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Nitrate Destruction Literature Survey and Evaluation Criteria

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EXECUTIVE SUMMARY

This report satisfies the initial phase of Task WP-2.3.4 Alternative Sodium Recovery Technology, Subtask 1; Develop Near-Tank Nitrate/Nitrite Destruction Technology. Some of the more common anions in carbon steel waste tanks at SRS and Hanford Site are nitrate which is corrosive, and nitrite and hydroxide which are corrosion inhibitors. At present it is necessary to periodically add large quantities of 50 wt% caustic to waste tanks. There are three primary reasons for this addition. First, when the contents of salt tanks are dissolved, sodium hydroxide preferentially dissolves and is removed. During the dissolution process the concentration of free hydroxide in the tank liquid can decrease from 9 M to less than 0.2 M. As a result, roughly half way through the dissolution process large quantities of sodium hydroxide must be added to the tank to comply with requirements for corrosion control. Second, hydroxide is continuously consumed by reaction with carbon dioxide which occurs naturally in purge air used to prevent buildup of hydrogen gas inside the tanks. The hydrogen is generated by radiolysis of water. Third, increasing the concentration of hydroxide increases solubility of some aluminum compounds, which is desirable in processing waste. A process that converts nitrate and nitrite to hydroxide would reduce certain costs. 1) Less caustic would be purchased. 2) Some of the aluminum solid compounds in the waste tanks would become more soluble so less mass of solids would be sent to High Level Vitrification and therefore it would be not be necessary to make as much expensive high level vitrified product. 3) Less mass of sodium would be fed to Saltstone at SRS or Low Level Vitrification at Hanford Site so it would not be necessary to make as much low level product. 4) At SRS less nitrite and nitrate would be sent to Defense Waste Processing Facility (DWPF) so less formic acid would be consumed there and less hydrogen gas would be generated.

This task involves literature survey of technologies to perform the nitrate to hydroxide conversion, selection of the most promising technologies, preparation of a flowsheet and design of a system. The most promising technologies are electrochemical reduction of nitrates and chemical reduction with hydrogen or ammonia.

The primary reviewed technologies are listed below and will be described in more detail later in the report.

1. Electrochemical destruction
2. Chemical reduction with agents such as ammonia, hydrazine or hydrogen
3. Hydrothermal reduction process
4. Calcination

Only three of the technologies on the list have been demonstrated to generate usable amounts of caustic; electrochemical reduction and chemical reduction with ammonia, hydrazine or hydrogen and hydrothermal reduction. Chemical reduction with an organic reactant such as formic acid generates carbon dioxide which reacts with caustic and is thus counterproductive. Treatment of nitrate with aluminum or other active metals generates a solid product. High temperature calcination has the potential to generate sodium oxide which may be hydrated to sodium hydroxide, but this is unproven.

The following criteria were developed to evaluate the most suitable option. The numbers in brackets after the criteria are relative weighting factors to account for importance.

1. Personnel exposure to radiation for installation, routine operation and maintenance {10}
2. Non-radioactive safety issues {10}
3. Whether the technology generates caustic and how many moles of caustic are generated per mole of nitrate plus nitrite decomposed {10}

4. Whether the technology can handle nitrate and nitrite at the concentrations encountered in waste {10}
5. Maturity of technology {7}
6. Estimated annual cost of operation (labor, depreciation, materials, utilities) {7}
7. Capital cost {6}
8. Selectivity to nitrogen as decomposition product (other products are flammable and/or toxic) {5}
9. Impact of introduced species {5}
10. Selectivity for destruction of nitrate vs. nitrite {5}
11. Cost of deactivation and demolition {3}

Each technology was given a score from one to five, five being most desirable, in each criterion. The results for the evaluation, in order from most to least promising was, Electrochemical, Chemical Reduction, Hydrothermal and Calcining. Another report [Steimke and Steeper, 2011] contains a flowsheet and design of an in-tank Electrochemical unit.

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ARP	Actinide Removal Process
DWPF	Defense Waste Processing Facility
HLW	High Level Waste
LAW	Low Activity Waste
MCU	Modular Caustic Side Solvent Extraction Unit
MST	Monosodium titanate
NAC	Nitrate to Ammonia and Ceramic
SRNL	Savannah River National Laboratory
SRS	Savannah River Site
WAC	Waste Acceptance Criteria
WTP	Waste Treatment Plant

1.0 Introduction

Savannah River Site (SRS) and Hanford Site both have dozens of tanks which contain as much as one million gallons of radioactive waste each. Both sites are in the process of stabilizing the waste for long term storage. Contents of waste tanks include large amounts of sodium hydroxide, sodium nitrate and sodium nitrite, with concentrations as great as 6 molar. The source of the nitrates was nitric acid used to dissolve reactor fuel and target assemblies and later neutralized with excess sodium hydroxide. Sodium nitrite was added as a corrosion inhibitor to protect carbon steel tanks. Hydroxide also serves as a corrosion inhibitor. Nitrate and nitrite can impact downstream disposition operations.

