sludge types currently existing within the engineered containers located in the KW Basin: 1) KE Basin-originating floor and pit sludge (SCS-CON-240, 250, and 260), 2) KW Basin-originating floor and pit sludge SCS-CON-210 and 220), and 3) KW Basin settler sludge (SCS-CON-230).

The KE Basin-originating floor and pit sludge was vacuumed into large containers in the KE Basin from 2004 to 2005 after SNF had been removed from the KE Basin. This sludge then was transferred by hose and multiple pumps to the SCS-CON-240, 250, and 260 engineered containers located in the KW Basin with the transfer completed in 2007. The majority of the radionuclide inventory in the KW Basin floor and pit sludge is from "fuel wash sludge," containing higher concentrations of uranium metal, fuel corrosion products, and likely ion-exchange materials from KE Basin from fuel cleaning and packaging operations in the KW Basin in 2000. The KW Basin floor and pit sludge also includes Grafoil pieces and particles from disintegration of this gasket material when lids were removed from the KW fuel storage canisters. Sludge originating from the KW Basin floor and pits has been consolidated into engineered containers SCS-CON-210 and 220. The finely particulate, high-uranium sludge from fuel washing activities that is less than 600 μm in diameter and initially collected in settling tanks now resides in engineered container SCS-CON-230.

Uranium metal reacts with water in K Basin sludge to form diatomic hydrogen gas (H_2) and uranium dioxide (or uraninite, UO_2) by way of uranium hydride (UH_3). Mechanistic studies show that hydrogen radicals ($H\cdot$) and UH_3 serve as intermediates in the reaction of uranium metal with water to produce H_2 and UO_2. Because H_2 is flammable, its release into the gas phase above K Basin sludge during sludge storage, processing, immobilization, shipment, and disposal is a concern to the safety of those operations.

Prior literature review and laboratory studies have been undertaken to identify methods that could be used to decrease the rate of H_2 gas generation from uranium metal corrosion in water present in sludge. Four means to decrease the H_2 evolution rate were identified for further experimental consideration: 1) decreased temperature; 2) reactant isolation (separation of the uranium metal from the water); 3) corrosion inhibition; and 4) hydrogen scavenging. The effect of decreased temperature could be inferred based on the known published rates of uranium metal reaction with water (Delegard and Schmidt 2009). Of the remaining three approaches, hydrogen scavenging appeared to be the most promising and testing of this alternative was performed (Sinkov et al. 2010). Some experimental studies in reactant isolation and corrosion inhibition were also conducted and documented (Sinkov et al. 2010).

Based on the literature review, sodium nitrate, sodium nitrite, Nochar Acid Bond N960 (salt of a low cross-linked polyacrylic acid), disodium hydrogen phosphate, hexavalent uranium [U(VI)], and chloride were tested for their effects on the rate of hydrogen generation from the reaction of uranium metal with water (Sinkov et al. 2010). Nitrate and nitrite, tested as corrosion inhibitors and hydrogen radical scavengers, were each effective; they decreased hydrogen generation rates in actual sludge by factors of about 100 to 1000 when used at 0.5 molar (M) concentrations. Higher attenuation factors were achieved in tests with aqueous solutions alone, and most of the hydrogen attenuation was due to radical scavenging as corrosion inhibition was generally less than a factor of 10. Nochar N960, a water sorbent used to isolate the reactant water from the uranium metal, decreased hydrogen generation in water by no more than a factor of three while disodium phosphate, a putative corrosion inhibitor, actually increased the corrosion and hydrogen generation rates slightly in water. Tests combining both Nochar and nitrate or nitrite showed excellent hydrogen attenuation; however, gas-forming side reactions, especially with nitrite, also were observed. Although U(VI) showed some promise in attenuating hydrogen, the effect was small and only initial testing was completed. A single test with chloride as sodium chloride (NaCl) showed no effect, confirming findings reported in other studies in simulated ocean water (Table 2 in Peterson [1966]) and in NaCl and calcium chloride ($CaCl_2$) solutions that were 2 M in chloride (Beard et al. 1971). Early work (Mollison et al. 1945) showed that uranium metal corrosion rate at 100°C decreased only marginally (by a factor of ~1.9) as NaCl concentration increased from 0 to 20 wt% or ~3.9 M.

Of the candidate agents tested, nitrate, NO_3^-, and nitrite, NO_2^- (added as their sodium salts) were determined to be the most promising for application to K Basin sludge operations because of their demonstrated high-hydrogen attenuation factors and small effect in decreasing the desired continued uranium metal corrosion. Of the two, nitrite has lower chemical capacity, greater toxicity, and was less efficacious than nitrate, producing unwanted gaseous products including nitric oxide (NO). Greater amounts of gas were found for tests that contained nitrite with organic constituents (e.g., Nochar N960) and simulant sludge containing ferrihydrite. Nitrite's capacity to scavenge its intermediate reduction products, which short-circuits their further reduction to ammonia, NH_3, leads to formation of gases of intermediate oxidation state (e.g., NO, N_2O, N_2). Ferrihydrite's influence was postulated to arise by the role it plays in mediating UO_2 oxidation by nitrite. In contrast, testing showed that nitrate produced little, if any, of the undesired NO gas but formed nitrite and ultimately NH_3 reduction product.

Hydrogen from the U–H_2O reaction poses significant challenges to the safety of the following planned sludge transport, storage, processing, and disposal activities:

- movement of sludge from its near-river K Basin location to T Plant
- storage and potential processing at T Plant or other location
- transport and disposal of the treated sludge as RH-TRU to WIPP.

Although the efficacy of nitrate in attenuating H_2 gas generation in water, simulated sludge, and genuine sludge was demonstrated in prior testing (Sinkov et al. 2010), the efficacy of nitrate in attenuating H_2 generation in waste forms suitable for WIPP has not yet been demonstrated except in limited testing of nitrate with Nochar. The WIPP waste forms must satisfy the requirement that drainable liquid constitutes no more that 1% of the waste volume. However, because of the presence of PCBs in the sludge, no drainable liquid is permitted for WIPP disposal.

Agents used to immobilize drainable liquids and thus help satisfy WIPP waste form requirements to limit or eliminate drainable liquid generally include Portland cement (PC) grout, Nochar, and inorganic sorbents (e.g., kitty litter, clay). Based on this experience, and the prior findings that Nochar and nitrate produce unwanted gases (Sinkov et al. 2010), tests were performed using PC, sepiolite clay, and a blend of PC and sepiolite clay. The tests investigate the influences of these agents on the corrosion rate and H_2 gas generation rate of simulated sludge in the absence and presence of added sodium nitrate salt.

1.2 Hydrogen Gas Mitigation Target

To prepare the sludge to meet WIPP waste acceptance criteria and to maximize the sludge quantity that can be loaded into each container, the quantity of hydrogen released from the reaction of uranium metal with the associated water must be diminished.

The following assessment illustrates the extent to which hydrogen release must be diminished to meet the shipping requirements of the RH-TRAMPAC (Remote-Handled Transuranic Waste Authorized Methods for Payload Control) based on assumed packaging and current estimates of the sludge uranium metal concentration. The basis of this assessment includes estimates of the quantities of various K Basin sludge streams that may be loaded to a 55-gal drum for disposal to WIPP as RH-TRU assuming no hydrogen gas mitigation, and assuming hydrogen mitigation features will reduce the hydrogen by a factor of 100. The present assessment only considers hydrogen generation from the uranium metal reaction with water and does not consider hydrogen generation by radiolysis that will further limit the quantity of uranium metal that may be present.

Criteria other than hydrogen generation also may limit sludge loading in the final waste container. For the sludge waste streams, these criteria include meeting limits for ^{239}Pu fissile gram equivalents

(FGEs), surface dose rate, and the volume of sludge that may be transferred in each of the three 55-gallon (or 30-gallon) drums packaged in a 72-B cask for disposal at WIPP. Based on physical constraints and preliminary operability considerations, the nominal volume of "as-settled sludge" that may be loaded into a 55-gallon drum to produce a final grouted waste form is about 80 L.

For fissile component loading purposes, the practical per-drum limit is 75 g ^{239}Pu FGE. The amount of sludge that can be delivered per drum necessarily decreases as the fissile concentration of the sludge increases. The design basis concentration of ^{239}Pu FGE in containers KW Basin SCS-CON-240, 250, and 260 is 702 ^{239}Pu FGE/m^3 (Table 2-3 of Johnson 2010); this means the 75-g ^{239}Pu FGE limit is met with 75/702 = 0.107 m^3 or 107 L. For design basis KW Basin container (SCS-CON-210 and 220) and settler sludge (SCS-CON-230) concentrations of 1560 and 7340 FGE/m^3, 75-g ^{239}Pu FGE is attained with 48 and 10.2 L of sludge, respectively.

The maximum uranium metal mass that can be loaded into a RH-TRU drum without exceeding the per-drum hydrogen gas generation rate limit of 7.0×10^{-8} moles of hydrogen per second is 25 g based on the assumptions and parameters given at the bottom of Table 1.1 for the nominal 500-µm diameter uranium metal found in SCS-CON-210, 220, 240, 250 and 260.[2] This assessment assumes no mitigation in the anoxic water-uranium metal reaction rate and no credit for uranium metal corrosion during storage prior to drum shipment to WIPP, but also does not take into account radiolytic hydrogen generation. Because the effective uranium metal diameter in SCS-CON-230 sludge is 375-µm, it has higher specific surface area than the 500-µm diameter uranium metal found in the other containers and the uranium metal mass limit is only about 19 g without hydrogen gas mitigation.

The design-basis uranium metal concentrations in each sludge type can be combined with the unmitigated 25- and 19-g uranium metal mass limits to calculate the maximum sludge volume that can be loaded in a drum based on the hydrogen gas generation rate. The maximum quantity for sludge held in SCS-CON-240, 250 and 260, which contains 6.0 g of 500-µm diameter uranium metal per liter, is 4.2 L, taking no credit for hydrogen rate attenuation by nitrate addition and the solidification matrix shown in Equation (1):

$$25 \text{ g U metal} \times \frac{\text{liter}}{6 \text{ g U metal}} = 4.2 \text{ liters} \tag{1}$$

By similar calculations, the per-drum loading for sludge from SCS-CON-210 and 220 (at 30 g uranium metal/liter) is 0.85 L and for SCS-CON-230 sludge is 0.37 L (at 52 g uranium metal/liter). With a hydrogen gas release attenuation factor of 100, the maximum settled sludge loadings as constrained by hydrogen gas generation rate would increase correspondingly by a factor of 100.

The above assessments are summarized in the analysis shown in Table 1.1. This analysis considers hydrogen generation, ^{239}Pu FGE, and "as-settled sludge" physical volume loading limits and shows that in the absence of hydrogen mitigation, drum loading is limited by hydrogen generation rate for sludge in all storage containers. However, if the hydrogen generation rate during shipment to WIPP can be reduced by a factor of 100, the sludge volume will be limited by either ^{239}Pu FGE loading (for SCS-CON-210, 220,

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[2] The value of 7.0×10^{-8} moles H_2 per second is an STP estimated limit that was provided on March 29, 2011, and based on interpretations of the Transuranic Waste Authorized Methods for Payload Control (TRAMPAC) and discussions with WIPP staff.

and 230) or by physical volume considerations (for SCS-CON-240, 250, and 260) and not by the amount of uranium metal available to react to form hydrogen in the container. Based on these evaluations, 100-fold hydrogen generation rate mitigation removes hydrogen generation as a limit in drum loading and affords a meaningful target performance for nitrate addition to K Basin sludge.

Table 1.1. RH-TRU Drum Loading Limits for K Basin Sludge Streams

Drum Loading Volumetric Limits			
Drum Load Limiting Factors	**Design Basis SCS-CON- 240, 250, 260**	**Design Basis SCS-CON-210, 220**	**Design Basis SCS-CON-230**
• **H_2 Generation with and without Mitigation**	**Maximum Design-Basis Settled Sludge Volume per Drum Based on H_2 Rate Limit, liters**		
No mitigation, no radiolysis; SNF rate(a)	4.2	0.85	0.37
H2 mitigation with target factor of 100(b)	420	85	37
• **^{239}Pu FGE**	**Maximum Design-Basis Settled Sludge Volume per Drum Based on 75-g ^{239}Pu FGE, liters(c)**		
	107	48	10.2
• **As-Settled Sludge Physical Volume**	**Maximum Design-Basis Settled Sludge Volume per Drum Based on Drum Volume, liters**		
	80	80	80
Load Limiting Parameter			
Hydrogen Mitigation Option	**Design Basis SCS-CON-240, 250, 260**	**Design Basis SCS-CON-210, 220**	**Design Basis SCS-CON-230**
No H_2 mitigation	H_2	H_2	H_2
100× H_2 mitigation	Drum Volume	^{239}Pu FGE	^{239}Pu FGE
Settled Sludge Design-Basis Values			
Parameter or Concentration	**Design Basis SCS-CON- 240, 250, 260**	**Design Basis SCS-CON-210, 220**	**Design Basis SCS-CON-230**
Maximum quantity uranium metal/drum, g(a)	25		19
U metal concentration, g U/liter(d)	6.0	30	52
Effective U metal particle size, μm(d)	500	500	375

(a) Drum gas generation is limited to 7.0×10^{-8} moles H_2/sec. The maximum uranium metal quantity is calculated based on the effective uranium metal particle size with uranium corroding at 60°C (WIPP transportation maximum) according to the SNF databook uranium metal corrosion rate law (Schmidt 2010). No H_2 production by water or organic radiolysis is considered in this evaluation.

(b) Target goal of solidified waste form with nitrate addition is to reduce H_2 generation rate 100-fold.

(c) The maximum sludge drum loading is 75 g of ^{239}Pu fissile gram equivalents (FGE). Containers KW Basin SCS-CON-240, -250, and -260 have 702 ^{239}Pu FGE/m^3 (design basis; Table 2-3 of Johnson 2010) and thus can hold 75/702 = 0.107 m^3 or 107 L. With FGE concentrations in design basis KW Basin container (SCS-CON-210 and 220) and settler sludge (SCS-CON-230) of 1560 and 7340 FGE/m^3, 75-g ^{239}Pu FGE is attained with 48 and 10.2 L of sludge, respectively.

(d) Sludge design-basis parameters found in Schmidt (2010).

2.0 Experimental Materials and Methods

Experiments were conducted using a simulated KW Basin-containerized sludge in the presence and absence of solution absorbents and with or without added sodium nitrate solution. All but two experiments contained 30 uranium metal beads of roughly 700-µm diameter weighing ~0.1 g in total. These beads are near in size to the ~560-µm uranium metal particle size observed in earlier analyses of K Basin sludge (Delegard and Schmidt 2009). The testing was performed in closed vessels designed to collect and contain the starting air and product gases with the test materials held at thermostatically controlled temperatures. Three test series were performed. The third series was split into identical experimental sets but at two different temperatures. Each test series and temperature had a control test containing only uranium metal beads and water.

The three test series followed test instructions approved by project and client personnel[3] and were conducted under the Radiochemical Processing Laboratory procedure for routine research operations.[4] Chemicals and materials used in the testing are described in Section 2.1, the corrosion experiments are described in Section 2.2, and the analytical methods are outlined in Section 2.3.

2.1 Chemicals and Materials

The sodium nitrate ($NaNO_3$) used as the hydrogen mitigation agent in these test series was reagent grade. Solutions were prepared with distilled and deionized (DI) water. Many of the tests were performed using simulated sludge. The sludge composition and compositions of the sludge ingredients are described in Section 2.1.1. The compositions and properties of the various tested water/solution immobilization agents are described in Section 2.1.2.

2.1.1 Simulated Sludge Composition

Components in the KW Basin-containerized sludge simulant include uranium metal, UO_2, $UO_3 \cdot 2H_2O$, ferrihydrite [$Fe_5O_7(OH) \cdot 4H_2O$; i.e., $Fe_2O_3 \cdot 1.8H_2O$], gibbsite [$Al(OH)_3$], Hanford Arid Lands Ecology Reserve (ALE) sand, Purolite NRW37 OIER, mordenite inorganic ion exchanger, Optimer 7194 Plus flocculating agent, and water. The sludge composition used in all testing was derived from the composition of a physical/chemical simulant designed to model the expected composition of sludge present in the KW Basin SCS-CON-240, -250, and -260 containers. The identities and distributions of the sludge constituents were informed by prior sludge characterization studies (Makenas et al. 1996, 1997, 1998, and 1999). The sludge component quantities required to prepare 2.776-g (dry basis) portions of simulated sludge, corresponding to about 3.264 mL of settled sludge, are shown in the right-hand column in Table 2.1.

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[3] Delegard CH. 2010. *Hydrogen Mitigation by Nitrate in KW Container Sludge Simulants and Waste Forms*. 53451-TI25, Pacific Northwest National Laboratory, Richland, Washington.
Delegard CH. 2010. *Hydrogen Mitigation by Nitrate in KW Container Sludge Simulants and Waste Forms – Round 2*. 53451-TI28, Pacific Northwest National Laboratory, Richland, Washington.
Delegard CH. 2010. *Hydrogen Mitigation by Nitrate in KW Container Sludge Simulants and Waste Forms – Round 3*. 53451-TI36, Pacific Northwest National Laboratory, Richland, Washington.

[4] *Routine Research Operations*. RPL-OP-001 (revision current at the time of testing), Pacific Northwest National Laboratory, Richland, Washington.

Table 2.1. KW Basin Simulated Containerized Sludge Basis and Composition

KW Basin Container Simulant – Physical/Chemical (Burbank 2010)		Uranium, OIER, and Mordenite Components Added			Target Quantities to Prepare 3.264 mL of Settled Sludge Simulant	
Material	**Amt., wt%**	**Material**	**Amt., wt%**	**Amt., g/mL**	**Material**	**Amt., g**
FeOOH or $Fe(OH)_3$	21.9	Ferrihydrite	21.9	0.186	Ferrihydrite	0.608
$Al(OH)_3$	7.8	$Al(OH)_3$	7.8	0.066	$Al(OH)_3$	0.217
Sand	14.7	ALE sand(a,b)	16.4	0.139	ALE sand	0.455(b)
Aggregate	16.9	OIER(b,c)	7.5	0.064	OIER	0.208(b)
		Mordenite(b,d)	7.7	0.066	Mordenite	0.213(b)
CeO_2 or equivalent	30.9	UO_2(e)	16.0	0.136	50:50 mol% UO_2:$UO_3\cdot 2H_2O$, (0.445 g UO_2, 0.530 g $UO_3\cdot 2H_2O$; 0.784 g U)	“W”(f)
Steel grit or equivalent	4.2	$UO_3\cdot 2H_2O$(e)	19.1	0.162		
Dense metal or alloy	3.6	U metal	3.6	0.0306	U metal	0.100
Total	100.0	Total	100.0	0.851	Total dry weight	2.776
					Added water	(f)
					Flocculating agent – 0.5 wt% Optimer 7194 Plus(g)	1.740

(a) ALE sand weight corresponds to the amount of sand in the physical/chemical stimulant, plus the aggregate left over after deducting the OIER and Mordenite weights.

(b) ALE sand in the first test series was 27.6 wt%, and OIER and mordenite were 2.0 wt% of dry ingredients. Target masses were 0.055 g OIER, 0.056 g mordenite, and 0.767 g ALE sand.

(c) The relative OIER amount corresponds to the amount in KE Basin sludge (1.05 m^3 OIER/18.4 m^3 total sludge) based on the density of OIER (Purolite 2007) and the assumptions the OIER ratio in KW Basin sludge is the same as that in KE Basin sludge, and the volume fractions water in settled OIER and settled sludge are equal.

(d) The relative mordenite amount is based on the amount in KE Basin sludge (20 ft^3, or 0.566 m^3, of mordenite in 18.4 m^3 total sludge); the assumption is the mordenite ratio in KW Basin sludge is the same as that in KE Basin sludge, and the assumption the volume fractions water in settled mordenite and settled sludge are equal.

(e) The UO_2 and $UO_3\cdot 2H_2O$ combined weights correspond to the sum of CeO_2 (or equivalent) and steel grit (or equivalent) weights where CeO_2 and steel grit are physical representations of particulate and agglomerated uranium oxide, respectively. The UO_2 to $UO_3\cdot 2H_2O$ distribution is 50:50 mole% U(IV) and U(VI), ±5% (i.e., 45:55 to 55:45).

(f) Water in wet $UO_2/UO_3\cdot 2H_2O$, “W” g, 1.740 g in the flocculating agent, and added water make 5.00 mL total $NaNO_3$ solution; 2.50 mL solution samples withdrawn to confirm $NaNO_3$ initial concentration by spectrophotometry or ion chromatography. Tests without $NaNO_3$ have 2.50 mL of water.

(g) From a 0.5 wt% dispersion of Optimer 7194 Plus, 1.740 g (or mL; containing 0.0087 g flocculant) is added to the sludge solid components. The flocculant amount is based on Moore and Duncan (2005) projections but adjusted downward to be ~55% of that projected according to later estimates of actual flocculant usage and losses.

The properties and compositions of the uranium metal, UO_2, $UO_3\cdot 2H_2O$, ferrihydrite, gibbsite, Hanford ALE sand, OIER, mordenite, and flocculating agent simulated sludge components are described in the following paragraphs.

The uranium metal used in the testing is of natural enrichment and in the form of nearly spherical beads. Prior energy dispersive spectroscopy showed aluminum and iron present in small but non-quantified concentrations. Spectrophotometric analyses of a solution produced by quantitatively dissolving a portion of the metal in nitric acid showed the uranium concentration in the metal to be 99.7±0.2 wt%. Analyses of the dissolved metal by kinetic phosphorescence showed the uranium concentration to be 100±1%.[5] Based on analyses of the gas products observed by corroding metal samples in hot water, carbon concentration in the uranium metal is estimated to be 73 parts per million parts of uranium (Delegard et al. 2004).

The uranium metal beads were cleaned of uranium oxide surface corrosion before experimental use by immersing the beads in either 2 M sodium carbonate (Na_2CO_3) solution containing 1% hydrogen peroxide (H_2O_2) or in ~6 M HNO_3 at room temperature until visibly shiny. The chemicals used in cleaning were reagent grade and discarded after use. The clean beads were rinsed with DI water, air dried, and often stored under ethanol until use. In all but two of the present experiments, 30 beads were used. The beads were individually selected for roundness and size such that the 30 beads weighed 0.10 to 0.11 g in total. Based on 19.04 g/cm^3 uranium metal density (Grenthe et al. 2006) for 30 beads weighing 0.1 g, the average bead diameter was about 693 μm. Three hundred uranium metal beads were used in the other two tests.

Mixtures of uranium dioxide (UO_2) and metaschoepite ($UO_3 \cdot 2H_2O$) were prepared by oxidation of UO_2 in aqueous suspension with a pure oxygen gas sparge (Sinkov et al. 2008). The target oxidation state distribution was 50±5 mole% U(IV), as UO_2, and 50±5 mole% U(VI), as $UO_3 \cdot 2H_2O$. Attainment of that distribution was established by spectrophotometry using an internal procedure.[6] The UO_2 was obtained by PNNL from an outside vendor who prepared it by reacting high-purity (99.96 wt%) uranium metal turnings in ~60°C water. The source uranium metal was isotopically depleted to 0.19% ^{235}U. The UO_2 has been kept under water in its original closed jars since preparation until needed for experiment. Characterization tests showed UO_2 to be nearly stoichiometric, of nominal 6-nm diameter intrinsic particle size, and containing larger agglomerates (Sinkov et al. 2008). The densities of the pure UO_2 and $UO_3 \cdot 2H_2O$ phases are 10.964 g/cm^3 and 5.00 g/cm^3, respectively (Grenthe et al. 2006).

The ferrihydrite used in the testing was identified as ferric oxide hydroxide by the vendor, Shepherd Chemical Company. The vendor found by X-ray diffractometry (XRD) analysis that the material contained significant 6-line ferrihydrite when synthesized in 2004. Subsequent XRD analysis by PNNL in 2009 found only hematite (α-Fe_2O_3 or Fe_2O_3; ~64%) and goethite (α-FeOOH or FeOOH; ~36%) according to Rietveld analysis of the diffraction pattern (Sinkov et al. 2010). As observed elsewhere (Jambor and Dutrizac 1998), the poorly crystalline hematite and goethite phases arise from slow room-temperature transformation of ferrihydrite. Ferrihydrite density is 3.93 g/cm^3.[7]

The aluminum hydroxide used for the Round 1 and Round 2 tests was reagent-grade chemical (JT Baker [now Mallinckrodt Baker, Inc.]). This material was identified to be gibbsite by prior XRD analyses. The aluminum hydroxide used in the Round 3 tests was Onyx OC1000, produced by Almatis,

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[5] Jones SA. 2009. *Sample Preparation for Determination of Uranium Metal Concentration in Sludge.* RPG-CMC-107, Revs. 0 and 1, Pacific Northwest National Laboratory, Richland, Washington.

[6] Delegard CH. 2009. *Sample Preparation and Analysis for Determining Uranium Oxide Oxidation States in K Basin Sludges*. RPG-CMC-255, Rev. 0, Pacific Northwest National Laboratory, Richland, Washington.

[7] Density data from Web Mineral: http://webmineral.com/Alphabetical_Listing.shtml. Accessed February 1, 2011.

Incorporated. According to vendor information, it is also gibbsite. Gibbsite density is 2.42 g/cm^3 (Anthony et al. 2011).

Hanford Site ALE sand contains quartz (SiO_2), anorthite ($CaAl_2Si_2O_8$), aegerine ($Fe_{0.5185}Al_{0.4815}Ca_{0.466}Na_{0.534}Si_2O_6$), mica [$KFe_3(Al_{0.24}Fe_{0.76}Si_3)O_{10}(OH)_2$], and microcline ($KAlSi_3O_8$) according to XRD analysis (Sinkov et al. 2010). The 2.39 g/cm^3 particle density for the Hanford ALE sand mixture was determined by water displacement.