Figures 1 and 2 illustrate the flow of materials in SRS waste processing. Waste tanks typically contain three layers; sludge, salt crystals and supernate (typically a saturated salt solution). The SRS stabilization process is to separate sludge from salt crystals and supernate in waste tanks. The salt and supernate predominantly contain non-radioactive salts but do contain radionuclides, primarily Cs-137, Sr-90 and actinides. The predominant non-radioactive salts are sodium nitrate, sodium nitrite and sodium hydroxide with lesser but significant concentrations of sodium aluminate, sodium carbonate and sodium sulfate. Strontium and soluble actinides are removed from the salt stream by absorbing it on granules of monosodium titanate (MST) and then adding the MST to the sludge as shown in Figure 2. Cesium is removed from the salt stream at the Modular Caustic Side Solvent Extraction Unit (MCU) using liquid phase ion exchange and then later that cesium is added to the sludge. The decontaminated salt stream is mixed with Portland cement, furnace slag and fly ash to form a cementitious material called Saltstone which is cast into large monoliths. Sludge is typically washed in Tank 51 to remove more salt, then pumped to Tank 40 and later to DWPF as shown in Figure 1. Sludge chemistry is adjusted by the appropriate additions of nitric acid, formic acid and other chemicals. Then sludge is mixed with glass frit and pumped to the Defense Waste Processing Facility (DWPF) Glass Melter. Molten glass is poured into stainless steel canisters ten feet tall and two feet in diameter.

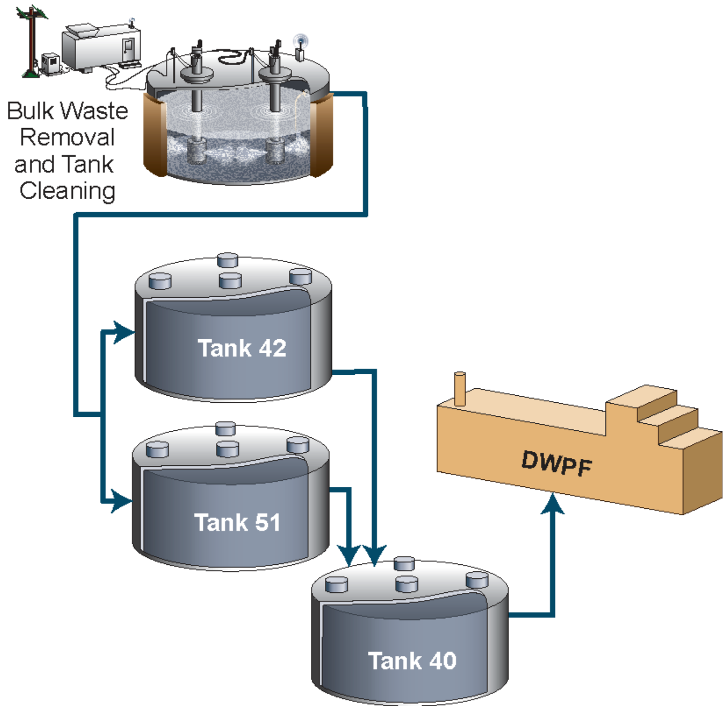

Figure 1 **SRS Sludge Process Diagram**

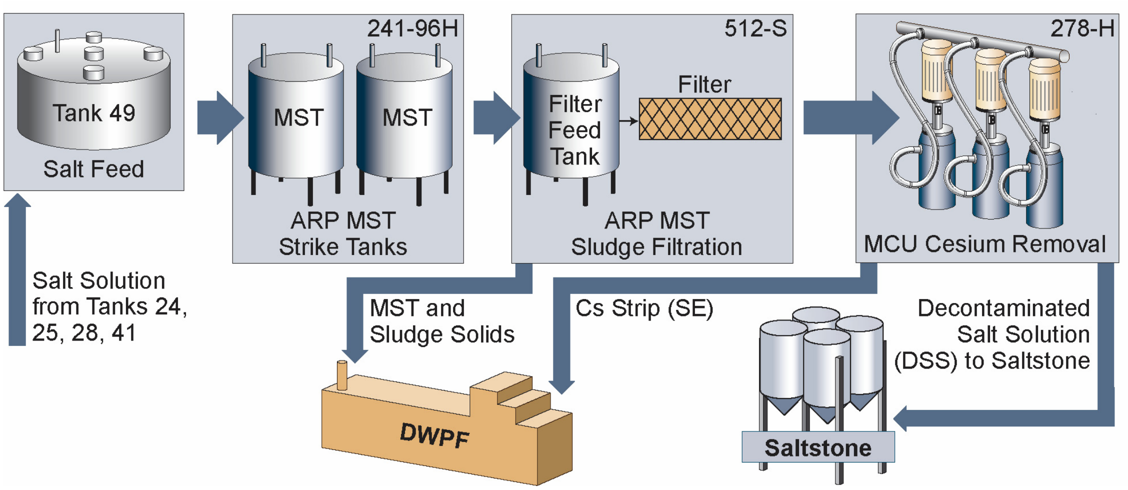

Figure 2 **SRS Salt and Supernate Process Diagram**

At Hanford Site the process is similar but with two major differences. Cesium is removed from the salt waste stream using solid ion exchange resin. Also, the decontaminated salt stream is mixed with crushed glass to form a Low Activity Waste vitrified product instead of a cementitious material.

At SRS nitrates and nitrites are encountered at several locations during processing. The great majority of those salts go to Saltstone which retards their release to groundwater. If nitrates and nitrites could be destroyed or converted to sodium hydroxide, the amount eventually released would be less. Although note that nitrate and nitrite concentrations in the stream sent to Saltstone are well below the Waste Acceptance Criteria (WAC) for Saltstone waste so the WAC limits are not by themselves reasons for destroying nitrates. Another place that nitrates and nitrites are encountered is in the sludge sent to DWPF because the sludge washing process leaves a significant amount of residual nitrate and nitrite. The sludge is pumped to the Slurry Receipt and Adjustment Tank (SRAT) where the addition of nitric acid and formic acid can cause generation of NO_x and hydrogen. Any nitrates and nitrites that are sent to the Glass Melter can also generate NO_x. At Hanford Site both High Level Waste (HLW) and Low Activity Waste (LAW) is eventually vitrified, with residual nitrates and nitrites generating NOx. The biggest benefits are for a technology that converts nitrate and nitrite to hydroxide. It would then be necessary to purchase less sodium hydroxide to be used for tank corrosion control and for waste processing. Also because less mass of sodium is added to the waste streams, less mass of sodium must be handled at Saltstone at SRS or LAW vitrification at Hanford Site.

2.0 Results of Literature Survey

2.1 Previous Reviews of Nitrate Destruction Techniques

Chemical reduction of nitrates can take place with a number of elements or compounds, inorganic reductants and organic reductants. Fanning [2000] reviewed the technologies and summarized in the following table nitrate chemical reducing agents for acidic or basic conditions and low or high concentrations of nitrate.

Table 1 Summary of Chemical Reduction Techniques

Reducing agent	acidic (A) or basic (B)	nitrate conc. L or H	nitrogen products	other products	reaction conditions
Al (s)	B	L, H	NH_3, NO_2- N_2	Al(OH)3	
Fe(s)	A	L	NO_2-	Fe+++	
Zn	B	L	NO_2-, NH_3 N_2	Zn++	catalyst
NH_4+	A	L	N_2O, N2		hi T&P, Cl-
NH_3	B	L	N_2, NO_2-	OH-	hi T&P
BH_4-	B	H	NO_2-, NH_3	$B(OH)_4$-, H_2	Cu++
HCO_2H	A	H	N_2O, NH_3	CO_2	Rh/C
	A, B	H	N_2	CO_2, H_2	hi T&P
NH_3OH+	A	L	N_2O		
NH_2OH	B	L	N2	OH-	Cu++
H_2	B	L	NO, N_2O, N_2	OH-	
Fe++	A	L	NO, N_2O, N_2	Fe+++	
	B	L	NH_3	$Fe(OH)_3$- OH-	Cu++, Ag+

The current interest for this report is in a process that generates hydroxide, functions with high concentrations of nitrate in basic conditions and does not generate solids such as metal compounds. None of the chemical reduction processes listed in Table 1 satisfy all requirements. High temperature reduction using formic acid works in basic solution at high nitrate concentrations, but generates carbon dioxide which reacts with hydroxide to form carbonate.

Fanning also reviewed nitrate reduction techniques using energy sources; electrochemical, photochemical and thermal. He stated that the electrochemical technique was being developed to destroy nitrates and nitrites in basic solutions including nuclear waste. Therefore, electrochemical destruction is a definite candidate and will be discussed in more detail later in this report.

In the photochemical technique, ultraviolet light, in the presence of catalysts, provides energy to generate oxygen species from nitrate and nitrite which react with organics to form carbon dioxide. The formation of carbon dioxide is undesirable so photochemical techniques are not promising.

Fanning said that thermal reduction uses temperatures up to 900°C and pressure up to 200 bar. Thermal reduction can be performed at the high end of the temperature range in the absence of reducing agents in which case the products are sodium oxide and nitrogen oxides. Sodium oxide may be hydrated to sodium hydroxide. Some reducing agents like formic acid contain carbon and are not acceptable. Others like hydrogen and ammonia can be considered. Therefore, thermal reduction with an inorganic reductant is still worth considering.

Taylor, Kurath and Guenther reviewed six nitrate destruction techniques in 1993.
1. Nitrate to Ammonia and Ceramic (NAC) reduces nitrate with elemental aluminum and with the addition of silica forms a solid product. It works with high concentrations of nitrate in a basic

environment. Because it forms a solid and does not generate caustic, it is not a candidate for further consideration.