The mordenite used in the testing was sodium mordenite LZM-5 from UOP, LLC. The LZM-5 was selected to substitute for the Norton Zeolon 900 mordenite used to remove radioactive cesium from the K Basins because Norton Zeolon 900 was no longer available for testing. Dry LZM-5 is nominally $Na_6Al_6Si_{42}O_{96}$, ignoring associated water, and is equivalent to $NaAlSi_7O_{16}$ for a Si:Al mole ratio of 7.0 (Ramachandran et al. 2005). The chemical composition of Zeolon 900 (containing 98% mordenite) is reported to have the formula $Na_2Al_2Si_{10}O_{24}$ for an Si:Al mole ratio of 5.0.[8] Natural mordenite, from which Norton Zeolon 900 was derived, varies little in composition in the field and has the nominal composition of $(Na_2,Ca,K_2)Al_2Si_{10}O_{24}\cdot 7H_2O$ (Passaglia 1975) and thus has identical metal:oxygen ratios to those reported for Zeolon 900. The density of natural mordenite is 2.125 g/cm^3 (Anthony et al. 2011).

Purolite NRW37, a 40:60 (by volume) mixture of strong acid cation (NRW100) and strong base anion (NRW400) resin, was the OIER used to control water quality in the K Basins and likewise was used in the sludge simulant. The particle density of the mixed resin, 1.12 g/cm^3, was calculated based on the distribution and densities of the individual components.[9]

Based on the particle densities of the individual solid sludge components and their proportions as described in Table 2.1, the particle density of the blended simulant sludge is 3.18 g/cm^3. The 2.776 g of dry solids used in each test calling for simulant sludge thus displaced 0.87 cm^3 of the total 3.26 cm^3 wet sludge volume.

Optimer 7194 Plus flocculating agent was used during K East Basin sludge consolidation operations, in the KE and KW sludge transfer operations, and in preparing the sludge simulant. The Optimer 7194 Plus used in simulant preparation was obtained from the Nalco distributor as a concentrate. The concentrate was diluted to a 0.5-wt% dispersion in water, and the diluted Optimer was introduced to the water-suspended sludge solids according to manufacturer's recommendations and in amounts corresponding to the cumulative values added to K Basin sludge.

2.1.2 Solidifying and Liquid-Absorbing Agents

The candidate sludge-solidifying and liquid-absorbing agents tested in the present investigative studies were American Society for Testing and Materials (ASTM International) Type I/II PC grout from Lehigh Cement Company, and three commercially available inorganic sorbents used for hazardous and radioactive aqueous waste solutions. The three solution sorbents tested were Aquaset II, Aquaset II G, and Aquaset II H (Fluid Tech 2010). All of the Aquaset agents contain sepiolite clay. Aquaset II and II

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[8] Hastings TW. 1997. FAX communication to I Papp (Numatec Hanford Corporation) from TW Hastings (Zeolyst International), no subject, May 19, 1997, Valley Forge, Pennsylvania.

[9] The NRW400 anion resin has a density of 1.07 g/cm^3 and the NRW100 cation resin has a density of 1.20 g/cm^3. They are represented, respectively, as 21.8 kg/ft^3 and 39.3 kg/ft^3 in the mixed NRW37 resin (Purolite 2007).

G are sepiolite clay in powder and granular forms, respectively, while Aquaset II H is a mixture of sepiolite clay and PC powders. Sepiolite clay particle density is 2.26 g/cm^3 (Anthony et al. 2011).

Unlike layer-type clays, which collapse in brines (such as the $NaNO_3$ solutions needed for hydrogen mitigation) and thus lose much of their abilities to retain solution, the sepiolite clays present in the Aquaset materials are needle-shaped and do not lose their sorptive capacity in brine.[10]

The selection of 2.50 mL of total solution volume arose from scoping tests of sludge-solidifying agent loading. Tests for 0.5 M and 2.0 M $NaNO_3$ sorption were performed with 1:1 weight ratios of nonradioactive dry simulated sludge, in which ceric oxide (CeO_2) was used in place of uranium oxides, and the candidate solidifying agents.[11] The incipient presence of free liquid for both 0.5 and 2 M $NaNO_3$ was shown at loadings corresponding to ~1.0 mL/g PC, ~1.1 mL/g Aquaset II H, and ~1.3 mL/g Aquaset II G. A test using 0.9 mL of 1 M $NaNO_3$/g Aquaset II powder was found to be dry.

Based on these findings, and to be conservative in recognizing that no free liquid is permitted in final waste packages destined for WIPP, the solution loading for the tests with sorbents was selected to be 0.9 mL/g sorbent (equivalent to 0.9 mL/g dry sludge solids). The vendor recommendation for Aquaset II application to aqueous solution only (no contained solids) is 2.4 mL/g, over two times greater than used in the present testing that also contained sludge solids. The proportions used in the present tests produced thick pastes. No further effort was made to optimize the sludge/solidifying agent formulation. Instead, the proportions of solidifying agent were selected to make a dry but workable waste form and provide the greatest challenge to nitrate solution contact with the contained uranium metal. Because the mass of dry sludge solids in the tests is 2.776 g (Table 2.1), the solution volume is 0.9 mL/g × 2.776 g = 2.50 mL. For consistency, the quantities of sludge solids and solution used in the sludge-only tests also were 2.776 g and 2.50 mL, respectively. Therefore, the weight ratio of solidifying agent to dry sludge used in testing was 1:1 as a conservative (high) estimate of solid absorbent demand to be applied in practice.

The particle volume of the 2.776 g of Aquaset II used in testing calling for this material was 1.228 cm^3, the particle volume of 2.776 g of Aquaset II G (density 2.20 g/cm^3) was 1.26 cm^3, and the particle volume of 2.776 g of PC (density ~3.15 g/cm^3) was 0.88 cm^3. The waste form volume immobilized with Aquaset II is expected to be the sum of the constituent simulated sludge solids, sodium nitrate solution, and added Aquaset II or 4.60 cm^3 for a combined mixture density of 1.79 g/cm^3 for 1 M $NaNO_3$.[12] The waste form volumes for the Aquaset II G products are greater than the corresponding sum of constituents because the granular Aquaset II G is merely added to the top of the settled sludge solids without mixing.

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[10] Attapulgite clays, which were proposed for use for the Mobile Grout Facility (Gilliam et al. 1987) and have acicular (needle-like) shapes similar to sepiolite clay (e.g., Aquaset II), were selected for their effectiveness to sorb the largely $NaNO_3$ Hanford Site tank waste brines. Plate-shaped bentonite clays typically used for water sorption (e.g., Aquaset) have interlayers that collapse in briny solutions and lose solution sorption effectiveness.

[11] This ratio was selected based on prior projected ~96-L maximum settled sludge loading in 220-L drums and estimated additional sorbent space allowed by the remaining drum freeboard and corresponds to the ~96-L volume-limited sludge loadings projected by British Nuclear Group America for grouted waste forms (Table 3-3 of Woodworth and Pillai 2007). See also Table 1.1 in the present report.

[12] The minimum vendor-suggested application rate for Aquaset II for solids-free aqueous high ionic concentration solution is ~3 lb per gallon (equivalent to ~0.36 g/mL solution; page 3 of http://www.fluid-tech-inc.com/library/FTI_Product_Description_1245450209.pdf). Up to 4 to 5 lb per gallon (0.48 to 0.60 g/mL) provides a thin peanut-butter consistency (telephone conversation with Scott Rowsell, Fluid-Tech Inc.). The present testing application rate with sludge solids present was 2.776 g/2.50 mL = 1.11 g/mL.

The waste form volumes for the PC products likely are close to the sum of the components (4.25 cm^3; 1.93 g/cm^3 density for 1 M $NaNO_3$) but PC products can swell or shrink upon curing. Scoping tests with non-radioactive sludge simulants showed that PC products swell resulting in lower product density.

The volumes after testing of the mixtures prepared with the Aquaset II and PC immobilizing agents were measured so that full-scale product densities and volumes could be forecast.

2.2 Corrosion Experiment Apparatus and Test Matrices

The H_2 gas mitigation afforded by treating simulated sludge and candidate sludge waste forms with nitrate at various concentrations was determined in gas generation test apparatus whose designs were based on prior test experience. Tests were conducted in three series. In each series, a single control test of uranium metal in water was performed. Except as noted in the following sentence, uranium metal quantities in each test were ~0.1 g, weighed to ±0.00001 g, and added as 30 uranium metal beads of nominal 700-µm diameter. The second tests in the first two series contained 300 ~700-µm diameter uranium metal beads (~1 g , weighed to ±0.00001 g) and were done in the presence of 0.5 M and 1 M sodium nitrate, $NaNO_3$, respectively. The remaining tests in each series were of simulated sludge or of simulated sludge to which solution absorbent or solidifying agent had been added and contained sodium nitrate solution concentrations ranging from 0 to 2 M.

For shipment of RH-TRU to WIPP, a 60-day shipping window with the package temperature at 60°C is assumed for purposes of estimating hydrogen gas concentrations within the shipping container. As a result, most of the hydrogen mitigation testing was conducted at 60°C with limited testing at higher temperatures; test durations at 60°C ranged from 28 to 56 days. The extent of anoxic uranium metal corrosion for 56 days at 60°C is equivalent to about 4.5 years at 20°C.

Series 1 and 2 tests were run at 60°C and started with brief (several-hour) intervals at 90°C to help overcome the induction times observed in prior tests of uranium corrosion at 60°C. The induction times were found for tests of uranium metal corrosion in water, simulated sludge, and simulated sludge with grout (Delegard et al. 2004). Half of the Series 3 tests were run at 80°C and the other half were run at 95°C. Because high temperatures were employed in the Series 3 tests, no preliminary elevated temperature period was used.

The 4-week times at 60°C for most tests should have achieved about 66-µm corrosion penetration, according to the nominal STP rate of uranium corrosion in the anoxic liquid water control tests, and corroded about 49% of the starting ~0.1-g uranium weight of the ~693 µm beads. The 8-week times at 60°C used in several tests in Series 2 should have removed about 132 µm of depth from the beads at the STP rate law and corroded about 77% of the starting uranium weight. The 10-day (240 hours) and 4-day (96 hours) time at 80°C and 95°C, respectively, would attain 96 µm, and 98 µm corrosion penetration, respectively, and corrode ~64% of the starting uranium weight. The actual experimental uranium metal corrosion rates were calculated by measuring weight losses over the time spans of the corrosion tests based on assumption of nearly spherical and uniform uranium metal bead shape and size.

In all of the tests in Series 1, the materials were contained in ~7-mL plastic vials held within heat-conducting water baths in 25-mL glass vials. The 25-mL vials were placed in thermostatted heat blocks controlled to 60°C. The inner plastic vials were used because scoping tests showed that PC-based agents swell upon curing and would break glass vials in which they were cast. The test apparatus diagram for Series 1 is shown in Figure 2.1.

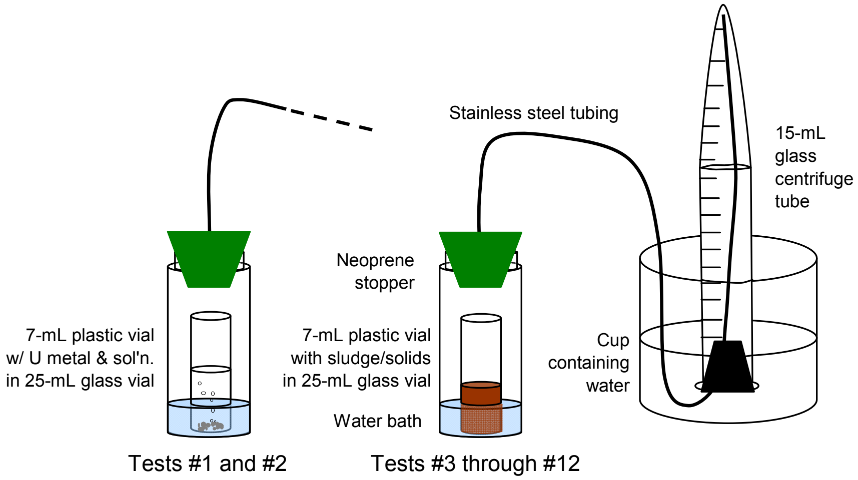

Figure 2.1. Sketch of Apparatus for Test Series 1 with 7-mL Sample Vial and 25-mL Gas Vial and Bath

Although useful data were obtained in Series 1, it was found that water evaporated from test materials in the inner vials, condensed on the walls of the outer glass vial, and reported to the water bath causing salt concentrations in the test materials to become higher than intended. Therefore, the apparatus used in Series 2 was modified to not require the inner bath (Figure 2.2). The design also conforms to the apparatus used in prior testing (Sinkov et al. 2010) but with a smaller (10-mL) glass vial to decrease the volume of contained air and attendant oxygen. Like the Series 1 tests, all Series 2 tests were run at 60°C.

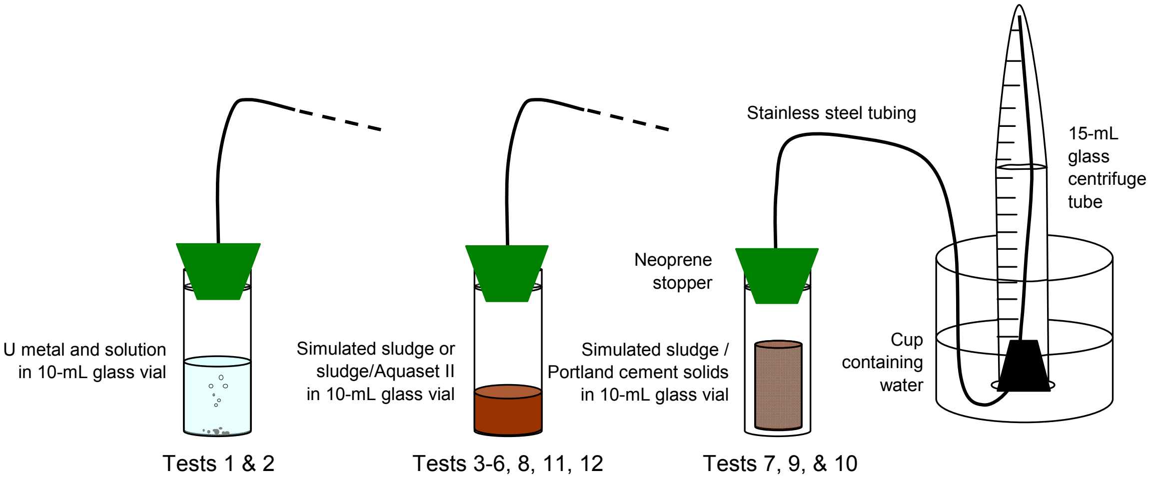

Figure 2.2. Sketch of Apparatus for Test Series 2 with 10-mL Gas Vial

Although the apparatus used for Series 2 decreased the volume of contained air and attendant oxygen, evaporative losses to the gas collection tube were found to be high because no opportunity for water reflux existed for the relatively short 10-mL tubes that were completely sheathed in the heater block. Therefore, the tests performed for Series 3 employed the taller 16-mL (4-dram) vials used in most prior testing (Sinkov et al. 2010) to allow water reflux to occur (Figure 2.3). The degree of reflux became more important for Series 3 because the experiments were conducted at 80°C and 95°C.

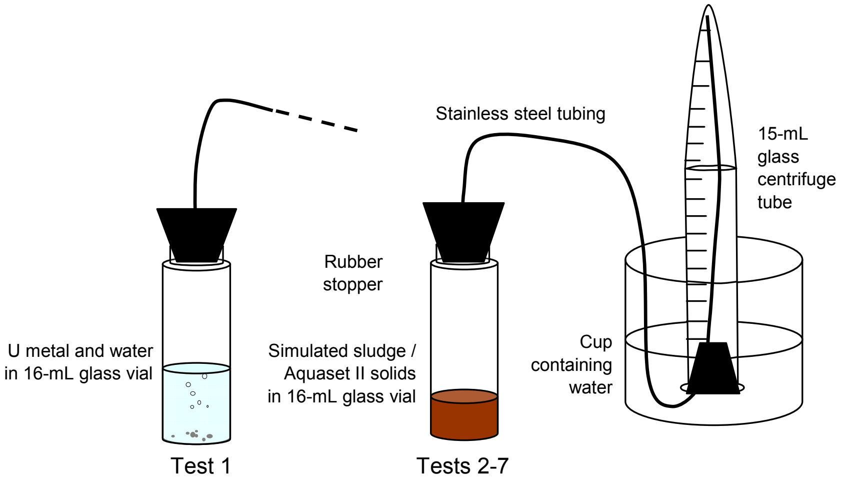

Figure 2.3. Sketch of Apparatus for Test Series 3 with 16-mL Gas Vial

The test matrix run under Series 1 is shown in Table 2.2. The candidate sludge solution absorption agents tested in Series 1 were Type I/II PC grout, Aquaset II H, and Aquaset II G.

Table 2.2. Series 1 Matrix for Hydrogen Mitigation Testing by Nitrate in Solidified Waste Forms

Test	Test Compositions[(a)]	Test Objectives
1	Water	Control to determine H_2 generation in water alone
2	1 M $NaNO_3$	To mimic KOP sludge[(b)]
3	Sim. sludge[(c)] in water	To determine H_2 generation in simulated sludge alone
4	Sim. sludge in 0.5 M $NaNO_3$	In comparison with Test 3, determine effects of nitrate concentration on H_2 mitigation in simulated sludge
5	Sim. sludge in 1 M $NaNO_3$	
6	Sim. sludge in 2 M $NaNO_3$	
7	Sim. sludge in 0.5 M $NaNO_3$ in PC	To determine the effectiveness of nitrate as functions of its concentration in PC/sludge
8	Sim. sludge in 2 M $NaNO_3$ in PC	
9	Sim. sludge in 0.5 M $NaNO_3$ in Aquaset II H	To determine the effectiveness of nitrate as functions of its concentration in sepiolite-PC (Aquaset II H)/sludge
10	Sim. sludge in 2 M $NaNO_3$ in Aquaset II H	
11	Sim. sludge in 0.5 M $NaNO_3$ in Aquaset II G	To determine the effectiveness of nitrate as functions of its concentration in granulated sepiolite (Aquaset II G)/sludge
12	Sim. sludge in 2 M $NaNO_3$ in Aquaset II G	

Sim. = Simulated.

(a) Tests 3-12 contained 30 (~0.1 g) uranium metal beads accurately weighed to ±0.00001 g, and 2.5 mL of total solution. Test 1 contained 5 mL water and 30 (~0.1 g) uranium metal beads weighed to ±0.00001 g.

(b) Test 2 contained 300 uranium metal beads weighing 1 g total, and used 5 mL of 1 M $NaNO_3$.

(c) The KW simulant sludge composition and preparation is in Table 2.1.

The PC and Aquaset II H (a mixture of sepiolite clay and PC powders) were blended with the sludge to form uniform mixtures and then allowed to cure. Both the PC and Aquaset II H mixtures cure to form hard-set materials with the Aquaset II H being weaker than the PC product. Aquaset II G, granular sepiolite clay of size ranging from dust to ~2-mm in diameter, was applied as prescribed to the moist waste from overhead without mixing. The liquid absorption occurs by wicking the supernatant solution into the sepiolite granules. Accordingly, the Aquaset II G was applied to the top of the settled simulant sludge material, without mixing, for the present testing. The primary objectives in Series 1 were to determine the effects of 0.5 and 2 M $NaNO_3$ concentration on H_2 gas attenuation for the three agents and to determine the effects of nitrate concentration (at 0, 0.5, 1, and 2 M) on uranium metal corrosion and H_2 attenuation in simulated sludge (~7 M $NaNO_3$ is saturated). The tests were run at ~60°C for about 4 weeks.

The Series 2 testing expanded the studies done under Series 1 to compare the hydrogen mitigation performances of simulated sludge with and without PC and Aquaset II (powdered sepiolite clay) and with and without added 1 M $NaNO_3$. Samples were processed at 60°C for 4- and 8-week durations. The test matrix for Series 2 is in Table 2.3.

Table 2.3. Series 2 Matrix for Hydrogen Mitigation Testing by Nitrate in Solidified Waste Forms

Test	Test Compositions[(a)]	Test Objectives
1	Water; 8 weeks	Control to determine H_2 generation in water alone
2	0.5 M $NaNO_3$ + 300 beads; 4 weeks[(b)]	Mimic KOP transfer; confirm prior test
3	Simulated sludge; water; 4 weeks[(c)]	Control tests of H_2 generation in simulated sludge
4	Simulated sludge; water; 8 weeks	
5	Sim. sludge; 1M $NaNO_3$; 4 weeks	Compare with Tests 3 and 4 to determine effect of nitrate as function of time
6	Sim. sludge; 1M $NaNO_3$; 8 weeks	
7	Sim. sludge; PC; water; 8 weeks	Determine H_2 generation in simulated sludge with solidifying agent (no nitrate)
8	Sim. sludge; Aquaset II; water; 8 weeks	
9	Sim. sludge; PC; 1 M $NaNO_3$; 8 weeks	Determine H_2 generation in simulated sludge, 1 M $NaNO_3$, and PC as function of time
10	Sim. sludge; PC; 1 M $NaNO_3$; 4 weeks	
11	Sim. sludge; Aquaset II; 1 M $NaNO_3$; 4 weeks	Determine H_2 generation in simulated sludge, 1 M $NaNO_3$, and Aquaset II as function of time
12	Sim. sludge; Aquaset II; 1 M $NaNO_3$; 8 weeks	

KOP = Knock-Out Pot.
Sim. = Simulated.
(a) Tests 3-12 contained 30 (~0.1 g) uranium metal beads accurately weighed to ±0.00001 g and contained 2.5 mL of total solution. Test 1 contained 5 mL water and 30 (~0.1 g) uranium metal beads weighed to ±0.00001 g.
(b) Test 2 contained 300 uranium metal beads weighing 1 g total and used 5 mL of 1 M $NaNO_3$.
(c) The KW simulant sludge composition and preparation is in Table 2.1.

The testing under Series 3 (Table 2.4) was performed to expand the Series 2 studies to compare H_2 attenuation in simulated sludge with and without Aquaset II and with and without 1 M $NaNO_3$. In some of the 60°C Series 1 and 2 tests, uranium metal-water induction times apparently were not overcome such that the more rapid uranium metal corrosion rates observed under anoxic conditions were not observed. The failure to attain anoxic corrosion made some test results difficult to interpret. Therefore, in Series 3 two sets of tests were conducted—one set was run at 95°C for 4 days and the other set at 80°C for 10 days.

Based on the STP Rate Law (Appendix G of Schmidt and Sexton 2009), the 80°C and 95°C temperatures with respective 10-day and 4-day reaction times would achieve anoxic aqueous uranium metal corrosion depths almost 50% greater than those attained for most tests under Series 1 and 2 which ran for 4 weeks at 60°C.

The compositions and material ratios used in Series 1, 2, and 3 are summarized in Table 2.5. The varying water quantities for different $NaNO_3$ quantities reflect the amounts needed to attain the target 2.50-mL solution volume.

Table 2.4. Series 3 Matrix for Hydrogen Mitigation Testing by Nitrate in Solidified Waste Forms

Test[a]	**Test Compositions**[b]	**Test Objectives**
1-xx	Water	Control to determine H_2 generation in water alone
2-xx	Sim.sludge[c]; water	Control tests of H_2 generation in simulated sludge
3-xx	Sim. sludge; 1M $NaNO_3$	Compare with Test 2 to determine effect of nitrate
4-xx	Sim. sludge; 1M $NaNO_3$; dup.	
5-xx	Sim. sludge; Aquaset II; water	Determine H_2 generation in sim. sludge with Aquaset II (no nitrate)
6-xx	Sim. sludge; Aquaset II; 1 M $NaNO_3$	Compare with Test 5 to determine effect of nitrate
7-xx	Sim. sludge; Aquaset II; 1 M $NaNO_3$; dup.	

Sim. = Simulated.

(a) Two sets of tests were run at xx=80°C and xx=95°C.

(b) Tests 2-7 contained 30 (~0.1 g) uranium metal beads accurately weighed to ±0.00001 g and contained 2.5 mL of total solution. Test 1 contained 5 mL water and 30 (~0.1 g) uranium metal beads weighed to ±0.00001 g.

(c) The KW simulant sludge composition and preparation is given in Table 2.1.

Table 2.5. Target Test Material Compositions and Material Ratios

Test[a]	**Target Component Weights, g**					**$[NO_3^-]$, M**	**Material Ratios**				
	U Metal	**Sl. Solids**[b]	**Water**	**$NaNO_3$**	**Sol. Agent**[c]		**NO_3^-: U, mol/mol**	**Sol'n.**[d]**: U, mL/g**	**Sol'n.: Sl. Solids, mL/g**	**Sol'n.: Total Solids, mL/g**	**Sol. Agent: Sl. Solids, g/g**
Series 1											
1	0.10	0.0	5.00	0.0	0.0	0.0	0.0	50	50	50	0
2	1.0	0.0	4.84	0.425	0.0	1.0	1.19	5	5	5	0
3	0.10	2.776	2.496	0.0	0.0	0.0	0.0	25	0.90	0.45	0
4	0.10	2.776	2.474	0.106	0.0	0.5	2.98	25	0.90	0.45	0
5	0.10	2.776	2.450	0.213	0.0	1.0	5.95	25	0.90	0.45	0
6	0.10	2.776	2.403	0.425	0.0	2.0	11.9	25	0.90	0.45	0
7	0.10	2.776	2.474	0.106	2.776[e]	0.5	2.98	25	0.90	0.45	1.0
8	0.10	2.776	2.403	0.425	2.776[e]	1.0	11.9	25	0.90	0.45	1.0
9	0.10	2.776	2.474	0.106	2.776[f]	0.5	2.98	25	0.90	0.45	1.0
10	0.10	2.776	2.403	0.425	2.776[f]	1.0	11.9	25	0.90	0.45	1.0
11	0.10	2.776	2.474	0.106	2.776[g]	0.5	2.98	25	0.90	0.45	1.0
12	0.10	2.776	2.403	0.425	2.776[g]	1.0	11.9	25	0.90	0.45	1.0
Series 2											
1	0.10	0.0	5.00	0.0	0.0	0.0	0.0	50	50	50	0
2	1.0	0.0	4.948	0.213	0.0	0.5	0.595	5	5	5	0
3	0.10	2.776	2.496	0.0	0.0	0.0	0.0	25	0.90	0.90	0
4	0.10	2.776	2.496	0.0	0.0	0.0	0.0	25	0.90	0.90	0
5	0.10	2.776	2.450	0.213	0.0	1.0	5.95	25	0.90	0.90	0
6	0.10	2.776	2.450	0.213	0.0	1.0	5.95	25	0.90	0.90	0
7	0.10	2.776	2.496	0.0	2.776[e]	0.0	0.0	25	0.90	0.45	1.0
8	0.10	2.776	2.496	0.0	2.776[h]	0.0	0.0	25	0.90	0.45	1.0

Table 2.5. (cont.)