2. Electrochemical Destruction, also discussed by Fanning, is an ambient temperature and pressure process that reduces nitrate and nitrite to hydroxide and the gases nitrogen, NO_x, and ammonia and will be discussed more later in this review.
3. Biological Denitration uses bacteria to convert nitrate to nitrogen gas and carbon dioxide. The process is slow and bacteria are not sufficiently sodium tolerant for this to work with SRS or Hanford waste. This technology will not be discussed further.
4. Chemical Reduction reduces nitrate with formic acid at about 100°C under acid conditions. It would be unacceptable to acidify caustic waste for reasons including cost, besides the only acceptable acid would be nitric acid. As mentioned earlier this process generates carbon dioxide which is unacceptable.
5. The Hydrothermal Process is a variation of Chemical Reduction but occurs at higher temperature and pressure, such as 350°C and 190 atm or up to supercritical conditions such as 525°C and 300 atm. It has been tested in both acidic and basic conditions with formic acid and ferrocyanide, etc. as reducing agents. However, a reaction that generates carbon dioxide is unacceptable in this application. Hydrothermal processing with inorganic reductants will be discussed more later in this report.
6. Calcination has been used to stabilize radioactive wastes at the New Waste Calcining Facility at Idaho National Engineering Laboratory. The facility heats waste mixed with sucrose to 500°C in a fluidized bed. Nitrates are destroyed but carbonates rather than sodium hydroxide are formed, so that type of calcining is not appropriate. Plasma torches have been tested for nitrate destruction at temperatures above 2000°C where they decompose nitrates to nitrogen gas and sodium oxide. Typically a carbon source is added so carbonates are generated. If the process could be applied without addition of carbon, sodium oxide could be hydrated to sodium hydroxide. However, this is not a proven technique.

Navetta [1997] reviewed four types of nitrate and nitrite destruction technologies for application to SRS radioactive wastes.

1. Navetta listed four types of Thermal Processes. The general principle is that sodium nitrate and sodium nitrite are decomposed to nitrogen, NO_x and sodium oxide in the range of temperatures from 600°C to 900°C. In principle, sodium oxide could be hydrated to sodium hydroxide.
    a. The Fluidized Bed Calciner was the same as discussed by Taylor, et al. Liquid waste is fluidized by hot air in a bed of fine dolomite particles. Dolomite cannot be heated too much because it decomposes at about 800°C releasing carbon dioxide.
    b. Plasma furnaces have been proposed for treating mixed wastes at temperatures between 1200°C and 1400°C. The process produces two molten phases, slag and metal.
    c. Navetta discusses a type of steam reforming in which the waste stream is heated to 1200°C to decompose the nitrates to NO_x and nitrogen gas.
    d. Vitrification produces a glass form and therefore no usable caustic.
2. The Hydrothermal Process was the same as described by Taylor, et al. Formic acid is reacted with the aqueous waste at supercritical conditions with temperatures between 350°C and 525°C and pressures between 190 and 300 atm.
3. The Chemical Reduction Process is also the same as described by Taylor, et al. Navetta mentions two reductants, formic acid and aluminum. The use of formic acid generates carbon dioxide which is a problem because it consumes hydroxide to form carbonate and the use of aluminum generates additional solid waste. Neither reductant generates hydroxide.

4. The Electrochemical Process which was mentioned earlier in this report.

A successful technology must generate hydroxide and operate with basic conditions and high concentrations of nitrate, nitrite and sodium. The process cannot generate solids or significant quantities of carbon dioxide. Based on the previous reviews of nitrate destruction technologies most options were ruled out. The remaining options for consideration are;
a. Electrochemical Reduction
b. Chemical reduction, but only with agents such as hydrogen, hydrazine or ammonia. Chemical reduction requires a catalyst.
c. Hydrothermal Process, but only when the reductant does not contain carbon and is not metallic and does not generate a solid product.
d. Calcination, but only performed in the absence of carbon compounds.

2.1.1 Electrochemical Reduction Literature Survey

Electrochemical reduction of nitrates and nitrites can be used to treat the liquid waste without the need for additional chemicals. In application there would be a battery of electrochemical cells, each with an anode and cathode, which perform oxidation and reduction, respectively. The cathode reactions are listed below. The most desirable cathode reaction forms nitrogen gas because ammonia and nitrous oxide probably require subsequent treatment, the reaction that forms hydrogen is parasitic and both ammonia and hydrogen can form explosive mixtures.

$NO_3- +H_2O + 2e- = NO_2- + 2OH-$
$2NO_2- + 3H_2O + 4e- = N_2O + 6OH-$
$NO_2- + 5H_2O + 6e- = NH_3 + 7OH-$
$NO_3- + 6H_2O + 8e- = NH_3 + 9OH-$
$NO_3- + 3H_2O + 5e- = 1/2N_2 + 6OH-$
$H_2O + e- = 1/2H_2 + OH-$

The anode reaction follows. Also, any organics present would tend to be oxidized at the anode.
$4OH- = O_2 + 2H_2O + 4e-$

The formation of hydrogen is an undesired side reaction and it increases in magnitude as nitrate and nitrite are depleted. The net result of the anode and cathode reactions is the formation of one mole of hydroxide for every mole of nitrate or nitrite decomposed to gas. The anode and cathode can be separated by a membrane, called divided mode, or no membrane used, called undivided mode. In divided mode, since hydroxide is depleted at the anode, care must be taken that the pH does not get too low which would precipitate aluminum compounds in the anolyte.

Hobbs [1995] tested a small electrolyzer with actual low level radioactive waste from SRS in both divided and undivided mode and destroyed as much as 97% of original nitrate. Chai, Hartsough and Genders [1995] tested a larger electrolyzer (0.21 m^2) on simulated Hanford and SRS waste in both divided and undivided modes with nickel electrodes. They concluded that lower than expected performance was due to chromate in the simulant being reduced to non-conductive chromium hydroxide at the cathode.

Steimke, Hobbs, Fowley and Steeper [1997] tested the same size electrolyzer as Chai, et al. with a simple waste simulant containing only sodium hydroxide, sodium nitrate and sodium nitrite and in both divided and undivided modes at a current density of 350 mA/cm^2. In undivided mode there was an induction period of 36 hours during which little nitrate was destroyed. During the subsequent 40 hours 70% of the nitrate was destroyed. About 70% of the electrical charge went to destroying nitrate and nitrite and the balance went to generating hydrogen. When the cell was operated in divided mode the nitrate concentration decreased immediately, decreasing by 30% in ten hours. About 85% of the charge was used to decompose nitrate and nitrite. The total voltage drop for the cell and power cables was 4.5 volts.

Duarte, Jha and Weidner [1998] addressed the problem of chromate in waste solutions forming chromium hydroxide at the cathode, which greatly reduces processing rates. They used nickel electrodes in an undivided cell at a current density of 160 mA/cm^2 with simulated waste solution; 1.95 M $NaNO_3$ + 0.6 M $NaNO_2$ + 1.33 M NaOH and varying concentrations of $Na_2Cr_2O_7$ which coverts to chromate. First they verified that even small concentrations of chromate (35 mg/L) interfered with nitrate destruction. They found that reversing the polarity of the electrodes at constant time intervals, typically 30 minutes, minimized the adverse effect of the chromium hydroxide film. Cell voltage was not stated in the paper.

Hobbs and Lambert [2002] proposed placing electrolyzers near the top of SRS waste tanks to convert nitrate to nitrite and/or hydroxide, both of which are corrosion inhibitors. They tested the concept on a small scale with a simple simulant that contained only sodium hydroxide, sodium nitrate and sodium nitrite. The cathode was always nickel and the anode was either nickel or platinum. They tested current densities of 10, 100 and 200 mA/cm^2. They found that hydroxide generation rate was proportional to current density, which was expected, and that more hydroxide was generated with the nickel anode than the platinum anode. They had hoped to generate both hydroxide and nitrite, but nitrite concentration always decreased, so both nitrate and nitrite were both reduced to hydroxide. Off gas was analyzed and contained concentrations of hydrogen ranging from 6% to 50%. Hydrogen production is an undesirable side reaction. Cell voltage was not stated.

Cheng, et al. [2005] were primarily interested in treating water having relatively low concentrations of nitrate, e.g. 16 mM, and also bicarbonate, chloride and sulfate. They used precious metal electrodes in a zero gap solid polymer electrode. With this system, a two day period was required to generate nearly full reaction of nitrates at the cathode and ammonia at the anode. Very low current densities, e.g. 1 mA/cm^2, favored production of nitrogen. The other products, which increased with current density, include ammonia at the cathode and nitrate at the anode. Nitrite production was negligible at either electrode. This study was conducted at limited pH values and wastes more alkaline than pH of 11.6 were not considered. The slow time of reaction and the side reactions at the electrodes present problems with this technique.

A number of different electrode compositions have been investigated to determine the best materials for nitrate destruction. Reyter, et al. [2008] were interested in decreasing the concentration of nitrates in drinking water to less than 45 mg/L. They tested copper electrodes but found that it demonstrates poor selectivity towards nitrogen gas. Instead it reduces nitrates to nitrites which are further reduced to ammonia. Nitrogen generation does not appear to occur. Furthermore, nitrites can also block the electrode surface from the nitrates, reducing the rate of denitration. Reyter, et al. [2010] reviewed the nitrate destruction literature and found a number of researchers who tested different electrode materials to maximize the production of nitrogen product or to maximize electrical efficiency. The authors tested nitrate destruction with iridium oxide on titanium electrodes. They found that they could achieve high selectivity to nitrogen product if they ran with relatively low current density, less than 80 mA/cm^2, and included 0.5 M chloride in the solution. Such low current densities would require the use of large electrochemical cells. Also, the addition of so much chloride is not an option for treatment of tank waste at SRS or Hanford Site, because chloride promotes stress corrosion cracking in steels.