Test(a)	**Target Component Weights, g**					**[NO_3^-], M**	**Material Ratios**				
	U Metal	**Sl. Solids(b)**	**Water**	**$NaNO_3$**	**Sol. Agent(c)**		**NO_3^-: U, mol/mol**	**Sol'n.(d): U, mL/g**	**Sol'n.: Sl. Solids, mL/g**	**Sol'n.: Total Solids, mL/g**	**Sol. Agent: Sl. Solids, g/g**
9	0.10	2.776	2.450	0.213	2.776(e)	1.0	5.95	25	0.90	0.45	1.0
10	0.10	2.776	2.450	0.213	2.776(e)	1.0	5.95	25	0.90	0.45	1.0
11	0.10	2.776	2.450	0.213	2.776(h)	1.0	5.95	25	0.90	0.45	1.0
12	0.10	2.776	2.450	0.213	2.776(h)	1.0	5.95	25	0.90	0.45	1.0
Series 3											
1-80	0.10	0.0	5.00	0.0	0.0	0.0	0.0	50	50	50	0
2-80	0.10	2.776	2.496	0.0	0.0	0.0	0.0	25	0.90	0.90	0
3-80	0.10	2.776	2.450	0.213	0.0	1.0	5.95	25	0.90	0.90	0
4-80	0.10	2.776	2.450	0.213	0.0	1.0	5.95	25	0.90	0.90	0
5-80	0.10	2.776	2.496	0.0	2.776(h)	0.0	0.0	25	0.90	0.45	1.0
6-80	0.10	2.776	2.450	0.213	2.776(h)	1.0	5.95	25	0.90	0.45	1.0
7-80	0.10	2.776	2.450	0.213	2.776(h)	1.0	5.95	25	0.90	0.45	1.0
1-95	0.10	0.0	5.00	0.0	0.0	0.0	0.0	50	50	50	0
2-95	0.10	2.776	2.496	0.0	0.0	0.0	0.0	25	0.90	0.90	0
3-95	0.10	2.776	2.450	0.213	0.0	1.0	5.95	25	0.90	0.90	0
4-95	0.10	2.776	2.450	0.213	0.0	1.0	5.95	25	0.90	0.90	0
5-95	0.10	2.776	2.496	0.0	2.776(h)	0.0	0.0	25	0.90	0.45	1.0
6-95	0.10	2.776	2.450	0.213	2.776(h)	1.0	5.95	25	0.90	0.45	1.0
7-95	0.10	2.776	2.450	0.213	2.776(h)	1.0	5.95	25	0.90	0.45	1.0

(a) Series 1 and 2 tests run at 60°C; Series 3 tests run at 80°C or 95°C as indicated in test number.
(b) Sl. solids are dry sludge solids weight. Does not include 0.0087 g Optimer or added $NaNO_3$. See Table 2.1 for dry simulant sludge composition.
(c) Sol. agent is solidifying agent.
(d) Sol'n. is water or $NaNO_3$ solution.
(e) Type I/II PC.
(f) Aquaset II H.
(g) Aquaset II G.
(h) Aquaset II.

The sequence of combining the simulated sludge, flocculating agent, nitrate solution, and solidifying or water-absorbing agent proceeded in that order and followed the expected sequence for plant operations. Sequences used for single selected tests in each of the three test series are in Figure 2.4 and show the sludge preparation steps through "Sludge Flocculation" to be identical. Variations arise in the amounts of $NaNO_3$ and types of solidification agent added, if any.

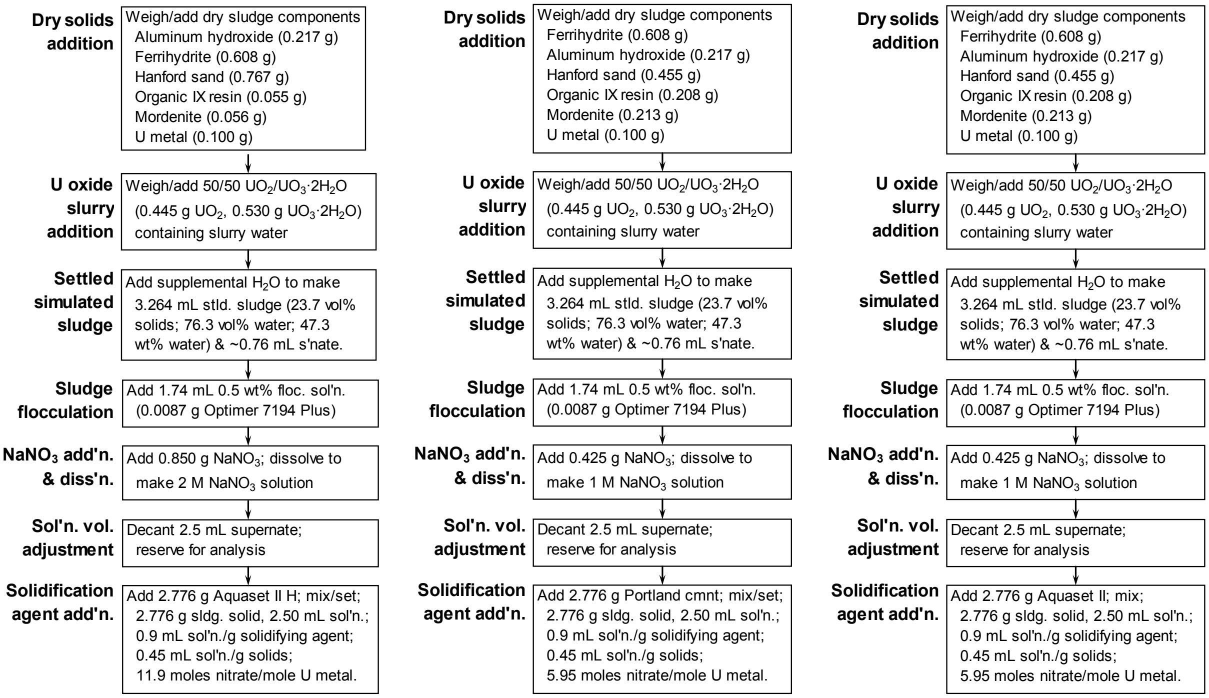

Figure 2.4. Sample Preparation Protocols for (left to right) Series 1–Test 10, Series 2–Tests 9 and 10, and Series 3–Tests 6 and 7

2.3 Analytical Methods

The objectives of the present studies were to determine the characteristics of the reaction of uranium metal with water in the presence of sludge simulant, sludge simulant with water-absorbing agent, and sodium nitrate solution. Characteristics of importance are the solution pH, corrosion of uranium metal, formation of gases (mostly H_2, but also oxides of nitrogen including nitric and nitrous oxides, NO and N_2O), consumption of gases (primarily oxygen, O_2), and the consumption and formation of dissolved nitrogenous species (nitrate consumption, nitrite and ammonia, NH_3, formation).

The pH measurements were conducted using a pH meter with glass electrode. The pH meter was calibrated using certified commercially available buffer solutions.

The uranium metal corrosion rate was calculated by gravimetric determination of mass loss of near spherical beads of uranium metal over the duration of the test at the measured test temperature. The uranium metal beads for most tests were selected such that 30 beads weighed ~100 mg. Test 2 in Series 1 and 2 used 300 beads weighing ~1 g in total. The average bead diameter was calculated based on the density of uranium metal (19.04 g/cm^3), the measured mass of the 30-bead groups, and assumption of identical spherical geometry. For example, this calculation shows that each of 30 uniform spherical uranium metal beads that together weigh exactly 0.100 g has a bead diameter of 693 µm. After testing, the uranium metal beads were retrieved from the test matrix, cleaned of surface corrosion layers by treatment in ~80°C concentrated phosphoric acid (H_3PO_4) containing 0.14 M sodium sulfate (Na_2SO_4), rinsed with water, air dried, and weighed. The cleaning procedure followed is the process used to free uranium metal of associated oxidized uranium in the PNNL uranium metal analysis procedure for sludge materials.[13]

The change in bead radius that occurred by corrosion during each test was divided by the elapsed time of testing at temperature to determine the corrosion rate. If applicable, adjustments were made in the elapsed time at temperature to account for the accelerated rate for the preliminary ~90°C heating used to overcome the induction time in the 60°C tests run in Series 1 and 2. Note bead retrieval was not possible and not attempted for the tests that used the hardened PC or Aquaset II H immobilization agents.

Gas analyses were performed by measuring volumetric changes in the contained gas collection space as shown by water-level differences in the test apparatus (see Figures 2.1, 2.2, and 2.3) and by sampling the gas and determining, by using an internal PNNL procedure[14], the gas composition at the conclusion of each test.

Ammonia concentrations produced by chemical reduction of nitrate were measured by ion selective electrodes using solutions of reagent ammonium chloride (NH_4Cl) for calibration. The method of standard additions was used to determine NH_3 solution concentrations.

Nitrate and nitrite concentrations were determined by ion chromatography according to an established PNNL procedure.[15] Analyses of other anions measurable by this method (fluoride, F^-; chloride, Cl^-; bromide, Br^-; sulfate, SO_4^{2-}; and phosphate, PO_4^{3-}) coincidentally present in the test solutions were determined adventitiously. However, all of these other analytes were present in less than quantifiable concentrations (F^-, <200 µg/mL; Cl^-, <500 µg/mL; Br^-, <1000 µg/mL; SO_4^{2-}, <1500 µg/mL; and PO_4^{3-}, <1500 µg/mL). Nitrite also was below its detection limit of 1000 µg/mL in all but one solution. The detection limit for nitrate was 1000 µg/mL.

The oxidation states of oxidized uranium materials present in the test sludges were determined by spectrophotometric analyses of their digestates prepared in ~80°C Na_2SO_4/H_3PO_4 solution. The interpretations of the spectra were performed by an established procedure.[16] The spectra of the test supernatant solutions both before and after heating were gathered for many tests to aid in understanding dissolved uranium speciation and to supplement nitrate and nitrite analysis information.

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[13] Jones SA. 2009. *Sample Preparation for Determination of Uranium Metal Concentration in Sludge.* RPG-CMC-107, Revs. 0 and 1, Pacific Northwest National Laboratory, Richland, Washington.

[14] Bos SJ. 2007. *Quantitative Gas Mass Spectrometry*. PNNL-98523-284, Rev. 2, Pacific Northwest National Laboratory, Richland, Washington.

[15] Lindberg MJ. 2004. *Determinations by Ion Chromatography (IC).* AGG-IC-001, Rev. 0, Pacific Northwest National Laboratory, Richland, Washington.

[16] Delegard CH. 2009. *Sample Preparation and Analysis for Determining Uranium Oxide Oxidation States in K Basin Sludges*. RPG-CMC-255, Rev. 0, Pacific Northwest National Laboratory, Richland, Washington.

3.0 Results

Results of the Series 1, 2, and 3 experiments to determine the effects of temperature and the presence and absence of sludge, immobilizing agent, and 0 to 2 M $NaNO_3$ on uranium metal corrosion rate and H_2 gas attenuation are summarized in Table 3.1. The results from the present Series 1, 2, and 3 tests were considered in combination with findings from previous testing (Sinkov et al. 2010). Results from the previous testing are shown in Appendix A for completeness.

The uranium metal corrosion rates in each test were determined by measuring the starting and ending masses of the uranium metal beads, calculating the difference in average bead diameter at the beginning and ending of each test (assuming identical spherical size and shape) for the time at reaction temperature to arrive at linear penetration rate. The nominal test temperatures were established by averaging temperatures logged manually over the test durations.

For tests in Series 1 and 2, which occurred at ~63°C, several hours of preliminary heating at ~90°C were imposed to overcome the lengthy and unknown induction time required to initiate anoxic corrosion rates observed in prior tests run at ~60°C, particularly those with grout immobilizing agents (Delegard et al. 2004). The times at higher temperature were accounted in reckoning the amount of corrosion based on the STP databook rate law ($\log_{10}$ rate, µm/h = 9.6942–3564.8/T; Schmidt and Sexton 2009; Appendix G). In this calculation, the effective time at the lower temperature was extended by the time at the ~90°C preliminary heating in inverse proportion to the ~7-fold more rapid rate at ~90°C compared with the rate expected at the ~63°C test temperature.

Test 1 in each of the three series contained only uranium metal beads and water without any sludge solids, nitrates, or water-immobilization agents. The uranium metal corrosion rate results of these tests were compared with the rate expected according to the STP rate law and thus aided in determining the validity of each test series. The expected STP uranium metal corrosion rates at the relevant test temperatures shown in Table 3.1 can be compared with the observed corrosion rates. For example, the rate expected at the 62.2°C average test temperature maintained in Series 1, based on the STP rate law, is 0.116 µm/hour. The rate expected at 62.4°C in the ~4-week interval used for some of the Series 2 tests is 0.117 µm/hour, while the rate expected at 63.5°C in the full ~8-week interval used in the balance of the Series 2 tests is 0.128 µm/hour. The rates expected in Series 3 were 0.398 µm/hour at 80°C and 0.972 µm/hour at 95°C.

Table 3.1. Uranium Metal Corrosion Rate and Hydrogen Generation Data

Test	[$NaNO_3$], M	Other Materials(a)	U Bead wt., mg		Corrosion Rate, µm/h	Corr. Rate Relative to STP Rate	Corr. Rate Attenuation Factor(b)	H_2 Produced, mmoles	H_2 Relative to STP Amt.	H_2 Attenuation Factor(b)
			Initial	Final						
Test Series 1, TI25 – STP rate at 62.2°C average temperature = 0.116 µm/h(c); 4 weeks										
1	0.0	None	97.56	98.27	-0.00101	-0.0087	-110	0.000268	0.00052	1900
2	1.0	None	1008.61	934.84	0.0106	0.092	11	0.000133	0.000025	40000
3	0.0	Sim. sludge	102.81	61.27	0.0670	0.59	1.7	0.227	0.42	2.4
4	0.5	Sim. sludge	108.38	97.99	0.0142	0.12	8.2	0.0232	0.042	24
5	1.0	Sim. sludge	101.87	61.59	0.0680	0.59	1.7	0.146	0.28	3.6
6	2.0	Sim. sludge	103.98	99.03	0.00684	0.059	17	0.000286	0.00053	1900
7	0.5	Sim. sludge in PC	103.89	ND(d)	ND(d)	ND(d)	ND(d)	0.000170	0.00032	3200
8	2.0	Sim. sludge in PC	105.78	ND(d)	ND(d)	ND(d)	ND(d)	0.000496	0.00090	1100
9	0.5	Sim. sludge in Aq. II H	94.26	ND(d)	ND(d)	ND(d)	ND(d)	0.000012	0.000024	42000
10	2.0	Sim. sludge in Aq. II H	97.27	ND(d)	ND(d)	ND(d)	ND(d)	0.000169	0.00033	3000
11	0.5	Sim. sludge in Aq. II G	102.58	95.66	0.00972	0.084	12	0.000298	0.00056	1800
12	2.0	Sim. sludge in Aq. II G	98.48	90.10	0.0122	0.11	9.5	0.000208	0.00040	2500
Test Series 2, TI28 – STP rate at 62.4°C average temperature = 0.117 µm/h(c), 4 weeks; STP rate at 63.5°C average temperature = 0.128 µm/h(c), 8 weeks										
1	0.0	None, 4 wks	107.69	58.99	0.0797	0.68	1.5	0.176	0.32	3.1
2	0.5	None, 4 wks	1002.53	268.86	0.154	1.3	0.76	1.06	0.20	4.9
3	0.0	Sim. sludge, 4 wks	107.72	51.41	0.0958	0.82	1.2	0.202	0.37	2.7
4	0.0	Sim. sludge, 8 wks	106.17	41.52	0.0584	0.46	2.2	0.117	0.14	6.9
5	1.0	Sim. sludge, 4 wks	101.37	91.08	0.0204	0.17	5.7	0.000118	0.00022	4400
6	1.0	Sim. sludge, 8 wks	104.59	78.07	0.0214	0.17	6.0	0.000067	0.000084	12000
7	0.0	Sim. sludge in PC, 8 wks	104.27	ND(d)	ND(d)	ND(d)	ND(d)	0.00229	0.0029	350
8	0.0	Sim. sludge in Aq. II, 8 wks	105.72	65.18	0.0299	0.23	4.3	0.0159	0.020	51
10	1.0	Sim. sludge in PC, 4 wks	106.22	ND(d)	ND(d)	ND(d)	ND(d)	0.000024	0.000044	23000
9	1.0	Sim. sludge in PC, 8 wks	110.54	ND(d)	ND(d)	ND(d)	ND(d)	0.000067	0.000080	13000
11	1.0	Sim. sludge in Aq. II, 4 wks	102.21	92.70	0.0138	0.12	8.5	0.000609	0.0012	870
12	1.0	Sim. sludge in Aq. II, 8 wks	105.01	89.94	0.0116	0.091	11	0.000031	0.000039	26000

Table 3.1. (cont.)

Test	$[NaNO_3]$, M	Other Materials[(a)]	U Bead wt., mg		Corrosion Rate, μm/h	Corr. Rate Relative to STP Rate	Corr. Rate Attenuation Factor(b)	H_2 Produced, mmoles	H_2 Relative to STP Amt.	H_2 Attenuation Factor[(b)]
			Initial	Final						
Test Series 3, TI36 – STP rate at 80.0°C average temperature = 0.398 μm/h[(c)], 10 days; STP rate at 94.1°C average temperature = 0.972 μm/h[(c)], 4 days										
1-80	0.0	None	99.24	47.81	0.289	0.73	1.4	0.226	0.42	2.4
2-80	0.0	Sim. sludge	99.45	41.58	0.393	0.99	1.0	0.171	0.34	3.0
3-80	1.0	Sim. sludge	100.95	91.87	0.0417	0.10	9.6	0.000224	0.00041	2500
4-80	1.0	Sim. sludge	103.03	93.88	0.0414	0.10	9.6	0.000156	0.00028	3600
5-80	0.0	Sim. sludge in Aq. II	98.18	67.77	0.155	0.39	2.6	0.105	0.19	5.1
6-80	1.0	Sim. sludge in Aq. II	102.40	90.00	0.0570	0.14	7.0	0.00470	0.0084	120
7-80	1.0	Sim. sludge in Aq. II	102.23	92.20	0.0458	0.12	8.7	0.00218	0.0039	260
1-95	0.0	None	99.41	65.86	0.704	0.72	1.4	0.215	0.58	1.7
2-95	0.0	Sim. sludge	101.61	64.94	0.971	1.00	1.0	0.163	0.53	1.9
3-95	1.0	Sim. sludge	101.99	84.86	0.156	0.16	6.2	0.000232	0.00041	2400
4-95	1.0	Sim. sludge	105.52	81.72	0.230	0.24	4.2	0.000178	0.00030	3300
5-95	0.0	Sim. sludge in Aq. II	101.22	78.33	0.261	0.27	3.7	0.0201	0.036	28
6-95	1.0	Sim. sludge in Aq. II	103.13	94.07	0.0967	0.10	10.0	0.00240	0.0042	240
7-95	1.0	Sim. sludge in Aq. II	103.63	88.48	0.172	0.18	5.6	0.00664	0.012	87

Sim. = Simulated.

Data marked by grey shading indicate tests for which initiation of full anoxic corrosion is doubtful or unknown. Test 5 in Series 1, also marked by grey shading, underwent dilution of the contained nitrate during testing. See text.

(a) Test durations, except for noted Series 2 tests, were ~4 weeks. All tests used 30 U metal beads except Tests 2 in Series 1 and 2, which used 300 beads. Except for tests with PC or Aquaset II H for which beads could not be recovered, 30 beads generally were recovered for each test having 30 beads originally; see footnote (d). For those tests having <30 beads recovered (either 28 or 29), the final beads masses were prorated to 30 beads. For Tests 2 in Series 1 and 2, 298 and 299 beads, respectively, were recovered and the final beads masses prorated to 300 beads.

(b) Attenuation factor = (Corrosion rate or amount of H_2 measured in experiment)/(corrosion rate or amount of H_2 according to STP rate law).

(c) Corrosion rate at average test temperature based on the STP rate law (Appendix G of Schmidt and Sexton 2009).

(d) ND = not determined. Uranium metal beads were not recovered from PC and Aquaset II H tests having cementitious matrices (see Section 3.2).

Results of several of the tests in Series 1 and 2 are questionable and are indicated by gray shading in Table 3.1. The reasons for the lack of confidence in these findings are summarized below:

- Test 1, Series 1. The observed corrosion rate for the control Test 1 in Series 1 was negligible compared with the STP rate law prediction. Therefore, this test obviously failed to enter into the anoxic corrosion rate regime despite the preliminary 2.3 hours of 92°C heating. In comparison, the uranium corrosion rate in Test 3 of Series 1 for simulated sludge, the only other test in Series 1 having no nitrate present, was 0.0684 μm/hour. This rate is credible, being ~60% of the 0.116 μm/hour rate predicted by the STP rate law.
- Tests 7, 8, 9, and 10, Series 1. Given the failure of Test 1 to fully enter the expected anoxic corrosion regime, the lack of uranium metal corrosion weight loss data for tests containing PC, and the fact that lengthy induction times also were observed for cementitious waste forms in prior sludge immobilization testing (Delegard et al. 2004), H_2 attenuation results are also in doubt for Tests 7 and 8 with PC and Tests 9 and 10 with Aquaset II H, which contains PC.
- Tests 7, 9, and 10, Series 2. The onsets of full anoxic corrosion for the three tests in Series 2 that used PC (Test 7, 9, and 10) also are in doubt based on the high H_2 attenuation coefficient observed for Test 7, which contained simulated sludge and PC but no added nitrate. Prior observations showed that grouted simulant sludge waste forms, including several based on PC, had negligible hydrogen attenuation under similar conditions (Delegard et al. 2004).
- Test 5, Series 1. The experimental findings for Test 5 in Series 1 are anomalous. This test studied the corrosion of uranium metal in simulated sludge containing 1 M $NaNO_3$. According to other studies described in present and prior reports (Sinkov et al. 2010), the presence of 1 M $NaNO_3$ should have decreased uranium metal corrosion by about a factor of 7 and attenuated H_2 generation by at least a factor of 1000. Instead, the corrosion and H_2 generation proceeded as if no nitrate were present. Subsequent analyses showed the initial 1 M nitrate concentration, confirmed by both anion chromatography and spectrophotometry, decreased—as shown by spectrophotometry—to ~0.02 M at the end of the test. The plastic vial holding the simulated sludge (Figure 2.1) had filled with solution by the end of the 4-week period at ~60°C. It is likely that during extended testing, the water condensate returned in the inner test vessel rather than draining to the water bath in which the vial was placed. The apparatus effectively functioned as a Soxhlet extractor in which condensate continuously collected in the inner vessel and overflowed to the outer vial, thus diluting the initial 1 M $NaNO_3$ in the test material to 0.02 M $NaNO_3$. No other inner test vessels in Series 1 had this behavior.

The average product density for the 1 M $NaNO_3$ (2.45 g H_2O; 0.213 g $NaNO_3$) tests prepared with 2.776 g each of dry sludge solids and Aquaset II (8.215 g total) is 1.54 ± 0.05 g/cm^3. This average and standard deviation are from six measurements, two each at the ~60°C, ~80°C, and ~95°C test temperatures (observed volumes were 5.20 and 5.20; 5.50 and 5.55; and 5.20 and 5.35 mL, respectively). If only the 60°C Aquaset II data are considered, the density is 1.58 g/cm^3. The lower observed densities compared with the 1.79 g/cm^3 value expected by summation of the solution and sludge and Aquaset II constituents likely reflect imperfect exclusion of gas pockets during preparation of these thick pastes. Lithostatic compression in full-scale products should increase product density to align more closely with the full 1.79 g/cm^3 value. The observed average density of the two 1 M $NaNO_3$ tests prepared with

2.776 g each of dry sludge solids and PC (8.215 g total) is 1.89 ± 0.03 g/cm^3. This value is only slightly less than the 1.93 g/cm^3 value projected by summing the constituent ingredients.

Effects of temperature, sludge, immobilization agent, and $NaNO_3$ concentration on uranium metal corrosion rate for the remaining valid tests are discussed in Section 3.1. Their effects on hydrogen gas mitigation are described in Section 3.2. The product gas compositions also are described in Section 3.2. In Section 3.3, findings from analyses of the products solutions for pH and nitrate, nitrite, and ammonia concentrations are examined in light of the uranium metal corrosion and gas products. Material balances for the series tests based on quantitation of the reactants and products are addressed in Section 3.4. Continued laboratory research to resolve remaining questions in implementation of H_2 gas mitigation by nitrate is proposed in Section 3.5. In all sections, results are discussed and compared with observations made in prior testing (Sinkov et al. 2010). In that work, effects of nitrate and other additives on uranium metal corrosion and hydrogen gas attenuation were investigated.

3.1 Effects of Experimental Variables on Uranium Metal Corrosion Rates

Respective effects of temperature and sodium nitrate concentration on uranium metal corrosion rates in aqueous solution, simulant sludge, and simulant sludge with immobilization agents are examined in Sections 3.1.1 and 3.1.2.

3.1.1 Effects of Temperature

Temperature effects on the corrosion of uranium metal in water, simulant sludge, and sludge with Aquaset II immobilizing agent both in the presence and absence of added 1 M $NaNO_3$ nitrate are shown in Figure 3.1. These data are presented in Figure 3.1 as the base-10 logarithm of corrosion rate versus the inverse absolute temperature (i.e., in Arrhenius coordinates) with the slope proportional to the reaction activation energy. The STP rate law, also plotted in Figure 3.1, has slope indicating reaction activation energy of 16.3 kcal/mole or 68.2 kJ/mole. Data used in Figure 3.1 include results from the present Series 1, 2, and 3 testing as well as data from similar prior tests (Sinkov et al. 2010).

Based on data spanning the studied ~60°C to 95°C temperature range, and with data sets having from three to nine points, the corrosion rate data for all of the six different systems follow Arrhenius dependencies that roughly parallel—and thus have activation energies near to—the STP rate law. Rates in water alone and in simulated sludge lie near or just slightly below the STP rate. Including Aquaset II with the simulated sludge decreases rates by about a factor of 3 below the STP rate. The addition of 1 M $NaNO_3$ to water only decreases the corrosion rate about a factor of 1.3 below that found for water alone and about a factor of 2 below the STP rate. However, addition of 1 M nitrate to simulated sludge decreases the corrosion rate by about a factor of 5 while addition of 1 M nitrate to sludge/Aquaset II mixture decreases the corrosion rate by ~2.5 compared with the respective nitrate-free analogues. Overall, the mixture of simulated sludge with Aquaset II and treated with 1 M $NaNO_3$ has a uranium corrosion rate about a factor of 8 to 10 lower than the STP rate law. The observed parallel adherence to the STP rate law in Arrhenius coordinates for these varied systems gives confidence to forecast behaviors to process-scale systems and lower temperatures.

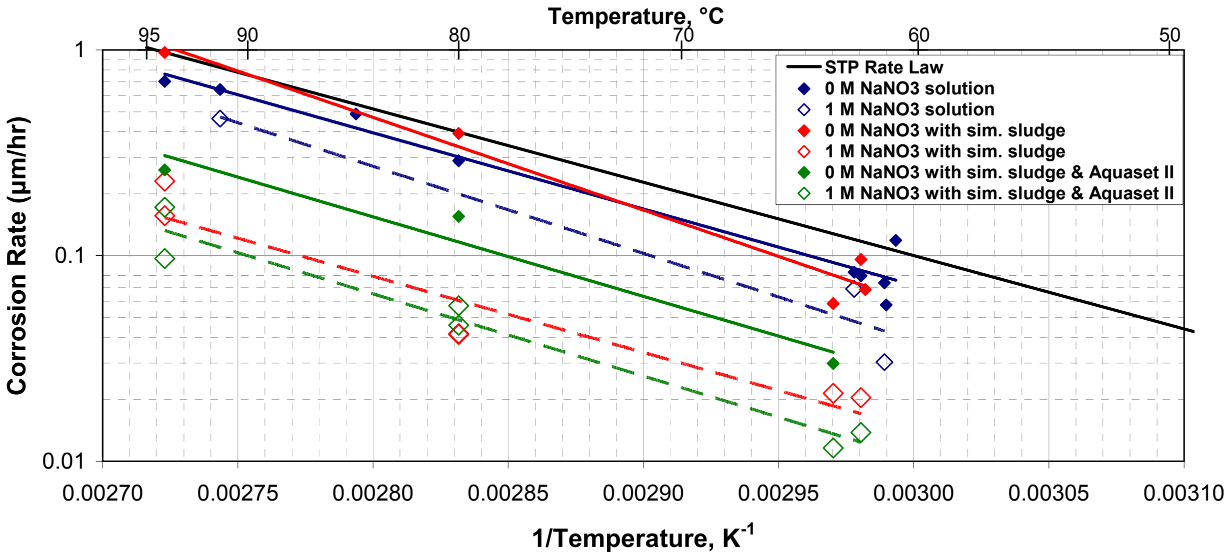


Figure 3.1. Uranium Metal Corrosion Rates in Aqueous Solution, KW Simulated Sludge, and KW Simulated Sludge/Aquaset II Blends with and without 1 M $NaNO_3$ as Functions of Temperature

3.1.2 Effects of Nitrate Concentration

Uranium metal corrosion attenuation factors for the tests described in Table 3.1 are plotted in Figure 3.2 as a function of nitrate concentration. Because of lack of evidence that anoxic corrosion of uranium metal was underway, data from the tests containing PC and Test 1 in Series 1 were not included. Data from Test 5, Series 1, is not included because of dilution of the contained nitrate. Those tests are indicated by grey shading in Table 3.1. Included for comparison in Figure 3.2 are uranium metal corrosion attenuation factor data found for prior tests in aqueous solution, solution with added UO_2, and simulated sludge (Sinkov et al. 2010). The attenuation factors for all tests were reckoned by comparing the corrosion rates observed in testing with the STP corrosion rates at the measured test temperature (i.e., the corrosion attenuation factor = [STP rate]/[measured rate]). The lines in Figure 3.2 are visual guides to the data trends.

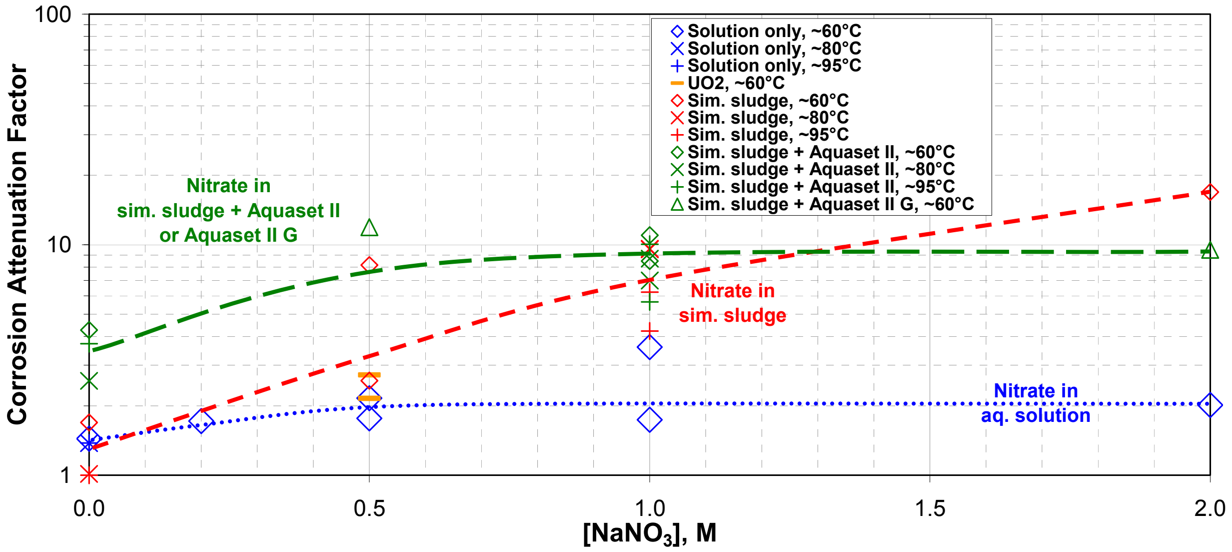


Figure 3.2. Uranium Metal Corrosion Rate Attenuation Factors in Aqueous Solution, KW Simulated Sludge, and KW Simulated Sludge/Aquaset II and II G Blends as Functions of $NaNO_3$ Concentration

The uranium metal corrosion rate in aqueous solution decreases by about a factor of 2, compared with the STP rate, between 0.5 M and 2 M $NaNO_3$. Addition of 1 M $NaNO_3$ to simulated sludge decreases the uranium metal corrosion rate about a factor of 7 compared with the STP rate, but values between about 4 and 10 were observed. The corrosion rate attenuations observed for UO_2 in 0.5 M $NaNO_3$ are in line with rate attenuations found at the same, greater, and lesser $NaNO_3$ concentrations for the full sludge simulant. The corrosion rate in 1 M $NaNO_3$ decreases about a factor of 8-10, again compared with the STP rate, for simulated sludge immobilized with Aquaset II or II G. The effect of temperature on the corrosion rate attenuation factor, compared with that predicted by the STP rate equation, is consistently biased for a given material type and nitrate concentration. This observation is an outcome of the fact that the Arrhenius plots for the various reaction media (solution, sludge, and sludge plus Aquaset II) in the presence and absence of 1 M $NaNO_3$ parallel the STP rate law as shown in Figure 3.1.

3.2 Effects of Experimental Variables on Hydrogen Generation Rates and Gas Compositions

Gas volumes and compositions for tests in Series 1 through 3 are shown in Appendix B. Hydrogen, from the corrosion of uranium metal in water, was present in all tests. Because Ar is present at constant concentration in air and is inert to chemical reaction, the observed O_2:Ar, N_2:Ar, and CO_2:Ar ratios give evidence of any reaction that might have produced or consumed O_2, N_2, and CO_2. Volumes of O_2, N_2, and CO_2 in the gas space at the beginning of each experiment were determined based on the initial gas volume at room temperature and the O_2, N_2, and CO_2 concentrations in normal air. For example, if the initial gas (air) volume in a test is 13.15 mL and air is 20.946 mole% (and vol%) O_2, the initial O_2 volume is 2.75 mL.

The O_2, N_2, and CO_2 quantities in the gas space at the end of each experiment were determined based on the initial gas volumes; the known concentrations of Ar, O_2, N_2, and CO_2 in air; and the Ar, O_2, N_2, and CO_2 concentrations measured in the gas samples taken at the end of each test. Because Ar does not react and is not produced in any of the tests, the ratio of the Ar concentration to the respective concentrations of O_2, N_2, and CO_2 indicates whether they are consumed or generated in the sampled gas space. The H_2 quantities at the end of each experiment were determined based on the total final room temperature gas volume and the measured H_2 concentration in the gas sample at the end of each test. Similar calculations were made for other gases, such as N_2O and NO_x, ordinarily found in negligible atmospheric concentrations. Although trace minor gas concentrations are found in air, initial H_2, CH_4, C_2H_x (i.e., ethane, ethylene, and acetylene, C_2H_6, C_2H_4, and C_2H_2, respectively), N_2O, and NO_x (or NO) concentrations were assumed to be zero.

The gas quantities expressed in volumes may be converted to moles using the Ideal Gas Law. The gas quantity calculations are shown in Table 3.2.

Table 3.2. Gas Quantity Calculations

Value	Gases Measured	Example Equation
Initial individual gas volume	O_2, N_2, CO_2	$V_{O_2,\text{initial}} = V_{\text{total, initial}} \times [O_2]_{\text{air}}$
Final individual gas volume	O_2, N_2, CO_2	$V_{O_2,\text{final}} = V_{\text{total, initial}} \times \frac{[Ar]_{\text{air}}}{[Ar]_{\text{final}}}[O_2]_{\text{final}}$
	All but O_2, N_2 and CO_2	$V_{H_2,\text{final}} = V_{\text{total, final}} \times [H_2]_{\text{final}}$

Moles of gas were calculated based on the Ideal Gas Law at 21°C (294 K) laboratory temperature:

$$\text{Moles of gas} = \frac{PV}{RT} = \frac{1\,\text{atm} \times V\,(\text{liters})}{\frac{0.082058\,\text{liter}\cdot\text{atm}}{\text{mole}\cdot\text{deg}} \times 294\,\text{deg}} = \frac{V\,(\text{mL})}{24{,}125\,\text{mL/mole}}$$

Oxygen was consumed in all tests based on O_2:Ar ratios. Oxygen consumption from the air cover gas caused overall gas volume decrease in many tests. In general, N_2 was consumed in tests without nitrate and produced in tests containing nitrate, but the quantities were small. Changes in CO_2 quantities also were small; in general, CO_2 was produced, likely by being displaced from solution in water by heating. Production of nitrous oxide (N_2O) was observed in many tests but the quantities generally were low. Methane (CH_4) produced by the reaction with water of uranium carbide (UC) present in the uranium metal (Bradley and Ferris 1962 and 1964), was observed in many of the tests and C_2H_x (i.e., ethane, ethylene, acetylene), also from hydrolysis of UC, was observed in fewer tests. Methane and C_2H_x were observed in products of prior tests of K Basin sludge (Delegard et al. 2000), metallic uranium fuel (Schmidt et al. 2003), and uranium metal beads (from the same source as used in the present tests: Delegard et al. 2004 and Sinkov et al. 2010). However, the absolute quantities of methane or C_2H_x were low in all cases.

Hydrogen was produced in widely varying amounts in tests from the three series. The H_2 gas attenuation afforded by nitrate in solution, simulated sludge, and simulated sludge containing Aquaset II immobilizing agent is discussed in Section 3.2.1. The comparisons use data from the Series 1, 2, and 3 testing and selected results from prior testing of H_2 attenuation (Sinkov et al. 2010). The individual gas analysis results for Series 1, 2, and 3 are discussed in Sections 3.2.2, 3.2.3, and 3.2.4, respectively.

3.2.1 Hydrogen Gas Attenuation

Earlier studies have shown that nitrate is effective in significantly diminishing hydrogen gas quantities evolved by the anoxic corrosion of uranium metal in water (Sinkov et al. 2010). Limited work within that study also investigated the effectiveness of nitrate in UO_2 slurries and in a full KW Basin-containerized simulant sludge. Tests of other potential H_2 suppression agents (e.g., nitrite, phosphate, Nochar Acid Bond 960, chloride, and hexavalent uranium) also were described in Sinkov et al. (2010) but are not addressed in the present report.

The objectives of the Series 1, 2, and 3 testing were to determine the effectiveness of nitrate in mitigating H_2 evolution in immobilized simulant sludge waste forms; to determine if the effectiveness is maintained over more extended periods (most of the prior tests had been performed at ~60°C for 4 weeks); to determine the effectiveness at temperatures other than ~60°C; to perform testing with and without added sludge, immobilization agents, and nitrate; and to vary nitrate concentration and immobilization agents. Immobilization agents tested include PC and three Aquaset products: Aquaset II (a sepiolite clay powder), Aquaset II G (granulated sepiolite clay), and Aquaset II H (a blend of sepiolite clay powder and PC). Nitrate concentrations ranged from 0 to 2 M as $NaNO_3$. Tests were run from about 4 to 8 weeks at ~60°C, 10 days at ~80°C, and 4 days at ~95°C.

As noted in Section 3.0, tests that contained PC (PC and Aquaset II H) and Test 1 of Series 1 did not appear to enter full anoxic corrosion while the nitrate in Test 5 of Series 1 was diluted by condensate. Therefore, H_2 mitigation data from these tests are inconclusive and are not considered in the analysis presented in this section. Data from Tests 2 from Series 1 and 2 are not discussed as the test materials are more prototypic of metal-rich Knock-Out Pot (KOP) sludge than of containerized sludge.

The H_2 attenuation factors observed for the remaining tests from Series 1, 2, and 3 are shown in Figure 3.3 with H_2 attenuation factors obtained in nitrate-free and nitrate-bearing systems based on prior related testing (Sinkov et al. 2010; see also Appendix A of the present report). The lines in Figure 3.3 are visual guides to the data trends only and are not statistical fits of the data. The H_2 attenuation factors were calculated as the H_2 generation amounts predicted by the STP rate law divided by the amounts measured in a particular test. Note that H_2 attenuation factors reported previously (Sinkov et al. 2010) were calculated as the quotient of the H_2 generation amounts observed in control Test 1 of the pertinent test series and the amounts measured for the individual test from that series. The H_2 attenuation factors for corrosion rate in the earlier tests were recalculated in the present report based on STP rate law values. Except for control Test 1 of Series 1 in the present testing, the measured H_2 amounts in the control tests in the present and prior (Sinkov et al. 2010) testing were near those expected based on the STP rate law. Note that because initial full anoxic corrosion was in doubt, no data are presented for tests containing PC or Aquaset II H (which itself contains PC).

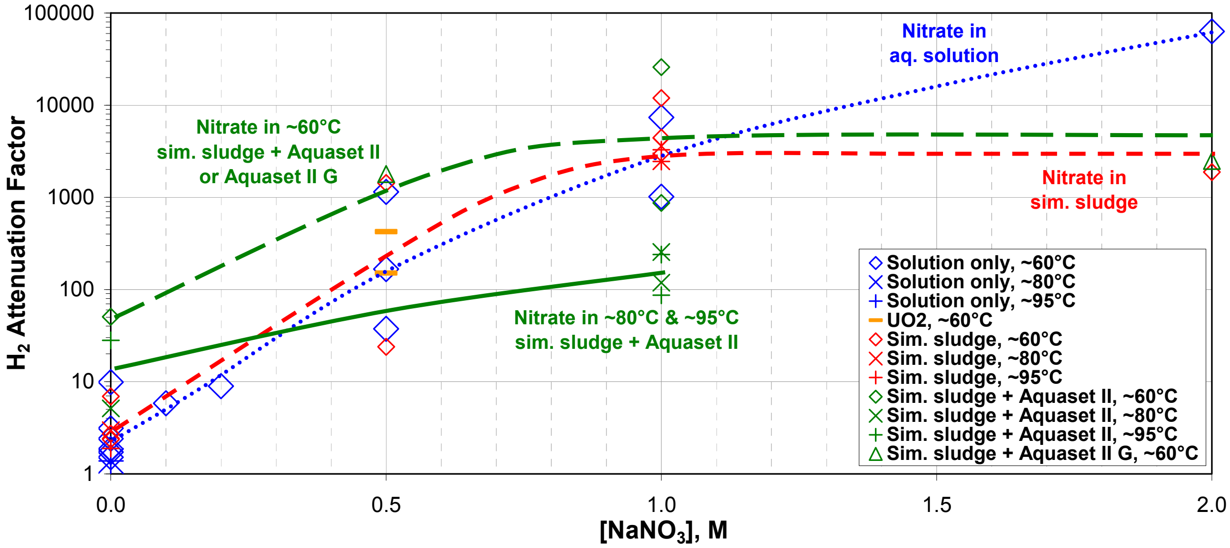


Figure 3.3. Hydrogen Attenuation Factors in Aqueous Solution, KW Basin Simulated Sludge, and KW Basin Simulated Sludge/Aquaset II and II G Blends as Functions of $NaNO_3$ Concentration

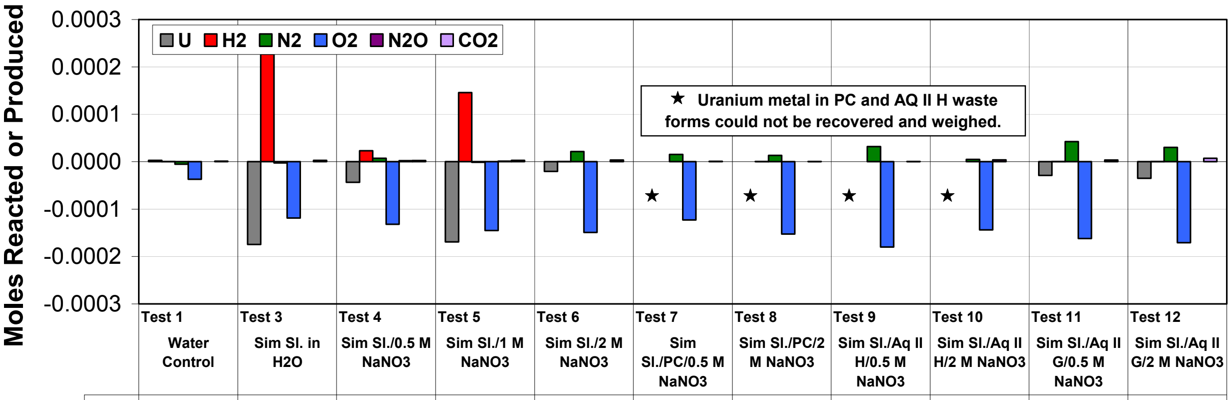
The effectiveness of nitrate in attenuating H_2 generation increases as nitrate concentration increases up to about 1 M $NaNO_3$. For uranium corroding in aqueous solution, the H_2 attenuation factor continues to increase up to at least 2 M $NaNO_3$ while no attenuation factor increase in simulated sludge or simulated sludge plus Aquaset II or II G is noted above 1 M $NaNO_3$. In 1 M $NaNO_3$, H_2 attenuation factors are consistently 1000 or higher for aqueous solution and simulated sludge at all tested temperatures (~60°C, 80°C, and 95°C) and for simulated sludge, plus Aquaset II or II G at ~60°C. Some diminution of H_2 attenuation is seen for the ~80°C and ~95°C tests of simulated sludge and Aquaset II. Still, H_2 attenuation factors are around 100 to 200 at 1 M $NaNO_3$ for the 80°C and 90°C test.

Part of the H_2 attenuation observed in Figure 3.3 can be attributed to attenuation of the corrosion rate as shown in Figure 3.2. For tests in solution, the H_2 attenuation factor that can be ascribed to corrosion inhibition is no more than a factor of 2. Therefore, if the observed H_2 attenuation factor is 1000, half is due to decreases in the corrosion rate, and the balance (a net attenuation factor of at least 500) is due to hydrogen radical scavenging or other hydrogen removal mechanisms. For simulated sludge and simulated sludge with Aquaset II or II G immobilization agent in 60°C 1 M $NaNO_3$, the corrosion rate attenuation factors are about 8 to 10 and thus the net H_2 attenuation factors, which range from about 1000 to 30000, decrease by no more than an order of magnitude.

3.2.2 Gas Analysis Results for Series 1

Test Series 1 was performed to examine the effectiveness of nitrate to retard H_2 generation in simulated sludge immobilized with PC, Aquaset II H, and Aquaset II G. Nitrate concentrations used for each immobilization agent were 0.5 and 2 M. Tests of the effect of varying $NaNO_3$ concentration (at 0, 0.5, 1, and 2 M) in simulated sludge also were performed. All tests were run at ~60°C for about 4 weeks.

The molar generation and consumption data for H_2, O_2, N_2, N_2O, and CO_2 gases and for uranium metal are shown in Figure 3.4. As noted earlier and in Figure 3.4, the uranium metal corrosion rate cannot be determined because uranium metal immobilized in cementitious solidification agents (PC and Aquaset II H) cannot be retrieved and weighed to determine the uranium metal weight loss.



	Test 1	Test 3	Test 4	Test 5	Test 6	Test 7	Test 8	Test 9	Test 10	Test 11	Test 12
U	2.98E-06	-1.75E-04	-4.36E-05	-1.69E-04	-2.08E-05	0.00E+00	0.00E+00	0.00E+00	0.00E+00	-2.91E-05	-3.52E-05
H2	2.68E-07	2.27E-04	2.32E-05	1.46E-04	2.86E-07	1.70E-07	4.96E-07	1.22E-08	1.69E-07	2.98E-07	2.08E-07
N2	-5.32E-06	-2.58E-06	6.95E-06	-1.21E-06	2.16E-05	1.55E-05	1.32E-05	3.18E-05	4.87E-06	4.21E-05	3.00E-05
O2	-3.72E-05	-1.19E-04	-1.32E-04	-1.45E-04	-1.49E-04	-1.23E-04	-1.53E-04	-1.80E-04	-1.44E-04	-1.62E-04	-1.71E-04
N2O	0.00E+00	0.00E+00	1.89E-06	1.06E-06	0.00E+00	0.00E+00	0.00E+00	0.00E+00	3.73E-06	0.00E+00	0.00E+00
CO2	1.13E-06	2.79E-06	2.39E-06	3.00E-06	3.41E-06	6.79E-07	5.88E-07	3.31E-07	1.09E-07	3.40E-06	6.89E-06

Figure 3.4. Moles of Uranium Metal Reacted and Moles of Gas Produced or Reacted in Series 1

It is apparent from Figure 3.4 that the uranium metal corrosion expected in control Test 1 failed to occur to any extent. If corrosion had occurred, about 0.00018 moles of uranium metal (0.18 millimoles of the initial ~0.42 millimoles of uranium metal) would have reacted. The forecast amount of corrosion is similar to the corrosion amount observed in Test 3. Stoichiometrically, about twice as many moles of H_2 would have been produced and some O_2 consumed. However, within experimental error, no uranium metal corrosion occurred and H_2 generation was less than 0.1% of the amount projected by the STP rate law. Only ~0.04 millimoles of O_2 were consumed. This lack of significant H_2 generation is consistent with the supposition that anoxic conditions were not attained. Therefore, this experiment failed to attain the expected more rapid anoxic uranium metal corrosion regime.

Given the failure of Test 1 to fully enter the expected anoxic corrosion regime, the apparent failure of Test 7 in Series 2 (simulated sludge in PC with no nitrate) to enter anoxic corrosion as shown by H_2 generation, the lack of uranium metal corrosion weight loss data for tests containing PC, and the fact that lengthy induction times also have been observed for cementitious waste forms in previous sludge immobilization testing (Delegard et al. 2004), H_2 attenuation results are in doubt for Tests 7 and 8 with PC and Tests 9 and 10 with Aquaset II H (which contains PC). The low amounts of H_2 evolved for Tests 7, 8, and 10 (~0.0002 to 0.0005 millimoles; Test 9 produced ~0.00001 millimoles of H_2) are similar to the amounts found for Tests 11 and 12 with sludge with Aquaset II G (~0.0002 to 0.0003 millimoles), which are known to have undergone uranium metal corrosion. However, it is doubtful the extended induction times previously observed for PC-bearing materials were overcome.

As noted in Section 3.0, the experimental findings for Test 5—which was to study the corrosion of uranium metal in simulated sludge containing 1 M $NaNO_3$—also were anomalous in that the uranium metal corrosion and H_2 production were much greater than would be expected based on similarly constituted tests. The likely anomaly arose because condensate returned to the inner test vessel (see Figure 2.1) to dilute the contained nitrate concentration about 50-fold. Therefore, uranium corrosion rate and H_2 attenuation results obtained for this test are not considered further in this report.

The gas analyses showed that O_2 was consumed in each test. Aside from control Test 1, which only contained uranium metal and water, the remaining tests contained simulant sludge, with and without solidifying agent, and all but one of these (Test 3) contained nitrate. Despite these variations, the O_2 consumptions for tests with simulant sludge were comparable at 0.12 to 0.18 millimoles. Most of the O_2 likely was consumed in oxidizing UO_2, present from uranium metal bead corrosion, to U(VI) compounds.