Katsounaros, et al. [2009] tested nitrate destruction on simulated liquid nuclear waste containing 1.8 M $NaNO_3$ + 0.55 M $NaNO_2$ + 1.16 M NaOH and for some tests 3.3 x 10^{-3} M Na_2CrO_4. They used a divided electrolyzer with a Nafion 117 membrane, a platinum foil anode and both tin and bismuth cathodes and galvanostatic (constant current) operation. They operated at current densities ranging from 65 to 450 mA/cm^2. Electrochemical cell voltage is the sum of the anode and cathode reversible potentials plus anode and cathode overpotentials plus resistive losses. Reversible potentials are defined as the potentials that drive the reactions at nearly zero rates. Overpotentials are the additional voltages required to drive the reactions at a usable rate. Normally designers of electrochemical cells try to choose electrode materials that have low overpotentials to decrease energy losses. However, Katsounaros, et al. intentionally chose cathode materials that have relatively high overpotentials. They found three beneficial results from the use of high overpotential cathode materials.

1. Current efficiency was generally very high, greater than 99%. They defined current efficiency as 100% minus the percentage of supplied current that went to generating hydrogen. Current efficiency decreased sharply when more than 85% of nitrate and nitrite had been destroyed.
2. Selectivity to nitrogen gas rather than other nitrogenous products was high, 82% for tin and 72% for Bi.
3. The presence of chromate did not change the results significantly. The authors attribute that benefit to the high overpotential which reduced Cr^{+6} to elemental Cr which is conductive, rather than reducing it to Cr^{+3} in the form of insoluble $Cr(OH)_3$ which is not conductive.

A disadvantage of the use of high overpotential cathodes is higher cell voltage, 6 volts at 450 mA/cm^2 and therefore higher energy consumption, about 100 watt-hours per gram of reduced nitrogen at the highest current density. Their longest run was ten hours, so long term performance with this technique is not known.

Navetta [1997] performed a cost analysis for an electrochemical denitration facility with a footprint of 60,000 square feet and operating life of 25 years designed to destroy 90% of the nitrates and nitrites in four million gallons of decontaminated salt waste per year. This dedicated facility was to be placed upstream of Saltstone. Note that the cost per gallon for treating contaminated salt solution would be more. Navetta assumed the salt solution to have 4.5 M nitrate and 1.0 M nitrite. He found that electrochemical treatment has an annual operating cost of \$4 M (\$8M in 2012) and a capital cost of \$22.5M (\$43.6M in 2012). Plant Cost Factors from Chemical Engineering magazine were used to escalate costs.

2.1.2 Chemical Reduction Literature Survey

Chemical reduction of nitrates can take place with a number of reductants, including formic acid, ammonia, glucose, urea, sodium, and hydroxylamine near ambient conditions. Chemical reduction usually requires the use of a catalyst. Ideally, introduced species are converted to gases to prevent the addition of additional chemicals into the waste stream. Chemical reduction with metals will not be considered here.

Hydrogen can be an effective means to reduce nitrates with minimal formation of unwanted compounds under the right catalytic conditions. Pintar, et al. [1996] and Pintar, et al. [1998] were interested in destroying nitrate in drinking water. They reduced the nitrate with hydrogen in the presence of Pd–Cu bimetallic catalyst on activated alumina at ambient conditions. The initial nitrate concentration was 100 mg/L. The hydrogen was diluted with both nitrogen and carbon dioxide. Carbon dioxide drove the reaction faster but is not usable for the present application. Using dilution with nitrogen two-thirds of the nitrate was destroyed in five hours. The alumina support might tend to dissolve in the high caustic conditions in salt waste.

Deganello, et al. [2000] tested reduction of nitrates in drinking water with hydrogen gas at ambient conditions using a palladium copper catalyst on pumice. Their best results were obtained either at pH 5.5 and in the presence of carbon dioxide, neither of which conditions is possible for the present case of interest.

D'Arino, et al. [2004] studied reduction of low concentrations of nitrates with hydrogen in the presence of catalysts, either 5% Pd or 5% Pt on tin oxide. The catalyst containing platinum was less selective, reacted more slowly and was more expensive than the palladium catalyst. Therefore platinum catalysts should not be considered for hydrogenation of nitrates. The palladium catalyst is formed from palladium chloride which costs $74.13 per gram (Science Lab, 2010). This corresponds to a catalyst cost of about $6/gram. Denitration can take up to two hours in a 100 ppm sample of nitrate with selectivity to ammonia of about 1 ppm. In order to have complete destruction of nitrate and nitrite, the pH of the solution must be kept low by an acetate buffer or addition of eight times more carbon dioxide than hydrogen, which is not an option for treating salt waste.