Nitrogen changes were small in all tests. Nitrogen was consumed in Tests 1 and 3 without nitrate and in Test 5 with its diminished nitrate concentration. The quantity consumed in control Test 1, containing water and uranium metal only, was 0.0053 millimoles, and was 0.0026 millimoles in Test 3 containing uranium metal in wet simulant sludge. Nitrogen consumption noted in the control tests from the previous study (Sinkov et al. 2010) was ascribed to nitrogen conversion to ammonia based on observations of ammonia in the test solutions and the lack of any nitrogen source other than atmospheric N_2. As will be seen in Section 3.3.4, ammonia was produced in Tests 1 and 3. From ~0.007 to 0.042 millimoles of N_2 was produced in all other Series 1 tests and evidently arose from the chemical reduction of nitrate contained in each of these tests.

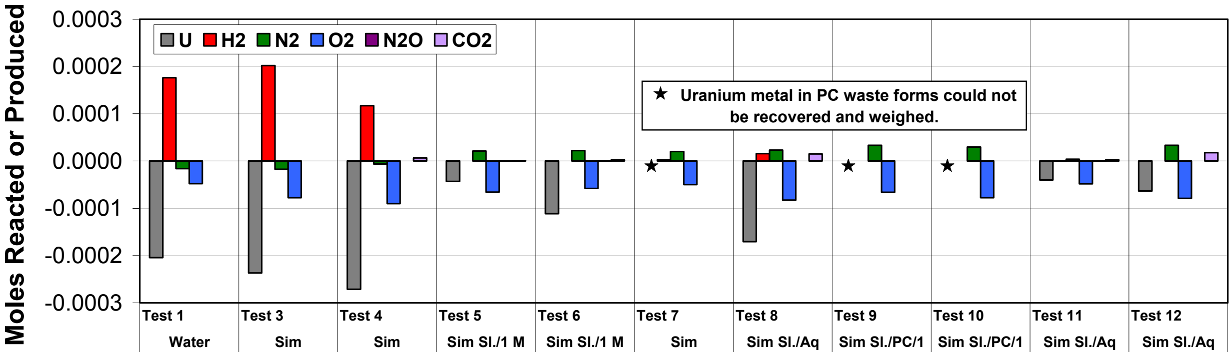
Small quantities of N_2O (nitrous oxide), ~0.001 to 0.003 millimoles, were found in three of the tests, all containing nitrate. Nitrous oxide was observed in previous tests but the levels generally were small with Test 11 in Series 5 of the past work (0.5 M $NaNO_3$ in simulated sludge [Sinkov et al. 2010]), producing ~0.0019 millimoles of N_2O while the analogous Test 4 in the present Series 1 produced ~0.0012 millimoles of N_2O. In contrast, ~0.42 millimoles of uranium metal were present in each test.

Very small amounts of carbon dioxide (CO_2) were evolved in each test, including control Test 1. The amounts ranged from about 0.0001 to 0.007 millimoles. The CO_2 likely arose from loss, due to heating, of CO_2 dissolved in water. No particular trend in amount of CO_2 and test parameter was observed.

3.2.3 Gas Analysis Results for Series 2

Test Series 2 was performed to further examine the effectiveness of nitrate to retard H_2 generation in simulated sludge; for these tests, nitrate was immobilized with PC and Aquaset II. Nitrate concentrations used for each immobilization agent were 0 and 1 M. To determine the effects of time, including depletion of uranium metal and nitrate, separate ~60°C tests were conducted for either 4 weeks or 8 weeks.

The molar generation and consumption data for H_2, O_2, N_2, N_2O, and CO_2 gases and for uranium metal are shown in Figure 3.5. As noted in Figure 3.5, uranium metal immobilized in the three tests with PC (Tests 7, 9, and 10) cannot be retrieved and weighed to determine the uranium metal weight loss and thus the amounts of uranium metal corroded.



	Test 1 Water Control, 4 wks	Test 3 Sim Sl./H2O/4 wks	Test 4 Sim Sl./H2O/8 wks	Test 5 Sim Sl./1 M NaNO3/4 wks	Test 6 Sim Sl./1 M NaNO3/8 wks	Test 7 Sim Sl./PC/H2O/8 wks	Test 8 Sim Sl./Aq II/H2O/8 wks	Test 9 Sim Sl./PC/1 M NaNO3/8 wks	Test 10 Sim Sl./PC/1 M NaNO3/4 wks	Test 11 Sim Sl./Aq II/1 M NaNO3/4 wks	Test 12 Sim Sl./Aq II/1 M NaNO3/8 wks
U	-2.05E-04	-2.37E-04	-2.72E-04	-4.32E-05	-1.11E-04	0.00E+00	-1.70E-04	0.00E+00	0.00E+00	-3.99E-05	-6.33E-05
H2	1.76E-04	2.02E-04	1.17E-04	1.18E-07	6.73E-08	2.29E-06	1.59E-05	2.42E-08	6.65E-08	6.09E-07	3.13E-08
N2	-1.63E-05	-1.73E-05	-6.28E-06	2.12E-05	2.18E-05	1.98E-05	2.32E-05	3.32E-05	2.95E-05	3.64E-06	3.32E-05
O2	-4.81E-05	-7.76E-05	-9.04E-05	-6.58E-05	-5.80E-05	-5.02E-05	-8.26E-05	-6.63E-05	-7.76E-05	-4.85E-05	-7.89E-05
N2O	1.07E-07	0.00E+00	0.00E+00	4.73E-07	6.71E-07	2.47E-08	6.27E-08	4.53E-08	5.10E-08	7.43E-07	1.88E-07
CO2	-1.23E-07	-7.30E-08	6.46E-06	8.39E-07	2.55E-06	-1.13E-07	1.51E-05	-7.15E-08	-1.43E-07	2.57E-06	1.78E-05

Figure 3.5. Moles of Uranium Metal Reacted and Moles of Gas Produced or Reacted in Series 2

As noted in Section 3.2.2 and also seen in Figure 3.5, uranium metal corrosion in Test 7, which contained simulated sludge and PC but had no added nitrate, produced only about 1% of the H_2 expected according to the Test 1 control and Test 3 that contains simulant sludge and no added nitrate. Therefore, Test 7 failed to enter the more rapid anoxic corrosion regime. This failure, the fact that uranium metal corrosion in PC-immobilized simulant sludge should occur at rates similar to the STP rate law although often with extended induction times (Delegard et al. 2004), and the inability to determine uranium metal corrosion in the solidified products, act to call into doubt the H_2 mitigation results for the companion Tests 9 and 10 that contained simulant sludge, PC, and 1 M $NaNO_3$. For the remaining tests, the presence of nitrate clearly led to H_2 attenuation.

Oxygen again was consumed in each test. Aside from control Test 1, which only contained uranium metal and water, the remaining 10 tests contained simulant sludge, with and without added PC or Aquaset II immobilizing agent. Four of the 10 contained no nitrate and test durations were either 4 or 8 weeks. Despite these variations, the O_2 consumptions for tests with simulant sludge, and even control Test 1 without sludge, were relatively consistent, ranging only from 0.05 to 0.09 millimoles compared with ~0.42 millimoles of uranium metal present in each test. No trend was observed in the amounts of O_2 consumed in the paired 4- and 8-week tests (i.e., O_2 consumption was not necessarily greater for the 8-week tests than for the otherwise similar 4-week tests). In addition, the observed O_2 consumptions were only about half those observed for the Series 1 tests, also run at ~60°C. The differences in O_2 consumptions between Series 1 and 2 may be due to differences in gas volume of the test vessel.

Nitrogen changes again were small in all tests with N_2 consumed in control Test 1 and simulant sludge Tests 3 and 4, all without nitrate. Surprisingly, nitrate-free Tests 7 and 8 (sludge plus PC and Aquaset II, respectively), produced N_2. All other tests, each of which contained 1 M $NaNO_3$ in their interstitial solutions, also produced N_2. The N_2 quantity consumed in control Test 1, containing water and uranium metal only, was 0.016 millimoles, and were 0.017 and 0.006 millimoles in Tests 3 and 4 containing uranium metal in wet simulant sludge and run for 4 and 8 weeks, respectively. These quantities are somewhat higher than observed in the analogous Series 1 control Test 1 and nitrate-free Test 3 with sludge. Again, N_2 consumption is likely due to nitrogen conversion to ammonia. In all other tests in Series 1, nitrogen was produced in quantities ranging from ~0.004 to 0.03 millimoles with the amounts not correlated with the presence of nitrate.

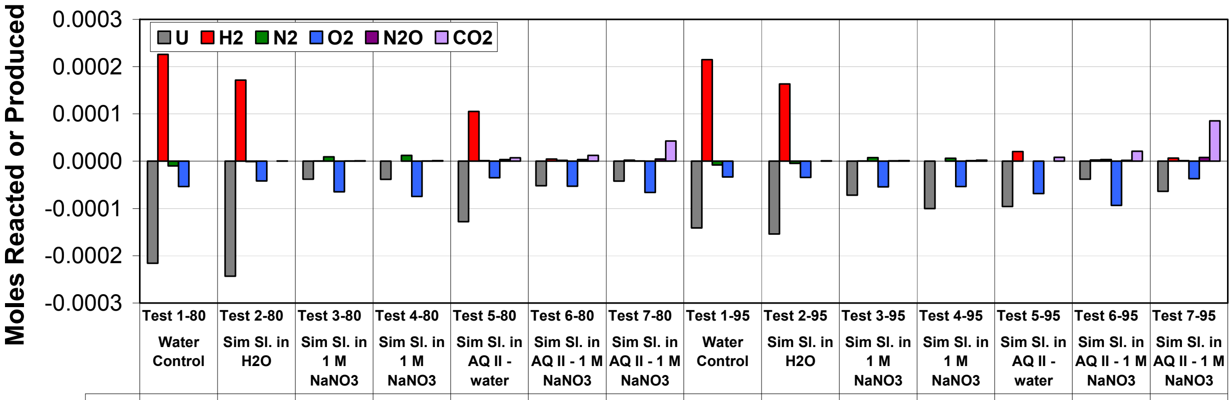
Quantities ranging from ~0.00002 to 0.015 millimoles of N_2O were found in 9 of the 11 tests. These quantities also were not dependent on whether or not nitrate was present.

Very small amounts of carbon dioxide (CO_2) also were evolved in the Series 2 tests with amounts ranging from about 0.00007 to 0.018 millimoles. Again, the CO_2 likely arose from loss of dissolved CO_2 due to heating. No particular trend in amount of CO_2 and the presence or absence of nitrate, simulated sludge, PC, or Aquaset II was observed.

3.2.4 Gas Analysis Results for Series 3

Test Series 3 was performed in two parts to separately examine the effects of temperature (at ~80°C and ~95°C) on the effectiveness of nitrate to retard H_2 generation in solution, in simulated sludge, and in simulated sludge immobilized with Aquaset II. Nitrate concentrations of 0 and 1 M as $NaNO_3$ were used. The 80°C test duration was 10 days; the 95°C test duration was 4 days. These test durations provided about 50% greater corrosion penetration depth than the depths experienced by the 4-week at 60°C conditions used for most other tests. Thus, the projected corrosion penetrations at 4 weeks (672 hours) at 60°C, 10 days (240 hours) at 80°C, and 4 days (96 hours) at 95°C are 66 μm, 96 μm, and 98 μm, respectively, according to the STP rate law.

Molar generation and consumption data for H_2, O_2, N_2, N_2O, and CO_2 gases and for uranium metal in Series 3 are shown in Figure 3.6.



	Test 1-80 Water Control	Test 2-80 Sim Sl. in H2O	Test 3-80 Sim Sl. in 1 M NaNO3	Test 4-80 Sim Sl. in 1 M NaNO3	Test 5-80 Sim Sl. in AQ II - water	Test 6-80 Sim Sl. in AQ II - 1 M NaNO3	Test 7-80 Sim Sl. in AQ II - 1 M NaNO3	Test 1-95 Water Control	Test 2-95 Sim Sl. in H2O	Test 3-95 Sim Sl. in 1 M NaNO3	Test 4-95 Sim Sl. in 1 M NaNO3	Test 5-95 Sim Sl. in AQ II - water	Test 6-95 Sim Sl. in AQ II - 1 M NaNO3	Test 7-95 Sim Sl. in AQ II - 1 M NaNO3
U	-2.16E-04	-2.43E-04	-3.81E-05	-3.84E-05	-1.28E-04	-5.21E-05	-4.21E-05	-1.41E-04	-1.54E-04	-7.20E-05	-1.00E-04	-9.62E-05	-3.81E-05	-6.36E-05
H2	2.26E-04	1.71E-04	2.24E-07	1.56E-07	1.05E-04	4.70E-06	2.18E-06	2.15E-04	1.63E-04	2.32E-07	1.78E-07	2.01E-05	2.40E-06	6.64E-06
N2	-1.01E-05	-9.85E-07	9.06E-06	1.23E-05	1.30E-06	1.76E-06	2.43E-07	-7.96E-06	-4.65E-06	7.42E-06	6.22E-06	-1.80E-07	3.18E-06	1.11E-06
O2	-5.38E-05	-4.20E-05	-6.50E-05	-7.45E-05	-3.54E-05	-5.31E-05	-6.60E-05	-3.37E-05	-3.44E-05	-5.41E-05	-5.38E-05	-6.85E-05	-9.34E-05	-3.73E-05
N2O	7.63E-08	9.12E-08	3.58E-07	4.10E-07	3.17E-06	3.22E-06	4.51E-06	7.38E-08	0.00E+00	9.75E-07	1.06E-06	1.07E-07	1.54E-06	7.82E-06
CO2	-4.83E-09	5.05E-07	6.44E-07	1.11E-06	7.09E-06	1.23E-05	4.27E-05	4.21E-08	9.62E-07	1.19E-06	1.90E-06	8.30E-06	2.10E-05	8.53E-05

Figure 3.6. Moles of Uranium Metal Reacted and Moles of Gas Produced or Reacted in Series 3

As expected, H_2 production was greatest for the nitrate-free Tests 1, 2, and 5 in both the 80°C and 95°C experimental sets. Greater uranium metal corrosion was observed in Test 2 for both 80°C and 95°C with simulated sludge than in their respective control Tests 1. Despite the greater uranium metal corrosion in the simulated sludge tests, however, relatively lower H_2 amounts were observed in the simulated sludge tests (compared with the control Tests 1) at both temperatures. This gives evidence that limited H_2 scavenging by sludge simulant components occurred in Tests 2 at both 80°C and 95°C. The apparent H_2 scavenging behavior by simulated sludge was not observed in comparing the analogous Test 1 and 2 Series 2 results at 60°C.

Oxygen was consumed in each test in amounts that varied relatively little with respect to changes in experimental parameters (presence or absence of simulated sludge and with or without Aquaset II or nitrate). The O_2 consumption ranged only from 0.03 to 0.09 millimoles, similar to the 0.05 to 0.09 millimole O_2 range observed in Series 2. Each test contained about 0.42 millimoles of uranium metal.

Nitrogen was consumed in nearly all nitrate-free tests (i.e., Tests 1-80, 2-80, 5-80, 1-95, and 2-95). Only Test 5-95, which contained simulated sludge and Aquaset II at 95°C, produced an insignificant amount (~0.0002 millimoles) of N_2. The remaining nitrate-bearing tests produced from 0.0002 to 0.01 millimoles of N_2. As discussed in this report, the N_2 consumed in the nitrate-free tests appears, at least to some extent, as ammonia whereas the N_2 production must arise from nitrate chemical reduction.

Small quantities of N_2O again were found in quantities ranging from 0.00007 to 0.008 millimoles. These levels are near those observed in the 60°C Series 2 tests. The N_2O quantities generally were greater for the tests containing simulated sludge, Aquaset II, and nitrate.

Control Test 1-80 consumed a trivial and experimentally insignificant amount of CO_2 (0.000005 millimoles). All other tests produced CO_2 in amounts ranging from 0.00004 to 0.09 millimoles. In general, more CO_2 was produced in Tests 6 and 7 that contained simulated sludge, Aquaset II, and nitrate and slightly less in Tests 5 with simulated sludge and Aquaset II but no nitrate.

3.3 Reactions and Stoichiometry

The experimental results discussed in Sections 3.1 and 3.2 and the results of prior testing (Sinkov et al. 2010) show that nitrate is effective in attenuating H_2 arising from the reaction of uranium metal with water. As observed by comparing Figures 3.2 and 3.3, some of the attenuation can be attributed to inhibition of the rate of the corrosion reaction itself. However, most of the H_2 attenuation is due to scavenging of the nascent hydrogen by nitrate. Besides H_2 attenuation, the introduction of $NaNO_3$ leads to chemical changes to the sludge and sludge/immobilization agent system in the solid and solution phases.

Results of examination of published literature findings and PNNL laboratory testing of H_2 mitigation by nitrate in solution, solution/UO_2 mixtures, and in simulated sludge have been described (Sinkov et al. 2010). Based on these considerations, the primary nitrate reduction product expected in the present tests is ammonia (NH_3), followed by nitrite (NO_2^-). However, gaseous nitrate reduction products including N_2O and N_2 also were observed with O_2 consumption.

Changes in pH, alterations in solid phase, and the generation of nitrate chemical reduction products are addressed in this section. The nitrate reduction reactions leading to gaseous products based on results from Section 3.2 are discussed in Section 3.3.1. Oxygen consumption data are in Section 3.3.2. The pH and solid phase alterations caused by $NaNO_3$ and the immobilization agents are in Section 3.3.3. The results of ammonia analyses are in Section 3.3.4 and the nitrite findings are in Section 3.3.5.

3.3.1 Nitrate Reduction to Form Gaseous Products

Gaseous nitrate reduction products, including N_2 and N_2O, were observed in nearly all tests as shown in Section 3.2. The reductions of nitrate to form N_2 and N_2O in the oxidation of uranium metal to form UO_2 are shown in Reactions 3.1 and 3.2, respectively:

$$5\ U_{(s)} + 4\ NO_3^-{}_{(aq)} + 2\ H_2O_{(l)} \rightarrow 5\ UO_{2\,(s)} + 2\ N_{2\,(g)} + 4\ OH^-{}_{(aq)} \qquad \text{Reaction 3.1}$$

$$2\ U_{(s)} + 2\ NO_3^-{}_{(aq)} \rightarrow 2\ UO_{2\,(s)} + N_2O_{(g)} + 2\ OH^-{}_{(aq)} \qquad \text{Reaction 3.2}$$

Unlike the previous testing, which also examined nitrite to mitigate H_2, no measurable NO (nitric oxide) or NO_2 were observed in the present tests that only examined the nitrate as a H_2 mitigation agent. Note nitric oxide reached significant levels in the previous testing for Test 11 of Series 5, which contained 0.5 M $NaNO_2$ with simulated sludge. Ferrihydrite was implicated in the vigor and unusual aspects of this gas-forming reaction (Sinkov et al. 2010).

3.3.2 Oxygen Reduction Reactions

Oxygen present in the apparatus gas spaces was consumed in all tests from Series 1, 2, and 3. The quantities consumed were relatively constant within the individual test series, ranging from about 0.12 to 0.18 millimoles in Series 1, at ~60°C, 0.05 to 0.09 millimoles in Series 2 at ~60°C, 0.04 to 0.07 millimoles in Series 3 at ~80°C, and 0.04 to 0.07 millimoles in Series 3 at ~95°C. The O_2 consumptions observed in the previous ~60°C testing with uranium metal in aqueous solution over varying $NaNO_3$ concentrations were similar to the Series 2 and 3 findings, ranging from about 0.04 to 0.06 millimoles (Sinkov et al. 2010). In the same set of experiments, O_2 consumption in tests with 0.5 M $NaNO_3$ in the presence of UO_2 and simulated sludge were slightly higher at ~0.05 to 0.07 millimoles. The greater O_2 consumption observed in the Series 1 tests might be related to the ~two-fold greater contained gas volume in its apparatus compared with the Series 2 and 3 apparatus (Appendix B).

Overall, only slight incremental O_2 consumption increase (average ~0.01 millimoles) was noted for tests containing simulant sludge or UO_2, with or without solidifying agent, compared with tests in the same test series containing solution only. At the same time, the uranium metal quantities corroded in the unmitigated control tests were about 0.17 millimoles. This implies the O_2 consumption is dominated by its reaction with uranium metal and the UO_2 freshly formed by its corrosion (Reactions 3.3), and not by oxidizing the UO_2 present in simulated sludge (shown in the present and earlier work; Sinkov et al. 2010) or by oxidizing UO_2 alone (Sinkov et al. 2010).

$$U_{(s)} + O_{2\,(aq)} \rightarrow UO_{2\,(s)} \qquad \text{Reactions 3.3}$$
$$UO_{2\,(s)} + 0.5\ O_{2\,(aq)} + 2\ H_2O_{(l)} \rightarrow UO_3\cdot 2H_2O_{(s)}$$

3.3.3 Solid Phase Alteration and pH

As seen in Reactions 3.6 (Section 3.3.4), 3.1, and 3.2, hydroxide ion (OH^-) is formed by reduction of nitrate to NH_3, N_2, and N_2O. The increase in OH^- concentration acts to raise the pH of the interstitial liquid. Reactions to lower the essentially neutral and poorly buffered pH of the starting simulated sludge also occur for all tests that contain added $NaNO_3$. It is likely the lower pH occurs by the reaction of sodium ion with the metaschoepite, $UO_3 \cdot 2H_2O$, present in the full sludge simulant by surface exchange of H^+ for Na^+ and to form compounds such as sodium compreignacite [$Na_2(UO_2)_6O_4(OH)_6 \cdot 7H_2O$; Reaction 3.4] or clarkeite [$Na(UO_2)O(OH)$; Reaction 3.5] (Sinkov et al. 2010):

$$6\ UO_3 \cdot 2H_2O_{(s)} + 2\ NaNO_{3\ (aq)} \rightarrow Na_2(UO_2)_6O_4(OH)_6 \cdot 7H_2O_{(s)} + 2\ HNO_{3\ (aq)} + H_2O_{(l)} \quad \text{Reaction 3.4}$$

$$UO_3 \cdot 2H_2O_{(s)} + NaNO_{3\ (aq)} \rightarrow Na(UO_2)O(OH)_{(s)} + HNO_{3\ (aq)} + H_2O_{(l)} \quad \text{Reaction 3.5}$$

It is seen that one-third mole of nitric acid (HNO_3) per mole of metaschoepite is produced in Reaction 3.4 to form sodium compreignacite while Reaction 3.5 produces one mole of HNO_3 per mole of metaschoepite in forming clarkeite.

To determine the effects of sodium nitrate on metaschoepite, an aqueous slurry of $UO_3 \cdot 2H_2O$ was contacted with 0.5 M $NaNO_3$ at ~95°C for 5 days. The product solids then were separated from the supernatant liquid, rinsed once with DI water, dried, and analyzed by XRD. A separate slurry sample of $UO_3 \cdot 2H_2O$ starting material was heated under the same conditions, separated from supernatant water, dried, and analyzed by XRD. Diffraction analysis confirmed the starting material was metaschoepite. However, the product of heating metaschoepite at 95°C in the presence of 0.5 M $NaNO_3$ could not be identified by XRD. The product pattern did not match metaschoepite, dehydrated schoepite (nominally $UO_3 \cdot 0.8H_2O$), clarkeite ($Na_2U_2O_7$; ICDD, International Centre for Diffraction Data, pattern 43-0347), $Na((UO_2)_4O_2(OH)_5)(H_2O)_5$ (ICDD pattern 75-8798), sodium compreignacite (Gorman-Lewis et al. 2008), or the patterns for the unnamed products formed by the 22°C reaction of metaschoepite in pH 5-buffered 0.01 M $NaNO_3$ solution for ~20 and ~56 days (Giammar and Hering 2004). The XRD patterns of the products of heating $UO_3 \cdot 2H_2O$ hydrothermally without and with 0.5 M $NaNO_3$ at ~95°C for 5 days are shown in Appendix C.

The pH also can be altered by the immobilizing agent. The PC and Aquaset II H agents contain PC. Upon full curing, PC has pore water pH of 10 to 11. The pH values observed before and after heating for the Series 1, 2, and 3 tests are in Table 3.3 and in Figure 3.7 with the lines in Figure 3.7 being visual guides to the data trends only and not statistical fits of the data.

Table 3.3. Test pH, Nitrate Quantities, and Nitrite and Ammonia Production

Test	[NaNO3], M	Other Materials	pH before Heating	pH after Heating	NO_3^-, mmoles		NO_2^-, mmoles	NH_3, mmoles(a)
					Before	After		
Test Series 1, TI25; 62.2°C								
1	0.0	None	6.53	8.74	–	–	–	0.00151
2	1.0	None; 300 U_{metal} beads	8.01	10.91	5.27	3.49	<0.109	0.0537
3	0.0	Sim. sludge	9.02	8.93	–	–	–	0.0607
4	0.5	Sim. sludge	5.08	4.23	1.23	(b)	(b)	0.00281
5	1.0	Sim. sludge	4.53	(b)	2.34	(b)	(b)	0.00325(c)
6	2.0	Sim. sludge	4.26	3.58	4.92	4.76	<0.054	0.00320
7	0.5	Sim. sludge in PC	4.90	(b)	1.19	(b)	(b)	0.00722(c)
8	2.0	Sim. sludge in PC	4.03	(b)	4.88	(b)	(b)	0.0000386(c)
9	0.5	Sim. sludge in Aq. II H	4.81	(b)	1.27	(b)	(b)	0.00457(c)
10	2.0	Sim. sludge in Aq. II H	4.25	(b)	4.88	(b)	(b)	0.0109(c)
11	0.5	Sim. sludge in Aq. II G	5.10	7.78	1.21	1.29	<0.725	0.00108
12	2.0	Sim. sludge in Aq. II G	4.12	7.77	4.80	3.50	<0.725	0.00169
Test Series 2, TI28; 62.4°C, 4 weeks; 63.5°C, 8 weeks								
1	0.0	None, 4 wks	7.12	7.52	–	–	–	0.00221
2	0.5	None, 4 wks; 300 U_{metal} beads	8.10	12.65	2.59	1.23	0.132	0.601
3	0.0	Sim. sludge, 4 wks	9.26	8.68	–	–	–	0.0000250
4	0.0	Sim. sludge, 8 wks	9.19	7.17	–	–	–	0.000445
5	1.0	Sim. sludge, 4 wks	4.46	5.53	2.41	2.38	<0.109	0.00108
6	1.0	Sim. sludge, 8 wks	4.50	6.76	2.48	2.37	<0.109	0.00377
7	0.0	Sim. sludge in PC, 8 wks	7.86	12.76	–	–	–	0.00176
8	0.0	Sim. sludge in Aq. II, 8 wks	9.27	8.63	–	–	–	0.000254
10	1.0	Sim. sludge in PC, 4 wks	4.23	12.63	2.33	1.99	<0.109	0.00153
9	1.0	Sim. sludge in PC, 8 wks	4.30	12.69	2.34	1.91	<0.109	0.00161
11	1.0	Sim. sludge in Aq. II, 4 wks	4.47	7.50	2.31	2.21	<0.109 <0.05(c)	0.000727
12	1.0	Sim. sludge in Aq. II, 8 wks	4.39	7.25	2.39	1.72	<0.109 <0.03(c)	0.000575

Table 3.3. (cont.)

Test	$[NaNO_3]$, M	Other Materials	pH before Heating	pH after Heating	NO_3^-, mmoles		NO_2^-, mmoles	NH_3, mmoles[a]
					Before	After		
Test Series 3, TI36; 80.0°C, 10 days; 94.1°C, 4 days								
1-80	0.0	None	7.29	7.57	–	–	–	0.000151
2-80	0.0	Sim. sludge	6.80	7.05	–	–	–	<0.00001
3-80	1.0	Sim. sludge	4.18	4.82	2.38	2.44	<0.109	0.000781
4-80	1.0	Sim. sludge	4.03	4.65	2.27	2.42	<0.109	0.000800
5-80	0.0	Sim. sludge in Aq. II	6.51	8.30	–	–	–	<0.00001
6-80	1.0	Sim. sludge in Aq. II	4.05	7.58	2.36	2.45	<0.217	0.000762
7-80	1.0	Sim. sludge in Aq. II	4.08	7.65	2.28	2.39	<0.217	0.000766
1-95	0.0	None	7.47	7.85	–	–	–	0.000244
2-95	0.0	Sim. sludge	6.95	7.00	–	–	–	0.00000802
3-95	1.0	Sim. sludge	4.14	4.77	2.34	2.40	<0.109	0.00362
4-95	1.0	Sim. sludge	4.08	4.98	2.41	2.33	<0.109	0.0108
5-95	0.0	Sim. sludge in Aq. II	6.48	8.35	–	–	–	0.0000367
6-95	1.0	Sim. sludge in Aq. II	4.15	7.33	2.31	2.32	<0.217	0.00190
7-95	1.0	Sim. sludge in Aq. II	4.10	7.51	2.28	2.44	<0.217	0.00236

Sim. = Simulated.

(a) Ammonia (NH_3) quantities include amounts found in both the sample vessel (plastic vial) and in the water bath in Series 1. For Series 1, water leach solutions were prepared for Aquaset II G materials but not for PC-immobilized materials (PC itself or Aquaset II H). For Series 2 and 3, water leach solutions were prepared from solidified samples for both PC- and Aquaset II-bearing materials.

(b) Solution sample was lost in Series 1, Test 5; result is for water bath only. Insufficient solution sample was available for pH and nitrate and nitrite analyses for Series 1, Tests 4, 7, 8, 9, and 10.

(c) Quantity estimates by spectrophotometry.

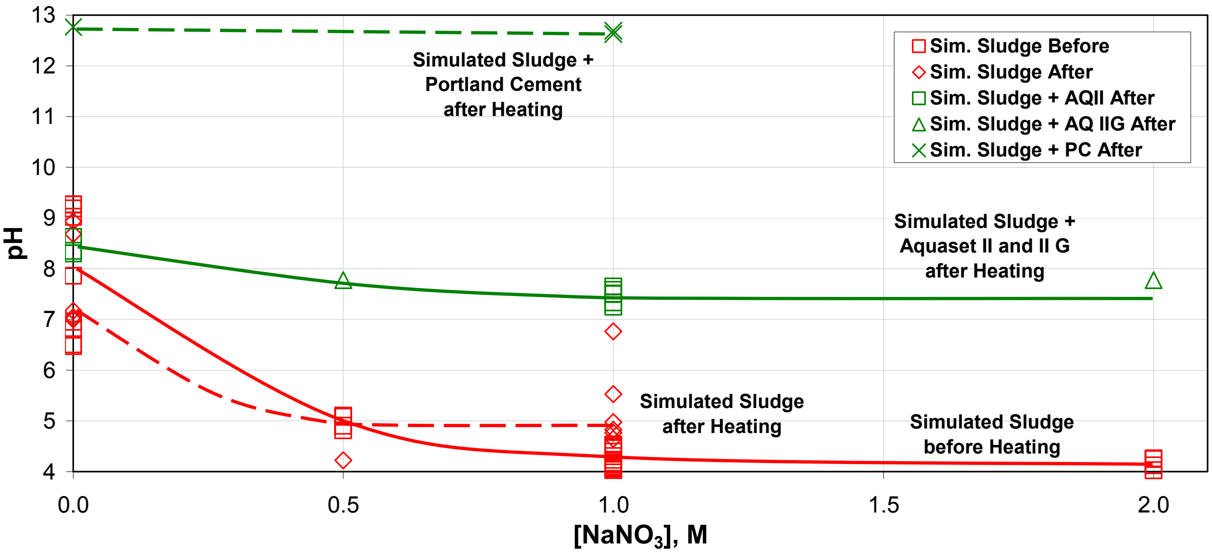


Figure 3.7. Simulated Sludge pH Before Heating and pH of Simulated Sludge with and Without Immobilization Agent after Heating as Functions of $NaNO_3$ Concentration

In agreement with Reactions 3.5 and 3.5, the initial pH decreases with increasing $NaNO_3$ concentration. In the absence of any immobilization agent and without nitrate, the initial simulant sludge pH ranges from about 6.5 to 9.2, is about 5.0 at 0.5 M $NaNO_3$, and about 4.2 at 1 to 2 M $NaNO_3$. The relatively high pH range observed for the sludge simulant in the absence of $NaNO_3$ is because the associated water has little buffering capacity. After heating to ~60-95°C, the pH of simulant sludge containing $NaNO_3$ generally remains low (pH ~5). However, sludge immobilized and heated with Aquaset II powder or the granular Aquaset II G is only slightly affected by nitrate concentration and decreases moderately from about 8.5 to 7.4 as nitrate concentration increases. The simulant sludge treated with PC and then heated has pH ~12.6 and is hardly affected by nitrate concentration. The high pH of the PC-bearing simulant sludge is because of the pH buffering provided by the calcium hydroxide, $Ca(OH)_2$, present in PC. Although it is not clear whether uranium metal corrosion occurred in the PC-bearing tests after heating, any hydrogen scavenging afforded by nitrate according to Reaction 3.6 (see Section 3.3.4) would produce NaOH and keep pH high.

3.3.4 Nitrate Reduction to Form Ammonia

As shown in Reaction 3.6, ammonia can be formed by chemical reduction of nitrate caused by uranium metal oxidation to UO_2:

$$2\ U_{(s)} + NO_3^-{}_{(aq)} + 2\ H_2O_{(l)} \rightarrow 2\ UO_{2\,(s)} + NH_{3\,(aq)} + OH^-{}_{(aq)} \qquad \text{Reaction 3.6}$$

According to measurements by selective ion electrode, ammonia was produced in quantifiable amounts ($\gtrsim 10^{-8}$ moles or $\gtrsim 0.00001$ millimoles) in most Series 1, 2, and 3 tests and was even found for all control Tests 1 that contained water and uranium metal beads and no added nitrate (Table 3.3). Only the Tests 2-80 and 5-80 in Series 3, both without added nitrate in the presence of sludge without and with added Aquaset II, respectively, had no quantifiable ammonia. The amounts of ammonia produced as functions of nitrate concentration are shown in Figure 3.8. The lines in Figure 3.8 are visual guides to the data trends and have no statistical meaning.

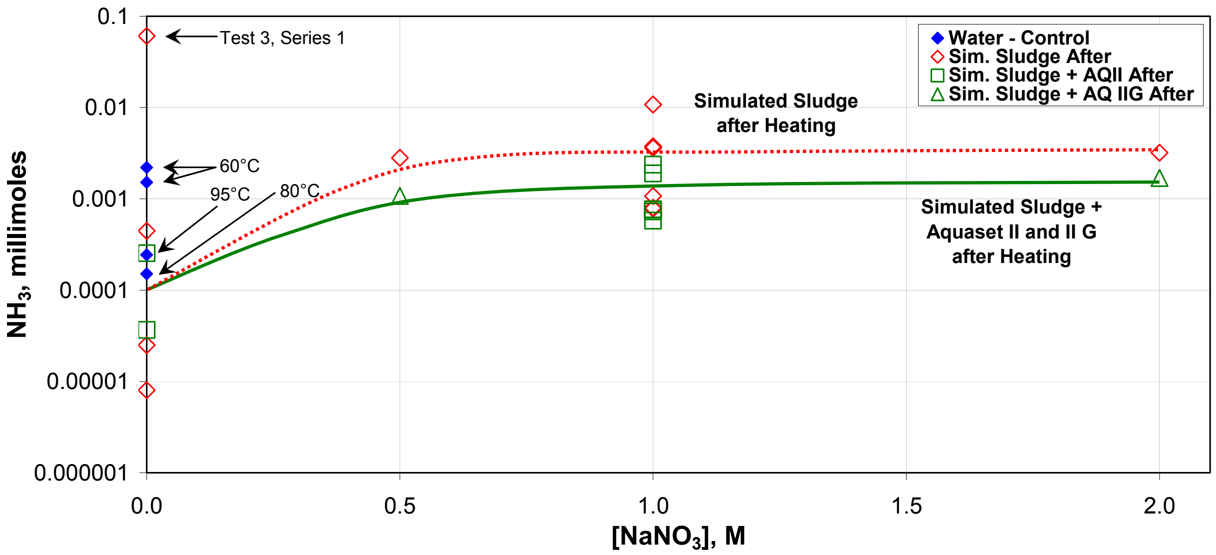


Figure 3.8. Ammonia Production for Sludge with and Without Immobilization Agent as Functions of $NaNO_3$ Concentration

Quantities of ammonia found in control Tests 1 are ~0.002 millimoles at 60°C from Series 1 and 2 and ~0.0002 millimoles at 80°C and 95°C in Series 3. The ~0.00002 to 0.0002 millimoles of NH_3 observed in similar ~60°C control tests from previous studies of uranium metal corrosion in water under air atmosphere (Sinkov et al. 2010) are at least a factor of 10 lower than in the present 60°C tests.

The ammonia amounts produced in tests with no nitrate varied widely. The ~0.06 millimole of NH_3 found in the ~60°C Test 3 of Series 1 (simulated sludge with no immobilization agent) is clearly much greater than the ~0.0001-millimole or lower amounts found for similar tests containing simulant sludge with no immobilizing agent (Tests 3 and 4 in Series 2 at ~60°C and Tests 2-80 and 2-95 in Series 3 at ~80°C and ~95°C, respectively). The reason for this great divergence is unknown.

The NH_3 quantities in the presence of nitrate are much more consistent. For sludge only, about 0.003 millimoles of NH_3 are found, while for simulant sludge blended with Aquaset II or with Aquaset II G added on top of the simulant sludge, ~0.001-0.002 millimoles of NH_3 are found. About 0.1 moles of NH_3 are formed per mole of uranium metal corroded.

The presence of 0.003 millimoles of NH_3 in 2.5 mL of interstitial solution is equivalent to 0.0012 M NH_3 (~20 ppm). This concentration is very small compared with the ~2.9 M NH_3 found in 5% household ammonia solution. At 20°C, the NH_3 vapor pressure above a 20 ppm NH_3 solution is ~11 ppm (Perman 1903), about 5 times above the 2.6 ppm olfactory threshold of detection of NH_3 (Smeets et al. 2007). The NH_3 vapor pressure is little affected by dissolved $NaNO_3$, even up to about 6 M concentration, and is negligibly affected by the NaOH produced in concentrations equimolar to those of the NH_3 (Sing et al. 1999). If all of the 0.42 millimoles of uranium metal had reacted and the nascent hydrogen were scavenged entirely by nitrate to form ammonia, the solution would become 0.084 M NH_3 (~1430 ppm), less than 3% of the concentration of household ammonia, and have a projected NH_3 vapor pressure at 20°C of ~8×10^{-4} atm. However, the present testing showed that only ~20% of the chemical equivalents of nitrate reduction by uranium metal resulted in NH_3. Therefore, the anticipated total NH_3

solution concentration upon complete uranium metal reaction would be ~0.017 M (~290 ppm) and provide a NH_3 vapor pressure of ~160 ppm in the drum head space.

3.3.5 Nitrate Reduction to Form Nitrite

Nitrite can form through nitrate chemical reduction by uranium metal oxidation to UO_2 per Reaction 3.7:

$$U_{(s)} + 2\ NO_3^-{}_{(aq)} \rightarrow UO_{2\,(s)} + 2\ NO_2^-{}_{(aq)} \qquad \text{Reaction 3.7}$$

In the previous testing of H_2 mitigation by nitrate, spectrophotometric analyses of nitrite were performed by measuring light absorbance at 354.9 nm ($\varepsilon_{max,\ 354.9\ nm} = 24.7$ l/mol·cm [Sinkov et al. 2010]).

In the present tests containing simulant sludge with its complement of metaschoepite, $UO_3{\cdot}2H_2O$, dissolved U(VI) appears in solutions at lower pH because of attack of U(VI) solid phases by the HNO_3 produced by Reactions 3.4 or 3.5. Depending on pH, the dissolved U(VI) species may include hydrolyzed monomers, dimers, and trimers at pH 4-6 but also can include carbonate complexes. The carbonate can arise from absorption of atmospheric CO_2 and from sludge sources or Aquaset II. All of these dissolved U(VI) species, as well as unknown constituents in the immobilizing agents or finely particulate matter, strongly increase in absorbance as wavelengths decrease below about 380 nm. Because of these strong absorptions, spectrophotometric quantitation of nitrite is compromised. Therefore, ion chromatography (IC) was used as an alternative means to measure nitrite.

Ion chromatographic measurements of nitrate and nitrite concentrations of most nitrate-bearing test solutions were performed both before and after heating. To obtain sufficient solution volume for analysis from the thick product sludge simulant and simulant/immobilization agent pastes, the media first had to be diluted in water by factors from about 2 to 13. Despite this preliminary dilution, additional sample dilution at times was required to eliminate overlap of the nitrate peaks from the 0.5, 1, and 2 M nitrate solutions used in Series 1, 2, and 3 onto the nitrite peak location in the ion chromatogram. As a result, the detection limit for nitrite by IC was 1000 µg/mL, equivalent to ~0.02 M nitrite, and the effective detection limit after applying the dilution factors ranged from ~0.02 M to ~0.29 M.

Only one of the analyzed product solutions, Test 2 in Series 2, had nitrite concentration above the analytical threshold. The 0.026 M nitrite measured for this test meant that 0.13 millimoles were produced in the 5 mL of test solution. The quantities of nitrite generated in the remaining analyzed tests that contained nitrate and sludge simulant were <0.05 millimoles to <0.7 millimoles. Detailed findings are shown in Table 3.3. This low sensitivity of the IC data because of dilution and interference from nitrate made quantitative assessment of nitrite participation in the Series 1, 2, and 3 tests impossible to judge.

Because of the difficulties in obtaining meaningful IC results, detailed examination of the spectra derived from Tests 11 and 12 of Series 2 were performed to determine if more sensitive estimates of nitrite concentration could be made. These two tests, containing simulated sludge treated with 1 M $NaNO_3$, immobilized with Aquaset II, and heated at ~60°C for 4 and 8 weeks, respectively, are of high interest for potential application of nitrate to immobilized waste forms. The spectral intensity near the 355-nm nitrite absorbance peak and the dilution factor of 2 means that the nitrite concentration for Test 11 was <0.002 M and the nitrite quantity generated was <0.05 millimoles; the nitrite concentration for Test 12 was <0.0012 M or <0.03 millimoles of nitrite generated (Table 3.3). Lower detection limits could not be attained because of strongly absorbing spectral interferences from dissolved U(VI) and perhaps contributions from the simulant sludge and Aquaset II. In comparison, as seen in Table 3.3, Tests 11 and 12 each produced about 0.006 millimoles of NH_3.

The paired IC results for nitrate concentration before and after the heating step were also examined to determine if significant depletion of the nitrate reagent could be detected. Amounts of nitrate present in the nitrate-bearing tests before and after heating are shown in Table 3.3. Except for Tests 2 in Series 1 and 2 (which are intended to emulate the KOP sludge and thus contain 10 times as many uranium metal beads as the other tests and have no simulant sludge or immobilizing agent), the amounts of nitrate present before and after heating are nearly identical. For the tests containing 1 M $NaNO_3$ (all found in Series 2 and 3), the average decrease in nitrate is 0.08 ± 0.24 millimoles out of the ~2.3 millimoles of nitrate originally present in each test. Thus, nitrate consumption was statistically undetectable.

The failure to discern nitrate consumption is not surprising because the maximum amount of uranium metal corroding in these tests, ~0.05 g (~0.2 millimoles) would consume only ~0.1 millimoles of nitrate and produce ~0.1 millimoles of NH_3 (Reaction 3.6). The loss of 0.1 millimoles of nitrate would be difficult to distinguish from the ~2.3 millimoles initially present in the 1 M $NaNO_3$ test solutions. If the less prevalent Reaction 3.7 to form nitrite were operating in the absence of Reaction 3.6, nitrate consumption and nitrite production would be ~0.42 millimoles. Observations of material balance are considered in the following section.

3.4 Material Balance

As discussed in Section 3.3, nitrate is reduced to form the nitrogen-bearing products nitrite, N_2O, N_2, and NH_3. The reactions of nitrate thus cannot be determined solely by decreases in its concentration but must be determined by the quantities of its reduction products. It is also surmised that NH_3 can form by reduction of atmospheric N_2. The chemical equivalent material balance for uranium metal corrosion to form UO_2 and U(VI) in the presence of nitrate, oxygen, and nitrogen is expressed in Equation (2):

$$\begin{aligned}\text{Equivalents of U corroded to } UO_2 + \text{equivalents of } UO_2 \text{ oxidized to U(VI)} = \\ \text{equivalents of } O_2 \text{ consumed to form } OH^- + \\ \text{equivalents of } H_2 \text{ produced from } H_2O \text{ reduction} + \\ \text{equivalents of } NO_2^- \text{ produced from } NO_3^- \text{ reduction} + \\ \text{equivalents of } N_2O \text{ produced from } NO_3^- \text{ reduction} + \\ \text{equivalents of } N_2 \text{ produced from } NO_3^- \text{ reduction} + \\ \text{equivalents of } NH_3 \text{ produced from } NO_3^- \text{ reduction} + \\ \text{equivalents of } NH_3 \text{ produced from } N_2 \text{ reduction.}\end{aligned} \qquad (2)$$

The oxidation of UO_2 was not measured in the present tests because the quantity of UO_2 present in the simulant sludge (1.65 millimoles) would overwhelm the maximum amounts of uranium metal corroded to UO_2 (no more than ~0.2 millimoles). However, as seen in Section 3.3.2, only about 0.01 millimoles additional O_2 was consumed (of ~0.04 to 0.06 millimoles total O_2 consumed) in tests containing simulant sludge or simulant sludge plus immobilizing agent compared with parallel tests with uranium metal alone. Therefore, the only UO_2 that was oxidized arose from uranium metal corrosion. Because prior testing showed that UO_2 is not oxidized by nitrate (Sinkov et al. 2010), the UO_2 oxidation that did occur was accomplished by O_2.

Based on the foregoing discussions and the gas analysis data presented in Section 3.2, the primary uranium metal and UO_2 oxidation and water, oxygen, nitrogen, and nitrate reduction half-reactions observed in the present testing are summarized in Table 3.4.

Table 3.4. Uranium Metal and UO_2 Oxidation and Water, Oxygen, Nitrogen, Nitrate, and Nitrite Reduction Half Reactions

Oxidations
Uranium Metal
$U + 4\ OH^- \rightarrow UO_2 + 2H_2O + 4\ e^-$
Uranium Dioxide
$UO_2 + 2\ OH^- + H_2O \rightarrow UO_3 \cdot 2H_2O + 2\ e^-$
Reductions
Water
$2\ H_2O + 2\ e^- \rightarrow H_2 + 2\ OH^-$
Oxygen
$O_2 + 2\ H_2O + 4\ e^- \rightarrow 4\ OH^-$
Nitrogen
$N_2 + 6\ H_2O + 6\ e^- \rightarrow 2\ NH_3 + 6\ OH^-$
Nitrate
$NO_3^- + H_2O + 2\ e^- \rightarrow NO_2^- + 2\ OH^-$
$2\ NO_3^- + 5\ H_2O + 8\ e^- \rightarrow N_2O + 10\ OH^-$
$NO_3^- + 3\ H_2O + 5\ e^- \rightarrow N_2 + 6\ OH^-$
$NO_3^- + 6\ H_2O + 8\ e^- \rightarrow NH_3 + 9\ OH^-$

The analytical findings and chemical material balances for most tests in the three test series are shown in Table 3.5. Because uranium metal present in the PC-bearing solidification agents (PC itself and Aquaset II H) could not be retrieved for weighing after corrosion, chemical material balances could not be obtained for Tests 7, 8, 9, and 10 in Series 1 and Tests 7, 9, and 10 in Series 2. Nitrate concentrations are not presented in Table 3.5 because the concentration changes were not sufficiently high to be registered with confidence and, more importantly, because the chemical changes for nitrate are determined more reliably by measurement of nitrate reduction products.

Table 3.5. Chemical Equivalents and Material Balance

Test	$[NaNO_3]$, M	Other Materials	Chemical Quantities, milliequivalents							Chemical Balance Ratio$^{(b)}$
			Reactants		Rct/Prd	Products				
			U	O_2	N_2	H_2	N_2O	NO_2^-	$NH_3^{(a)}$	
Test Series 1, TI25; 62.2°C										
1	0.0	None	-0.0119	0.1489	-0.0319	0.0005	0.0000	NM	0.0045	-0.08
2	1.0	None; 300 U_{metal} beads	1.2396	0.5013	0.2345	0.0003	0.0000	<0.22	0.4297	1.06
3	0.0	Sim. sludge	0.7148	0.4756	-0.0155	0.4539	0.0000	NM	0.1820	0.63
4	0.5	Sim. sludge	0.1746	0.5274	0.0695	0.0464	0.0151	NM	0.0225	0.26
5	1.0	Sim. sludge	0.6769	0.5804	-0.0121	0.2916	0.0085	NM	0.0260	0.76
6	2.0	Sim. sludge	0.0832	0.5971	0.2157	0.0006	0.0000	<0.11	0.0256	0.10
7	0.5	Sim. sludge in PC	NM	0.4915	0.1552	0.0003	0.0000	NM	0.0577	NM
8	2.0	Sim. sludge in PC	NM	0.6106	0.1316	0.0010	0.0000	NM	0.0003	NM
9	0.5	Sim. sludge in Aq. II H	NM	0.7200	0.3182	0.00002	0.0000	NM	0.0366	NM
10	2.0	Sim. sludge in Aq. II H	NM	0.5766	0.0487	0.0003	0.0299	NM	0.0871	NM
11	0.5	Sim. sludge in Aq. II G	0.1163	0.6491	0.4211	0.0006	0.0000	<1.45	0.0086	0.11
12	2.0	Sim. sludge in Aq. II G	0.1408	0.6832	0.3001	0.0004	0.0000	<1.45	0.0135	0.14
Test Series 2, TI28; 62.4°C, 4 weeks; 63.5°C, 8 weeks										
1	0.0	None, 4 wks	0.8184	0.1925	-0.0978	0.3528	0.0009	NM	0.0066	1.48
2	0.5	None, 4 wks; 300 U_{metal} beads	12.3285	0.2948	-0.5225	2.1214	0.0209	0.26	4.8094	1.83
3	0.0	Sim. sludge, 4 wks	0.9463	0.3104	-0.1038	0.4041	0.0000	NM	0.0001	1.32
4	0.0	Sim. sludge, 8 wks	1.0863	0.3614	-0.0377	0.2342	0.0000	NM	0.0013	1.82
5	1.0	Sim. sludge, 4 wks	0.1729	0.2632	0.2115	0.0002	0.0038	<0.22	0.0086	0.35
6	1.0	Sim. sludge, 8 wks	0.4456	0.2319	0.2183	0.0001	0.0054	<0.22	0.0262	0.92
7	0.0	Sim. sludge in PC, 8 wks	NM	0.2008	0.1190	0.0046	0.0002	NM	0.0052	NM
8	0.0	Sim. sludge in Aq. II, 8 wks	0.6813	0.3303	0.1392	0.0317	0.0005	NM	0.0003	1.88
10	1.0	Sim. sludge in PC, 4 wks	NM	0.2654	0.3321	0.00005	0.0004	<0.22	0.0122	NM
9	1.0	Sim. sludge in PC, 8 wks	NM	0.3105	0.2948	0.0001	0.0004	<0.22	0.0099	NM
11	1.0	Sim. sludge in Aq. II, 4 wks	0.1597	0.1942	0.0364	0.0012	0.0059	<0.10	0.0058	0.66
12	1.0	Sim. sludge in Aq. II, 8 wks	0.2532	0.3155	0.3324	0.0001	0.0015	<0.06	0.0035	0.39

Table 3.5. (cont.)