Other chemical reductants have a number of other safety concerns that factor into their viability. Reactors using formic acid are prone to runaway reactions. Reactants may continue to be added and temperature increased to speed a slow reaction. Once the reaction starts to pick up, it may be difficult to stop. Runaway reaction has also been a problem in the past with hydroxylamine forming hydroxylammonium nitrate. Explosions have occurred at Hanford Site (Department of Energy, Feb. 1998, p.1) and at Concept Sciences Inc. in Allentown, Pennsylvania (WSWS, 1999). Although the accidents could probably have been avoided with proper care, hydroxylammonium nitrate is highly explosive.

2.1.3 Hydrothermal Chemical Reduction Literature Survey

Hydrothermal Chemical Reduction has similarities with Chemical Reduction but is performed at much higher temperatures and pressures, but may not require a catalyst. The reaction can occur in a continuously stirred tank reactor (CSTR), which is easier to scale up than electrochemical cells. Cox, et al. [1994] tested hydrothermal nitrate destruction with six reducing agents in basic solution, pH=13, 3 wt% nitrate solution. Reactions were conducted in a batch reactor at temperatures ranging from 200°C to 350°C and pressures from 40 atm to 190 atm. The reductants were ammonia, formate, urea, glucose, methane and hydrogen. The reductants, in order of effectiveness from best to worst, were formate, glucose, urea, hydrogen, ammonia and methane. Unfortunately, the three most effective reductants generate no net hydroxide. The best reductant that also generated hydroxide was hydrogen, but nitrate conversion in two hours was only 18%.

The high temperatures and pressures take place in supercritical water, which presents two safety problems. First, supercritical water is highly corrosive to carbon and stainless steels and leaks in the reactor material are of great concern. High levels of salts in waste further increase corrosion rates. Second, high pressures aggravate problems with leaks because higher pressures increase the flow rate through any reactor leaks. A reactor leak could contain significant amounts of radioactivity that would create hazards for personnel and the surrounding environment. The combination of radioactivity and highly pressurized steam pose safety hazards that require extensive planning to avoid. Both hazards are applicable to ammonia and formate. Ammonia has the additional hazard of excess ammonia forming a flammable gas while formate reactions have the potential to run away if not controlled.

Long term corrosiveness of a supercritical solution of water and salts to the denitration reactor is a major concern. It may be necessary to construct the reactor from a highly resistant material such as niobium, Inconel, or zirconium. Before a reactor could be built, coupons of prospective materials would have to be tested in salt waste under supercritical conditions. In the presence of basic solution, hydrogen embrittles the niobium (MTI, 2010). Even if niobium was viable, construction of tanks made from niobium do not offer a cost-effective alternative. Niobium costs about $75 a pound (Periodic Table of the Elements, 2010), which is over 40 times more expensive than 316 stainless steel—estimated at $1.84 per pound (E-Stainless Steel, 2010). Zirconium appears to be a viable construction material because of its ability to resist strongly basic solutions (MTI, 2010). Against the oxidizing conditions of supercritical water, zirconium proved to effectively resist supercritical corrosion when it is alloyed with chromium and iron. An alloy of Zr-1.0Cr-0.2Fe shows only 20 g/m^2 of weight loss in a 135 day period (Jeong, 2005, p.1373). Salts in the waste are expected to increase the rate of corrosion and must be considered.

Navetta [1997] estimated the cost of the hydrothermal process for use of formic acid as the reductant. The total capital cost was $29M of which $1.5M was for the high pressure reactor. Those costs would be doubled in 2012 dollars. Navetta did not mention whether the high pressure reactor price included expensive corrosion resistant materials or assumed stainless steel. The Present Value of the Life Cycle Cost was $168M or twice that in 2012 dollars.

2.1.4 Calcining Literature Survey

Calcination is a conceptually simple technology. Waste is heated to temperatures in the range from 600^{o}C to 800^{o}C, which first evaporates water and then decomposes nitrates and nitrites to sodium oxide and NO_x. Calcination is an energy intensive process that costs about $140/gal or $130/kg nitrate according to Taylor, et al. [1993]. A drawback of this technology is that sodium nitrate can cake onto and inside the main components of the calciner. This means high levels of maintenance may be required on the calciner.

Operating the calciner at 900^{o}C is possible but creates a higher energy requirement. At that temperature nitrates are reduced to gases, mostly NOx compounds. Nitrogen selectivity is expected to be low. Sodium forms sodium oxide and remains in the bed material along with other metals and their compounds [Navetta, 1997]. Sintering can plug up the reactors with sodium and other alkali metals compounds. If sintering problems can be alleviated, the products of the calciner should be an off-gas high in NOx compounds with a solid product that remains on the bed media. The off-gas must be treated before it can be released into the atmosphere.

Navetta [1997] estimated the cost of a Plasma Arc System for calcining waste. He found that the operating cost was $10.2M, 65% of which was for electricity and the Present Value was $289M.