Test	$[NaNO_3]$, M	Other Materials	Chemical Quantities, milliequivalents							Chemical Balance Ratio[b]
			Reactants		Rct/Prd	Products				
			U	O_2	N_2	H_2	N_2O	NO_2^-	NH3[a]	
Test Series 3, TI36; 80.0°C, 10 days; 94.1°C, 4 days										
1-80	0.0	None	0.8642	0.2154	-0.0606	0.4515	0.0006	NM	0.0008	1.29
2-80	0.0	Sim. sludge	0.9724	0.1680	-0.0059	0.3429	0.0007	NM	0.0001	1.90
3-80	1.0	Sim. sludge	0.1526	0.2601	0.0906	0.0004	0.0029	<0.22	0.0089	0.42
4-80	1.0	Sim. sludge	0.1538	0.2979	0.1226	0.0003	0.0033	<0.22	0.0092	0.35
5-80	0.0	Sim. sludge in Aq. II	0.5110	0.1415	0.0078	0.2103	0.0254	NM	0.0001	1.35
6-80	1.0	Sim. sludge in Aq. II	0.2084	0.2126	0.0176	0.0094	0.0258	<0.43	0.0101	0.76
7-80	1.0	Sim. sludge in Aq. II	0.1685	0.2641	0.0024	0.0044	0.0361	<0.43	0.0101	0.53
1-95	0.0	None	0.5638	0.1346	-0.0477	0.4294	0.0006	NM	0.0007	1.00
2-95	0.0	Sim. sludge	0.6162	0.1376	-0.0279	0.3266	0.0000	NM	0.0000	1.33
3-95	1.0	Sim. sludge	0.2879	0.2163	0.0742	0.0005	0.0078	<0.22	0.0290	0.88
4-95	1.0	Sim. sludge	0.3999	0.2151	0.0622	0.0004	0.0084	<0.22	0.0863	1.07
5-95	0.0	Sim. sludge in Aq. II	0.3846	0.2740	-0.0011	0.0402	0.0009	NM	0.0001	1.22
6-95	1.0	Sim. sludge in Aq. II	0.1522	0.3734	0.0318	0.0048	0.0123	<0.43	0.0152	0.35
7-95	1.0	Sim. sludge in Aq. II	0.2546	0.1491	0.0111	0.0133	0.0626	<0.43	0.0189	1.00

Sim. = Simulated.

Data marked by grey shading indicate tests for which initiation of full anoxic corrosion is doubtful or unknown.

Test 5 in Series 1, also marked by grey shading, underwent dilution of the contained nitrate during testing. See beginning of Section 3.0.

(a) For tests without nitrate, equivalents of NH_3 are reckoned as 3 times the number of moles of NH_3 found in the test solutions based on atmospheric N_2 reduction. For tests with nitrate, equivalents of NH_3 are 8 times the number of moles of NH_3 found in the test solutions based on nitrate reduction.

(b) The chemical balance ratio is the ratio of the number of chemical equivalents oxidized to the number of chemical equivalents reduced. The number of chemical equivalents oxidized includes U metal oxidized to UO_2 as measured by U metal weight loss. The chemical equivalents reduced include O_2 reduction to H_2O or OH^- as measured by O_2 consumption, H_2O reduction to H_2 as measured by H_2 formation, N_2 reduction to NH_3 (in nitrate-free systems) as measured by NH_3 formation, and NO_3^- reduction to NO_2^-, N_2O, N_2, and NH_3 as measured by formation of these nitrate reduction products. The contribution from UO_2 oxidation to U(VI) by O_2 in simulant sludge was not accounted because of the large quantity of UO_2 in simulant sludge compared with the small amount of UO_2 from U metal corrosion and the small incremental amount of O_2 consumption observed comparing tests with and without simulated sludge. Nitrate oxidation of UO_2 has been found to be negligible (Sinkov et al. 2010).

The chemical material balances provided in Table 3.5 are the arithmetic ratios of the number of chemical equivalents oxidized (uranium metal oxidized to UO_2) to the number of chemical equivalents reduced (H_2O reduced to H_2, O_2 reduced to H_2O and OH^-, N_2 reduced to NH_3 for nitrate-free tests, and NO_3^- reduced to NO_2^-, N_2O, N_2, and NH_3). Ideally, the number of oxidation and reduction reaction chemical equivalents should be equal and the chemical balance ratio should be 1.00. The observed ratios vary widely around 1 (average 0.91 ± 0.58 at 1 σ, excluding values from invalid tests indicated by shading in Table 3.5). Chemical balance ratios less than 1 indicate that materials being oxidized are under accounted or that materials being reduced are over accounted with the converse true for chemical balance ratios greater than 1.

In the present 1 M $NaNO_3$ tests with simulated sludge and Aquaset II, about 60% of the observed uranium metal corrosion and the entire subsequent product UO_2 oxidation to $UO_3 \cdot 2H_2O$ occurred by reaction with O_2. The remainder of the uranium metal oxidation was anoxic to form a quantity of H_2 corresponding to an attenuation factor of 1000 and, mediated by nitrate, form N_2, N_2O, and NH_3. Ignoring the contribution of the oxic reactions of uranium metal and UO_2 with O_2, the Test 7-95 (Series 3) observations are described by Reaction 3.8:

$$U_{(s)} + 0.882\ NO_3^-{}_{(aq)} + 0.587\ H_2O_{(l)} \rightarrow \qquad \text{Reaction 3.8}$$
$$UO_{2\,(s)} + 0.002\ H_{2\,(g)} + 0.042\ N_{2\,(g)} + 0.351\ N_2O_{(g)} + 0.096\ NH_{3\,(aq)} + 0.882\ OH^-{}_{(aq)}$$

The idealized stoichiometry presented in Reaction 3.8 varies moderately for similarly constituted Series 2 and 3 tests. In addition, because of insufficient analytical sensitivity, nitrite was not observed in any of the present tests. Therefore, Reaction 3.8 does not include nitrite although nitrite may be present as determined in prior testing (Sinkov et al. 2010). As a result, somewhat different relative amounts of nitrate consumption and hydrogen, nitrogen, and nitrous oxide gas and ammonia and nitrite solute production may be observed in other experiments.

Idealized stoichiometries for the reaction of nitrate with corroding uranium metal in solution only and in simulated sludge also were determined based on experimental observations. The stoichiometry in 1 M $NaNO_3$ solution but without simulated sludge or Aquaset II , as found in Test 4 in Series 4 and approximated by analogous tests from the earlier study (Sinkov et al. 2010), is shown in Reaction 3.9. Problems in detecting nitrite by spectrophotometry in the presence of dissolved U(VI) may have been the reason no measurable nitrite was found in this prior test.

$$U_{(s)} + 0.968\ NO_3^-{}_{(aq)} + 0.688\ H_2O_{(l)} \rightarrow \qquad \text{Reaction 3.9}$$
$$UO_{2\,(s)} + 0.004\ H_{2\,(g)} + 0.62\ NO_2^-{}_{(aq)} + 0.004\ N_2O_{(g)} + 0.34\ NH_{3\,(aq)} + 0.348\ OH^-{}_{(aq)}$$

The idealized stoichiometry observed in simulated sludge containing 1 M $NaNO_3$, based on Test 6 of Series 2 in the present experimental set and approximated by analogous tests in the present study, is shown in Reaction 3.10.

$$U_{(s)} + 0.7653\ NO_3^-{}_{(aq)} + 0.4799\ H_2O_{(l)} \rightarrow \qquad \text{Reaction 3.10}$$
$$UO_{2\,(s)} + 0.0008\ H_{2\,(g)} + 0.34\ N_{2\,(g)} + 0.0105\ N_2O_{(g)} + 0.0643\ NH_{3\,(aq)} + 0.7653\ OH^-{}_{(aq)}$$

The precisions of the chemical quantities observed in the actual testing are much less exact than those shown in the exactly balanced idealized Reactions 3.8, 3.9, and, 3.10. Nevertheless, the overall reaction product distributions reflected in the stated reactions indicate the shifts in product distribution and lesser shifts in nitrate demand that occur as the uranium metal corrosion system in 1 M $NaNO_3$ becomes complicated by the presence of sludge components and by the additional presence of Aquaset II.

The quantities of reactants and products, taken from Reactions 3.8, 3.9, and 3.10 and normalized to one mole of uranium corroded, are displayed in Figure 3.9. This figure shows that despite changes in the relative amounts of the nitrite, nitrous oxide, nitrogen, and ammonia products, about 0.77 to 0.97 moles of nitrate are required per mole of uranium corroded and complementary mole of UO_2. Nitrite production is only observed in aqueous solution; no nitrite is found for tests that included the sludge simulant. As noted in Section 3.3.5, analytical difficulties are experienced in quantifying nitrite in the presence of

U(VI) by spectrophotometry and in quantifying nitrite in the presence of nitrate by IC. However, it might also be true that little nitrite would remain in tests containing sludge simulant owing to its consumption by reaction with the UO_2 present in the simulant, possibly abetted by ferrihydrite (see Sections 3.4 and 3.2.4, respectively, of Sinkov et al. 2010). More sensitive techniques to quantify nitrite are required to examine this postulate.

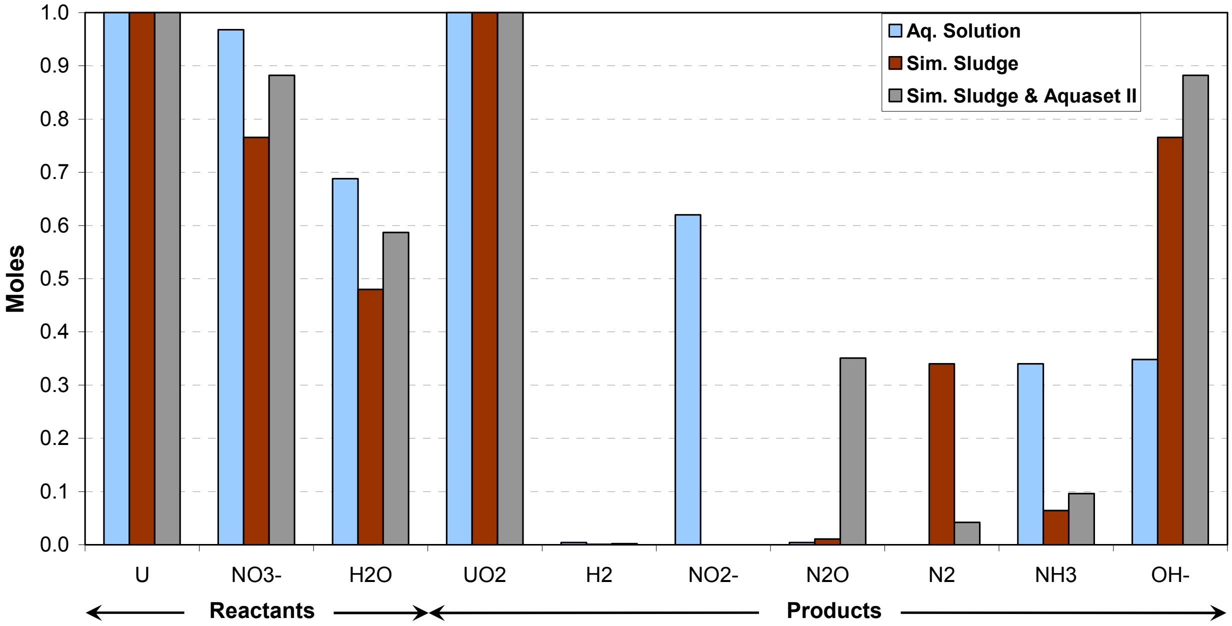


Figure 3.9. Uranium Metal Anoxic Corrosion Reaction Stoichiometries in 1 M $NaNO_3$ in Aqueous Solution, Simulated Sludge, and Simulated Sludge with Aquaset II

For uranium metal corrosion in 1 M $NaNO_3$ solution only (Reaction 3.9 and Figure 3.9), nitrate reduction products are mostly nitrite and ammonia. Nitrate reduction during uranium metal oxidation in simulated sludge containing 1 M $NaNO_3$ produces mostly nitrogen gas followed by ammonia and a small fraction of nitrous oxide (Reaction 3.10 and Figure 3.9). For uranium metal corrosion in mixtures of simulated sludge and Aquaset II in 1 M $NaNO_3$ (see Reaction 3.8 and Figure 3.9), the dominant nitrate reduction product is nitrous oxide, distantly followed by ammonia and nitrogen gas.

According to Reaction 3.8, about 0.9 moles of nitrate are consumed per mole of uranium metal reacted in simulated sludge immobilized in Aquaset II. Conservative conditions used in the present testing, including high uranium metal loading (3.6 wt%, dry basis) and dry WIPP-ready simulant sludge / Aquaset II pastes containing only 0.45 mL of sodium nitrate solution per gram of combined simulated sludge and Aquaset II clay, led to high uranium metal-to-nitrate ratios. At these conservative but process-relevant test conditions and even assuming one mole of nitrate consumption per mole of uranium, nitrate still was present at about 6 times the stoichiometric requirement. According to Reaction 3.8, ~0.016 M NH_3 will be present in the interstitial product solution after complete uranium metal corrosion. This NH_3 concentration is low and equivalent to a ~190-fold dilution of 5% household ammonia solution. Even if all hydrogen from complete uranium metal corrosion were scavenged to form NH_3, the ending NH_3 concentration in the interstitial solution of the thickened WIPP simulant sludge paste would be 0.084 M or a ~35-fold dilution of household ammonia solution.

3.5 Additional Questions

The present testing confirms prior work that nitrate is an effective agent to attenuate H_2 generation from the corrosion of uranium metal in water and in simulated K Basin sludge. In addition, testing demonstrates that the effectiveness of nitrate also extends to potential candidate solidified K Basin waste forms for WIPP disposal and, at 1 M nitrate concentration and hydrogen attenuation factors of about 1000 or greater, readily meets the target attenuation factor of 100, which is achieved at about 0.5 M $NaNO_3$. Additional testing is recommended to investigate remaining issues in application of this technology and to substantiate further the utility of nitrate to attenuate H_2 generation in K Basin sludge storage, treatment, transportation, and ultimate disposal.

Testing with genuine sludge begins under strictly inert conditions, achieved using sealed and neon-backfilled reaction vessels as was done in earlier gas generation testing (e.g., Schmidt et al. 2003), may be warranted so that interferences due to oxygen consumption are minimized, and to further validate the performance of nitrate for actual K Basin sludge materials. Within such testing, long-term tests to examine the potential reactions at expected sludge storage temperatures may be considered. Parameters to be measured include temperature, phase changes, gas volume and composition, uranium metal weight losses, nitrite and ammonia formation from nitrate, and sludge volume and strength as a function of storage time. Testing to date has occurred at ~60°C to 95°C. Therefore, nitrate should be tested for its efficacy in application to K Basin sludge at lower temperatures representative of its potential application (e.g., trans-site shipment, long-term onsite storage, and processing for WIPP disposal). The testing could be incorporated as part of long-term testing envisioned to determine sludge mechanical properties. However, longer-term testing at lower temperatures could be inconclusive if the uranium metal in the test matrix does not overcome the induction period necessary to enter the anoxic corrosion regime. In a previous test of actual sludge and water at ~30°C hot cell conditions, 10,000 hours were inadequate to overcome the induction period (Schmidt et al. 2003) even though other samples of the same sludge material entered anoxic corrosion at temperatures as low as 40°C (Delegard et al. 2000). Yet other sludge samples generated appreciable hydrogen gas at ~30°C hot cell temperatures even following air sparging (Makenas et al. 1997). Therefore, neither extended induction times nor aeration cannot be relied upon to avoid uranium metal corrosion by water to generate hydrogen.

Nitrate also should be tested for its impact on diminishing the H_2 arising from radiolysis especially in the presence of solidifying agents. The attractiveness of pursuing this avenue of investigation would be increased if credit for decreasing radiolytic H_2 could be obtained from WIPP authorities. Such credit would allow greater waste loading for containers destined for WIPP.

Based on reviews of radiolysis research in aqueous solution, nitrate forms nitrite and diatomic oxygen with the radiolytic yield (G value) increasing with increasing nitrate concentration (Pikaev 1960). A factor-of-6 decrease in the radiolytic H_2 yield in 1 M $NaNO_3$ is expected compared with water only (see Figure 1 of Meisel et al. 1991) while direct studies show gamma radiolytic H_2 yield decreases by a factor of 4 to 5 in 1 M $NaNO_3$ compared with the yield in pure water (Figure 3.10). In a separate study, researchers found that ~0.8 M nitrate in water used to prepare a Savannah River Site simulant tank waste grout attenuated gamma radiolytic H_2 by about a factor of 3 compared with grouted waste in the absence of nitrate (from Table 3 of Bibler 1978). Radiolysis of the nitrate contained in the grouted waste also produced O_2 and small quantities of N_2O. Simulated low- and intermediate-level reprocessing waste solution containing 300 g $NaNO_3$ per liter (~3.5 M) was immobilized in cement and subjected to gamma radiolysis (Möckel and Köster 1982). As the waste (and nitrate) cement matrix loading increased, radiolytic H_2 attenuation increased by factors of ~5 to ~10 compared with cement containing no nitrate. Oxygen was not formed in the nitrate-free cement tests but constituted ~60% of the product gas when nitrate was present with the balance of the gas product being H_2. In a third study with grouted waste, addition of sufficient $NaNO_3$ to the make-up water used to prepare the grouted waste form to achieve ~0.43 M $NaNO_3$ (1 wt% $NaNO_3$ in the waste form) decreased the radiolytic H_2 generation rate by a factor of ~3 compared with tests without $NaNO_3$ (Lewis and Warren 1990). The Portland cement grout formulation also contained fly ash and (blast furnace) slag while the waste contained lithium and potassium chloride.

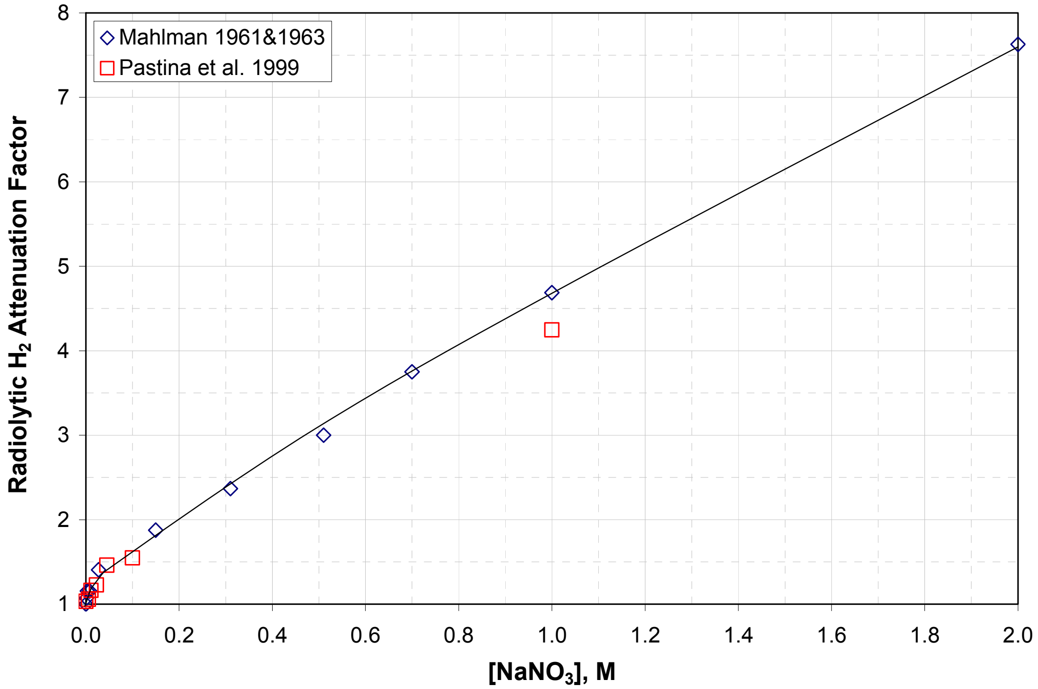


Figure 3.10. Radiolytic Hydrogen Attenuation Factor as a Function of $NaNO_3$ Concentration in Water

The radiolysis studies show that some nitrate loss by radiolysis may occur in nitrate-amended stored K Basin sludge or immobilized sludge awaiting shipment to WIPP. Fortunately, the nitrite product from nitrate radiolysis itself is also very effective in attenuating H_2 generation from anoxic corrosion of uranium metal (Sinkov et al. 2010). Ultimately, radiolysis of the product nitrite in aqueous solution also could lead to nitrate by reaction with peroxide radicals such that a secular equilibrium between nitrate and nitrite is established. Because added components such as dissolved gas, sludge solids, and immobilization agents can alter nitrate radiolytic decomposition rates and H_2 attenuation (Flakowski et al. 1995), investigation of nitrate concentration changes in radiolytic fields for K Basin sludge and solidifying agent mixtures is recommended.

The acceptability of any product waste for WIPP disposal must be determined. Objection to the use of nitrate is unlikely given its ubiquity in prior wastes disposed to WIPP from the Rocky Flats Site and the Hanford Site but its application to the K Basin sludge may be an issue. Depending on the desired implementation strategy, management of the excess nitrate solution, and the impact of lower pH caused by reaction of sodium ion with metaschoepite also must be evaluated.

Future testing should be tailored to actual target waste streams (e.g., settler tank and container sludge, orphan materials in sludge processing, and decommissioning and decontamination rubble) to meet specific functional design criteria within the particular points of operational insertion such as storage, treatment, or shipping.

4.0 Conclusions

Laboratory experimentation was conducted to determine the effects of nitrate to lower the rate of H_2 generation from the reaction of uranium metal with water in simulated sludge and in simulated sludge mixed with water-immobilization agents. The tests, run under controlled temperature conditions at ~60°C, 80°C, and 95°C, used nearly spherical high-purity uranium metal beads and simulated sludge meant to emulate KW Basin-containerized sludge. The gas space above all reacting mixtures was air.

The immobilization agents tested were PC, a commercial blend of PC with sepiolite clay (Aquaset II H), granulated sepiolite clay (Aquaset II G), and sepiolite clay powder (Aquaset II) and the mass of solidification agent added was identical to the mass of solids present in the simulated sludge. The solution fraction in each test was 0.9 mL per gram of sludge solids or 0.45 mL per gram of combined sludge solids and immobilization agent. In all cases except tests with Aquaset II G, the simulated sludge was mixed intimately with the immobilization agent before testing commenced with the raw mixtures having a thick paste consistency. For Aquaset II G, the granulated clay was added to the top of the settled sludge/solution mixture according to application directions provided by the manufacturer.

The reaction progress was monitored by measuring the gas volume, the extent of uranium metal corrosion (as determined by weight loss), the concentrations of nitrate reduction product (nitrite and ammonia), and the final gas compositions and quantities. The uranium metal corrosion rates were determined by measuring the weight changes in the uranium metal beads using the known uranium metal density and assuming isotropic penetration and spherical bead geometry. Because the uranium metal beads remaining after testing of the hardened waste forms containing PC could not be retrieved and weighed, no information on corrosion rates in these media could be determined. The observed corrosion rates were compared with rates forecast from the STP rate law at the individual test temperatures. The ratios of the STP forecast corrosion rates to the observed rates were calculated to find the uranium metal corrosion rate attenuation factors.

Hydrogen generation quantities were determined by gas volume and composition analyses. The analyzed quantities were compared with quantities expected based on non-attenuated H_2 generation of the same uranium metal materials at full anoxic rate forecast at the test temperature by the STP rate law. The ratios of the expected to the observed H_2 productions were calculated to arrive at H_2 attenuation factors.

The uranium metal corrosion rate and H_2 generation data for the present tests were compared and combined, where appropriate, with results of earlier tests performed for the STP (Sinkov et al. 2010). The combined data were evaluated to help determine trends in performance for the solution-only, simulant sludge, and sludge/immobilization agent systems as functions of $NaNO_3$ concentration and test temperature.

The uranium metal corrosion rates for six systems of aqueous solution, KW Basin-simulated sludge, and KW Basin-simulated sludge/Aquaset II blends with and without 1 M $NaNO_3$ paralleled the STP rate law for uranium metal corrosion in anoxic water as plotted in Arrhenius coordinates. Therefore, these various systems showed similar activation energies over the studied ~60°C to ~95°C temperature range. Rates in water alone and in simulated sludge lie near or just slightly below the STP rate while the nitrate-free system of Aquaset II with simulated sludge decreases rates by about a factor of 3 below the STP rate. In 1 M $NaNO_3$, the corrosion rate decreases about a factor of 1.3 below that found for water alone and about a factor of 2 below the STP rate. However, addition of 1 M nitrate to simulated sludge decreases the corrosion rate by about a factor of 5 while addition of 1 M nitrate to sludge/Aquaset II mixture decreases the corrosion rate by ~2.5 compared with the respective nitrate-free analogues. Overall, mixed pastes of simulated sludge with Aquaset II and treated with 1 M $NaNO_3$ have uranium metal corrosion rates about a factor of 8 to 10 lower than the STP rate law. The observed parallel adherence to the STP rate law in Arrhenius coordinates for these varied systems gives confidence to forecast behaviors to process-scale systems and lower temperatures.

The uranium metal corrosion rate in aqueous solution decreases by about a factor of 2, compared with the STP rate, between 0.5 M and 2 M $NaNO_3$. Addition of 1 M $NaNO_3$ to simulated sludge decreases the uranium metal corrosion rate about a factor of 7 compared with the STP rate but values between about 4 and 10 are observed. The corrosion rate attenuation observed for UO_2 in 0.5 M $NaNO_3$ in prior testing (Sinkov et al. 2010) is in line with rate attenuations found at the same, greater, and lesser $NaNO_3$ concentrations for the full sludge simulant. The corrosion rate decreases about a factor of 8 to 10 compared with the STP rate for simulated sludge in 1 M $NaNO_3$ immobilized with Aquaset II or II G.

Of most interest to STP researchers was that significant H_2 mitigation still was provided for in immobilized simulant sludge waste forms containing Aquaset II or Aquaset II G clay. Regrettably, results on H_2 mitigation for tests with PC and Aquaset II H (which contains PC) were inconclusive because of suspected failure of these tests to overcome their induction times and enter fully into the anoxic corrosion regime.

The effectiveness of nitrate in attenuating H_2 generation increases as nitrate concentration increases up to about 1 M $NaNO_3$. For uranium corroding in aqueous solution, the H_2 attenuation factor continues to increase up to at least 2 M $NaNO_3$ while no attenuation factor increase in simulated sludge or simulated sludge plus Aquaset II or II G was found above 1 M $NaNO_3$. In 1 M $NaNO_3$, H_2 attenuation factors are consistently 1000 or higher for aqueous solution and simulated sludge at all tested temperatures (~60, 80, and 95°C) and for simulated sludge plus Aquaset II or II G at ~60°C. Some diminution of H_2 attenuation is seen for the ~80°C and ~95°C tests of simulated sludge and Aquaset II. However, even at these higher temperatures, H_2 attenuation factors around 100 to 200 at 1 M $NaNO_3$ were found.

Part of the H_2 attenuation observed is attributed to attenuation of the corrosion rate. For tests in solution, the H_2 attenuation factor that can be ascribed to corrosion inhibition is no more than a factor of two. Therefore, if the observed H_2 attenuation factor is 1000, half is due to decrease in the corrosion rate and the balance (a net attenuation factor of at least 500) is due to hydrogen radical scavenging or other hydrogen removal mechanisms. For simulated sludge and simulated sludge with Aquaset II or II G immobilization agent in 60°C 1 M $NaNO_3$, the corrosion rate attenuation factors are about 8 to 10 and thus the net H_2 attenuation factors, which range from about 1000 to 30000, decrease by no more than an order of magnitude.

As shown in prior testing and confirmed in the present experiments, the scavenging of hydrogen by nitrate forms dissolved ammonia and hydroxide ion (OH^-). These products have the effect of raising the interstitial solution pH. However, even before the nitrate can react to scavenge nascent hydrogen, the sodium from the added sodium nitrate exchanges onto metaschoepite and displaces hydrogen ion (H^+). This displacement has the effect of lowering solution pH and ultimately converting some of the metaschoepite to sodium-bearing hexavalent uranium compounds.

The initial pH for systems containing simulant sludge and its constituent metaschoepite decreases with increasing $NaNO_3$ concentration. Thus, in the absence of any immobilization agent and without nitrate (or native buffering agents), the initial simulant sludge pH ranges widely from about 6.5 to 9.2 but decreases to pH ~5.0 at 0.5 M $NaNO_3$ and becomes pH ~4.2 at 1 to 2 M $NaNO_3$. After heating to ~60°C to 95°C, the simulant sludge containing $NaNO_3$ solution remains at pH ~5. However, the pH of sludge immobilized and heated with Aquaset II powder or with the granular Aquaset II G is only slightly affected by sodium concentration and decreases moderately from about 8.5 to 7.4 as sodium concentration increases from 0 to 0.5, 1, and 2 M. Simulant sludge treated with PC and then heated has pH ~12.6, is little affected by sodium concentration and, instead, dominated by the pH buffering provided by the calcium hydroxide intrinsic to the PC. Even though significant uranium metal corrosion may not have occurred in the PC- and sodium-bearing tests after heating, any hydrogen scavenging by nitrate only would have produced NaOH (and ammonia) and kept the pH high.

Besides ammonia and hydroxide, nitrate reduction produces dissolved nitrite and nitrogen and nitrous oxide gases. The reactions that produce nitrogen and nitrous oxide also produce hydroxide ion. Analyses of gases in the test apparatus also showed extensive but relatively constant oxygen consumption. Limited nitrogen gas consumption was evident in tests without added nitrate.

Based on the gas and solution concentration analyses, the respective gas and solution volumes, and the masses of uranium metal corroded, material balances could be calculated for most tests. The material balances could not be determined for the tests using the PC solidification agents because the final uranium metal masses could not be measured. In determining the chemical material balance, the number of chemical equivalents for oxidation reactions (uranium metal oxidizing to UO_2) should match the number of chemical equivalents for reduction reactions (water reduction to hydrogen gas, oxygen gas reduction to water and hydroxide ion, nitrogen gas reduction to ammonia for nitrate-free tests, and nitrate reduction to nitrite, nitrous oxide, nitrogen gas, and ammonia). As such, the chemical balance, calculated as the number of oxidized chemical equivalents divided by the number of reduced chemical equivalents, should be unity. The observed chemical balance ratios vary widely around 1 (average 0.91 ± 0.58 at 1 σ) but indicate the major reactions are accounted. Closure of the material balances from the testing confirms the basic chemistry of nitrate addition to the matrices tested is understood.

Valuable additional information has been obtained on nitrate's ability to attenuate H_2 gas generation from solution, simulant sludge, and especially simulant sludge with immobilization agents. Characteristics of the associated reactions also were determined. Present testing confirms prior work that nitrate effectively attenuates H_2 generation from uranium metal corrosion in water and in simulated K Basin sludge, and shows nitrate remains effective in potential candidate solidified K Basin waste forms for WIPP disposal. Further investigations should be performed to confirm that the performances observed to-date in simulant sludge and sludge/immobilization agent systems extend to lower temperatures and to genuine sludge. Tests in the presence of radiation fields also should be performed to determine not only the ability of nitrate to attenuate radiolytic H_2 but also to determine if significant nitrate depletion occurs by radiolysis.

The acceptability of any product waste for WIPP disposal also must be determined. Although objection to nitrate itself is unlikely given its ubiquity in prior wastes disposed to WIPP from the Rocky Flats Site and the Hanford Site, introduction of nitrate to the sludge for hydrogen mitigation from actively corroding uranium metal may be of concern to WIPP. Depending on the implementation strategy, the management of the excess nitrate solution, and the impact, if any, of lower pH caused by reaction of sodium ion with metaschoepite also must be evaluated. Future testing should be tailored to actual target waste streams (e.g., settler tank and container sludge, orphan materials in sludge processing, and decommissioning and decontamination rubble) to meet specific functional design criteria within the particular points of operational insertion such as storage, treatment, or shipping.

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Appendix A

Uranium Metal Corrosion Rate and Hydrogen Generation Data from Earlier Testing (Sinkov et al. 2010)

Table A.1. Uranium Metal Corrosion Rate and Hydrogen Generation Data from Earlier Testing (Sinkov et al. 2010)

Test	$[NaNO_3]$/ $[NaNO_2]$, M	Other Materials	U Bead wt., mg		Corrosion Rate, μm/h	Corr. Rate Relative to STP Rate	Corr. Rate Attenuation Factor(a)	H_2 Produced, mmoles	H_2 Relative to STP Amt.	H_2 Attenuation Factor(a)
			Initial	Final						
Test Series 1 – Rate at 91.4°C average temperature = 0.821 μm/h(b)										
1	0.0/0.0	None	114.07	69.92	0.642	0.78	1.3	Not measured.		
2	1.0/0.0	None	104.14	72.87	0.464	0.56	1.8	Not measured.		
3	3.0/0.0	None	101.45	81.01	0.296	0.36	2.8	Not measured.		
4	6.0/0.0	None	116.43	97.68	0.244	0.30	3.4	Not measured.		
5	0.0/6.0	None	103.61	94.92	0.119	0.14	6.9	Not measured.		
Test Series 2 – Rate at 84.8°C average temperature = 0.774 μm/h(b)										
1	0.0/0.0	None	101.09	55.27	0.451	0.90	1.1	Not measured.		
2	0.0/0.1	None	109.26	85.25	0.201	0.40	2.5	Not measured.		
3	0.0/1.0	None	95.07	80.11	0.134	0.27	3.7	Not measured.		
4	0.0/3.0	None	111.55	97.82	0.109	0.22	4.6	Not measured.		
5	6.0/0.0	None	106.68	85.66	0.178	0.35	2.8	Not measured.		
Test Series 3 – Rate at 60.9°C average temperature = 0.106 μm/h(b)										
1	0.0/0.0	None	112.39	45.73	0.119	1.12	0.89	0.276	0.54	1.9
2	0.0/0.0	0.2 g Nochar/g solution	108.53	49.17(c)	0.105	0.99	1.01	0.197	0.39	2.5
3	0.0/0.0	0.2 g Nochar/g solution	108.18	50.70(c)	0.101	0.96	1.05	0.218	0.44	2.3
4	0.0/0.0	0.5 g Nochar/g solution	101.38	50.08(c)	0.0926	0.88	1.1	0.126	0.27	3.8
5	0.0/0.0	0.5 g Nochar/g solution	107.37	58.86(c)	0.0818	0.78	1.3	0.104	0.21	4.8
6	0.0/0.0	1.0 g Nochar/g solution	107.01	58.19	0.0827	0.78	1.3	0.150	0.30	3.3
7	0.1/0.0	None	108.08	57.84	0.0850	0.80	1.2	0.0859	0.17	5.8
8	0.0/1.0	None	103.12	92.13	0.0164	0.16	6.4	0.0000479	0.00010	10000
9	0.0/0.1	None	113.15	97.12	0.0228	0.22	4.6	0.00664	0.013	78
10	0.1/0.0	0.2 g Nochar/g solution	107.29	Remaining beads were not recovered.(d)				0.0421	0.085	12
11	0.0/1.0	0.2 g Nochar/g solution	Test not performed.							
12	0.0/0.1	0.2 g Nochar/g solution	105.79	Remaining beads were not recovered.(d)				0.0000672	0.00014	7300

Table A.1. Uranium Metal Corrosion Rate and Hydrogen Generation Data from Earlier Testing (Sinkov et al. 2010) (Cont.)

Test	$[NaNO_3]$/ $[NaNO_2]$, M	Other Materials	U Bead wt., mg		Corrosion Rate, µm/h	Corr. Rate Relative to STP Rate	Corr. Rate Attenuation Factor$^{(a)}$	H_2 Produced, mmoles	H_2 Relative to STP Amt.	H_2 Attenuation Factor$^{(a)}$
			Initial	Final						
Test Series 4 – Rate at 62.6°C average temperature = 0.120 µm/h$^{(b)}$										
1	0.0/0.0	None	99.38	61.71	0.0831	0.69	1.4	0.281	0.66	1.5
2	0.2/0.0	None	99.81	67.33	0.0697	0.58	1.7	0.0472	0.11	9.0
3	0.5/0.0	None	105.24	77.70	0.0555	0.46	2.2	0.0117	0.027	37
4	1.0/0.0	None	100.91	68.53	0.0689	0.57	1.7	0.000416	0.00098	1000
5	2.0/0.0	None	100.69	72.31	0.0594	0.50	2.0	0.00000655	0.000016	63000
6	0.0/0.2	None	101.05	87.09	0.0275	0.23	4.4	0.0000148	0.000035	28000
7	0.0/0.5	None	106.19	83.72	0.0441	0.37	2.7	0.00000613	0.000014	72000
8	0.0/0.75	None	102.69	82.43	0.0404	0.34	3.0	0.0000117	0.000028	36000
9	0.0/1.0	None	102.81	89.48	0.0259	0.22	4.6	0.00000821	0.000019	52000
10	0.5/0.0	UO_2	104.07	76.69	0.0556	0.46	2.2	0.00102	0.0024	420
11	0.0/0.5	UO_2	104.30	80.72	0.0471	0.39	2.5	0.00210	0.0048	210
12	0.0/0.0	0.07 M Na_2HPO_4	104.60	44.43	0.194	1.62	0.62	0.530	1.5	0.65
Test Series 5 – Rate at 61.4°C average temperature = 0.109 µm/h$^{(b)}$										
1	0.0/0.0	None	96.17	61.38	0.0736	0.67	1.5	0.228	0.56	1.8
2	0.0/0.2	None	104.59	103.86	0.00127	0.012	86	0.0000766	0.00018	5600
3	0.0/0.5	None	100.12	98.57	0.00278	0.025	39	0.0000150	0.000036	28000
4	0.0/0.75	None	102.82	99.76	0.00542	0.050	20	Gas sample lost.		
5	0.5/0.0	None	98.64	68.17	0.0619	0.57	1.8	0.00247	0.0060	170
6	1.0/0.0	None	103.15	86.77	0.0304	0.28	3.6	0.0000578	0.00014	7400
7	0.0/0.5	UO_2	99.22	87.77$^{(c)}$	0.0214	0.25	4.0	0.00292	0.0071	140
8	0.5/0.0	UO_2	103.12	81.87	0.0401	0.37	2.7	0.00282	0.0066	150
9	0.0/0.5	0.01 g Nochar	98.89	82.21	0.0319	0.29	3.4	0.00000717	0.000017	58000
10	0.0/0.5	0.0087 g Optimer 7194 Plus	96.87	95.94	0.00170	0.016	64	0.00000369	0.0000091	110000
11	0.0/0.5	3.264 mL sim. sludge	96.37	79.12	0.0337	0.31	3.2	0.000527	0.0013	770
12	0.5/0.0	3.264 mL sim. sludge	102.38	86.47	0.0425	0.39	2.6	0.000220	0.00070	1400

Table A.1. Uranium Metal Corrosion Rate and Hydrogen Generation Data from Earlier Testing (Sinkov et al. 2010) (Cont.)

Test	$[NaNO_3]$/ $[NaNO_2]$, M	Other Materials	U Bead wt., mg		Corrosion Rate, µm/h	Corr. Rate Relative to STP Rate	Corr. Rate Attenuation Factor[(a)]	H_2 Produced, mmoles	H_2 Relative to STP Amt.	H_2 Attenuation Factor[(a)]
			Initial	Final						
Test Series 6 – Rate at 61.3°C average temperature = 0.109 µm/h[(b)]										
1	0.0/0.0	None	105.39	72.72	0.0576	0.53	1.9	0.0471	0.10	9.9
2	0.5/0.0	None	105.63	60.16	0.0847	0.78	1.3	0.000405	0.00087	1100
3	0.0/0.5	None	104.97	96.68	0.0134	0.12	8.1	0.00000728	0.000016	64000
4	0.0/0.0	~0.5 mL KE Floc Comp	102.86	80.03	0.0394	0.36	2.8	0.0235	0.052	19
5	0.5/0.0	~1.2 mL KE Floc Comp	104.32	87.63	0.0278	0.26	3.9	0.000258	0.00056	1800
6	0.0/0.5	~1.5 mL KE Floc Comp	104.92	93.08	0.0193	0.18	5.6	0.0000267	0.000058	17000
7	0.0/0.0	~2.0 mL KC-2/3 Comp	106.22	91.45	0.0241	0.22	4.5	0.0000135	0.000029	35000
8	0.5/0.0	~1.8 mL KC-2/3 Comp	102.17	96.89	0.00858	0.079	13	0.0000760	0.00017	6000
9	0.0/0.5	~1.8 mL KC-2/3 Comp	103.59	97.37	0.0100	0.092	11	0.000280	0.00061	1600

(a) Attenuation factor = (Corrosion rate or amount of H_2 measured in experiment)/(Corrosion rate or amount of H_2 according to STP rate law).

(b) Corrosion rate at average test temperature based on the STP rate law (Appendix G of Schmidt and Sexton 2009).

(c) 22, 23, 27, and 28 beads recovered, respectively, in Tests 2, 3, 4, and 5 of Series 3 and 29 beads in Test 7 of Series 5; final bead weights were pro-rated by factors of 30/22, 30/23, 30/27, 30/28, and 30/29, respectively. All 30 beads were recovered in the other tests except Tests 10 and 12 in the third test series.

(d) Uranium metal beads were not recovered in these tests because of the difficulty in separating the residual beads from Nochar and because the Nochar-salt mixtures showed high reactivity precluding its applicability and acceptability for WIPP.

Appendix B

Initial and Final Gas Volumes and Gas Compositions for Test Series 1, 2, and 3

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Initial and Final Gas Volumes and Gas Compositions for Test Series 1, 2, and 3

Table B.1. Initial and Final Gas Volumes and Gas Compositions for Test Series 1, 2, and 3

Test	[$NaNO_3$], M	Other Materials	Gas Vol., mL		Gas Concentrations, mole percent							
			Initial	Final	Ar	CO_2	N_2	O_2	H_2	CH_4	N_2O	C_2H_x
Air(a)	–	–	–	–	0.934	0.0385	78.079	20.946	0.00005	0.0002	0.00003	–
Test Series 1, TI25;4 weeks, 62.2°C												
1	0.0	None	27.00	25.90	0.97	0.105	80.6	18.3	0.025	0.002	<0.005	<0.001
2	1.0	None; 300 U_{metal} beads	32.85	35.55	1.01	0.058	86.3	12.7	0.009	0.003	<0.005	<0.001
3	0.0	Sim. sludge	29.25	27.65	0.83	0.243	69.2	9.9	19.8	0.011	<0.005	<0.001
4	0.5	Sim. sludge	29.25	32.35	1.02	0.178	85.9	11.0	1.73	0.003	0.141	<0.001
5	1.0	Sim. sludge	29.15	28.95	0.93	0.250	77.7	8.9	12.15	0.0145	0.0885	0.0065
6	2.0	Sim. sludge	29.65	34.55	1.04	0.238	88.9	9.8	0.02	<0.001	<0.005	<0.001
7	0.5	Sim. sludge in PC	27.70	31.50	1.03	0.052	87.6	11.3	0.013	<0.001	<0.005	<0.001
8	2.0	Sim. sludge in PC	28.10	31.50	1.06	0.045	89.9	8.9	0.038	<0.001	<0.005	<0.001
9	0.5	Sim. sludge in Aq. II H	27.95	29.55	1.07	0.027	92.6	6.2	0.001	0.064	<0.005	<0.001
10	2.0	Sim. sludge in Aq. II H	27.65	29.15	1.06	0.009	89.1	9.5	0.014	0.018	0.309	<0.001
11	0.5	Sim. sludge in Aq. II G	27.90	32.65	1.04	0.251	91.0	7.7	0.022	<0.001	<0.005	<0.001
12	2.0	Sim. sludge in Aq. II G	27.55	31.35	1.06	0.530	91.6	6.8	0.016	0.001	<0.005	<0.001
Test Series 2, TI28; 62.4°C, 4 weeks; 63.5°C, 8 weeks												
1	0.0	None, 4 wks	9.90	14.00	0.77	0.007	61.1	7.6	30.4	0.0185	0.0185	0.004
2	0.5	None, 4 wks; 300 U_{metal} beads	18.60	48.10	0.52	0.015	39.7	6.3	53.2	0.0455	0.131	0.0065
3	0.0	Sim. sludge, 4 wks	12.20	16.75	0.82	0.021	65.2	4.9	29.1	0.0225	<0.005	0.0045
4	0.0	Sim. sludge, 8 wks	10.90	11.30	0.88	1.375	71.9	0.9	25.0	0.016	<0.005	<0.001
5	1.0	Sim. sludge, 4 wks	12.45	11.65	1.02	0.220	89.8	9.0	0.0245	0.001	0.098	<0.001
6	1.0	Sim. sludge, 8 wks	12.00	9.55	1.00	0.590	88.3	10.0	0.0170	0.001	0.1695	<0.001
7	0.0	Sim. sludge in PC, 8 wks	10.15	8.50	1.00	0.013	88.7	9.7	0.650	0.001	0.007	<0.001
8	0.0	Sim. sludge in Aq. II, 8 wks	10.25	9.45	1.00	3.840	89.5	1.6	4.05	0.005	0.016	<0.001
10	1.0	Sim. sludge in PC, 4 wks	11.30	7.80	1.04	0.011	93.2	5.8	0.0150	0.001	0.0115	<0.001
9	1.0	Sim. sludge in PC, 8 wks	11.90	10.70	1.01	0.025	91.7	7.3	0.0075	0.001	0.014	<0.001
11	1.0	Sim. sludge in Aq. II, 4 wks	9.75	8.45	1.04	0.750	88.0	10.0	0.174	0.001	0.212	<0.001
12	1.0	Sim. sludge in Aq. II, 8 wks	9.45	5.80	1.01	4.930	93.2	0.9	0.0130	0.002	0.078	<0.001
Test Series 3, TI36; 80.0°C, 10 days; 94.1°C, 4 days												
1-80	0.0	None	13.10	18.40	0.75	0.030	60.8	8.8	29.6	0.029	0.01	0.002
2-80	0.0	Sim. sludge	13.60	22.00	0.82	0.113	68.4	11.9	18.8	0.0145	0.01	<0.001
3-80	1.0	Sim. sludge	16.45	14.40	1.02	0.145	86.3	12.4	0.0375	<0.001	0.06	<0.001
4-80	1.0	Sim. sludge	15.60	13.20	1.03	0.231	88.2	10.4	0.0285	0.001	0.075	<0.001
5-80	0.0	Sim. sludge in Aq. II	12.60	17.80	0.84	1.26	70.5	12.8	14.25	0.010	0.43	<0.001
6-80	1.0	Sim. sludge in Aq. II	13.45	12.75	0.99	2.38	83.1	12.1	0.89	0.001	0.61	<0.001
7-80	1.0	Sim. sludge in Aq. II	14.20	12.95	0.96	7.50	80.3	10.0	0.407	0.001	0.84	<0.001
1-95	0.0	None	12.40	17.80	0.72	0.036	59.0	11.1	29.1	0.021	0.01	<0.001
2-95	0.0	Sim. sludge	14.10	19.80	0.80	0.174	66.2	12.9	19.9	0.013	<0.005	<0.001
3-95	1.0	Sim. sludge	16.00	13.00	1.00	0.234	84.8	13.7	0.043	<0.001	0.181	<0.001
4-95	1.0	Sim. sludge	16.10	12.60	1.00	0.346	84.6	13.8	0.034	<0.001	0.202	<0.001
5-95	0.0	Sim. sludge in Aq. II	12.45	10.75	1.01	1.78	84.4	8.3	4.51	0.008	0.024	<0.001
6-95	1.0	Sim. sludge in Aq. II	13.95	9.65	1.05	4.12	88.4	5.4	0.6	0.001	0.384	<0.001
7-95	1.0	Sim. sludge in Aq. II	13.85	14.30	0.84	13.4	70.4	13.0	1.12	0.002	1.32	<0.001

(a) Air composition from NOAA (1976) was adjusted for current atmospheric CO_2 concentration (Keeling et al. 2008) and renormalized.

Appendix C

XRD of Metaschoepite after Five Days at 95°C with and Without 0.5 M $NaNO_3$

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XRD of Metaschoepite after Five Days at 95°C with and Without 0.5 M NaNO3

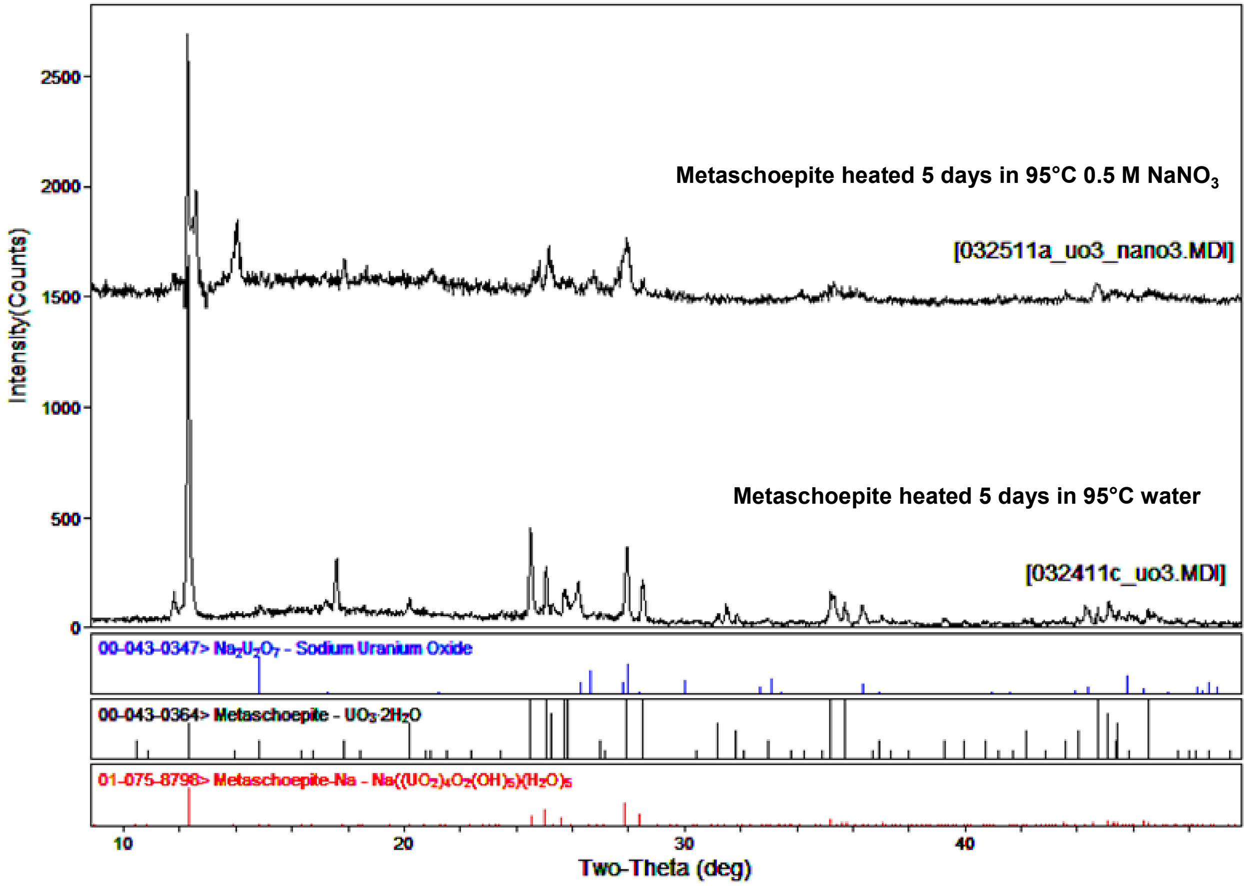

Figure C.1. XRD Scans of Metaschoepite Heated to 95°C for Five Days in Water and in 0.5 M NaNO$_3$

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