2.2 Possible Locations for Nitrate Destruction Hardware

This assignment called for reviewing technologies that could be implemented "Near Tank". One way to achieve that requirement is to place the hardware in a trailer positioned near tanks and later moved to other tanks. Supernate would be pumped out of the tank, through the equipment which would convert nitrate and nitrite to hydroxide and then back into the tank. Because the supernate is radioactive, lead shielding 3" thick would be required to protect workers. Another "Near Tank" location is to suspend the hardware in the tank, either above or below the liquid level. This would largely solve the shielding problem and decrease concerns about liquid leaks. However, it would be necessary to ensure that the presence of the hardware, any introduced chemicals and any generated chemical species would not cause damage to the tanks or risk an explosion. It would also be necessary to ensure that the weight of the equipment did not damage the tank. A third option is a dedicated facility for nitrate destruction that is fed contaminated salt solution. This option is not "Near Tank". Supernate would be pumped from tanks to this facility and then back to the tanks after nitrate destruction. A fourth option is to locate a dedicated facility after strontium and cesium had been removed, which at SRS would be downstream of the Salt Waste Processing Facility (SWPF). It would handle decontaminated waste so much less shielding would be required.

Either dedicated nitrate destruction facility described above might employ Caustic Recycle, which is an electrochemical process. Sodium ions pass through a membrane from the waste containing anode side of the cell to the cathode side and hydroxide is consumed at the anode and generated at the cathode. The net result is that the waste solution is depleted in sodium hydroxide and a clean sodium hydroxide solution, as much as 50 wt% is formed. Radioactive anolyte would require a ceramic membrane which is limited to low current density, e.g. 50 mA/cm^2. Low current density requires larger electrochemical cells and larger capital investment. A Nafion membrane and much larger current density could be used for decontaminated solution. Recycled caustic could be pumped to locations of need, such as waste tanks. A possible disadvantage of placing the facility downstream of the SWPF is that some effort was expended to decontaminate the salt solution and that relatively clean product would be pumped back to contaminated tanks.

The Electrochemical Technology and Chemical Reduction could potentially be placed in any of the four locations because they are ambient temperature and pressure processes that have relatively modest off-gas requirements. Hydrothermal and Calcining would have to be placed in a dedicated facility, either in the vicinity of tanks or downstream of SWPF. The reasons are that both processes require high temperature. Also, Calcining has challenging off-gas requirements and Hydrothermal requires high pressure.

2.3 Advantages of Nitrate and Nitrite Destruction at SRS

The three primary advantages of converting nitrate and nitrite to hydroxide are a) waste tank protection, b) making some aluminum compounds found in the waste tanks more soluble which results in sending more mass to Saltstone at SRS or Low Activity Vitrification at Hanford Site and less mass to High Level Waste Vitrification and c) reducing processing issues associated with nitrates and nitrites. SRS Waste Tanks were constructed from carbon steel and therefore are susceptible to stress corrosion cracking. Nitrite and hydroxide act as corrosion inhibitors, while halides, sulfate and nitrate are corrosive. Hoffman and Coleman [2008] tested coupons and determined that carbon steel is protected by hydroxide concentrations of at least one molar. For lower concentrations of hydroxide the steel will be protected if nitrite molarity is at least 1.66 times nitrate concentration.

One possible application of conversion of nitrate to hydroxide is during dissolution of Salt Tanks which was modeled by Pike [2005] for Salt Tank 25. Figure 3 shows that when the contents of Salt Tank 25 are dissolved the concentrations of the two corrosion inhibitors in the liquid, hydroxide and nitrite, are initially high, 9.5 M and 1.5 M, and nitrate concentration is low. However, by the third batch of the dissolution process the concentration of hydroxide decreases to less than one molar and the concentration of nitrate increases to more than 7 M. The tank would be out of compliance with Corrosion Controls [Cole, 2002] and it would be necessary to add large quantities of sodium hydroxide to the tank.

A second reason to generate caustic is to compensate for losses. Radiolysis in the tanks generates hydrogen gas. Air is purged through the tanks to prevent the accumulation of a flammable mixture. Most of the carbon dioxide in the air reacts with hydroxide to form carbonate [Hobbs and Wallace, 1985, Hobbs, 1987]. Partially as a result of reaction of hydroxide, consumption of the corrosion inhibitors hydroxide and nitrite at SRS exceeds 100,000 gallons per year [Hobbs and Lambert, 2002].

A third reason to generate caustic is aluminum compound solubility. Martino and Poirier [2010] calculated that approximately 40,000 gallons of 50 wt% caustic must be added to Tank 21H to increase the pH to 2.75 so that precipitation of aluminum compounds will not occur in MCU. Also, increasing the concentration of hydroxide in waste tanks will increase the solubility of some aluminum compounds. Therefore, more aluminum would be sent to Saltstone, a relatively inexpensive process, and less to High Level Waste vitrification.

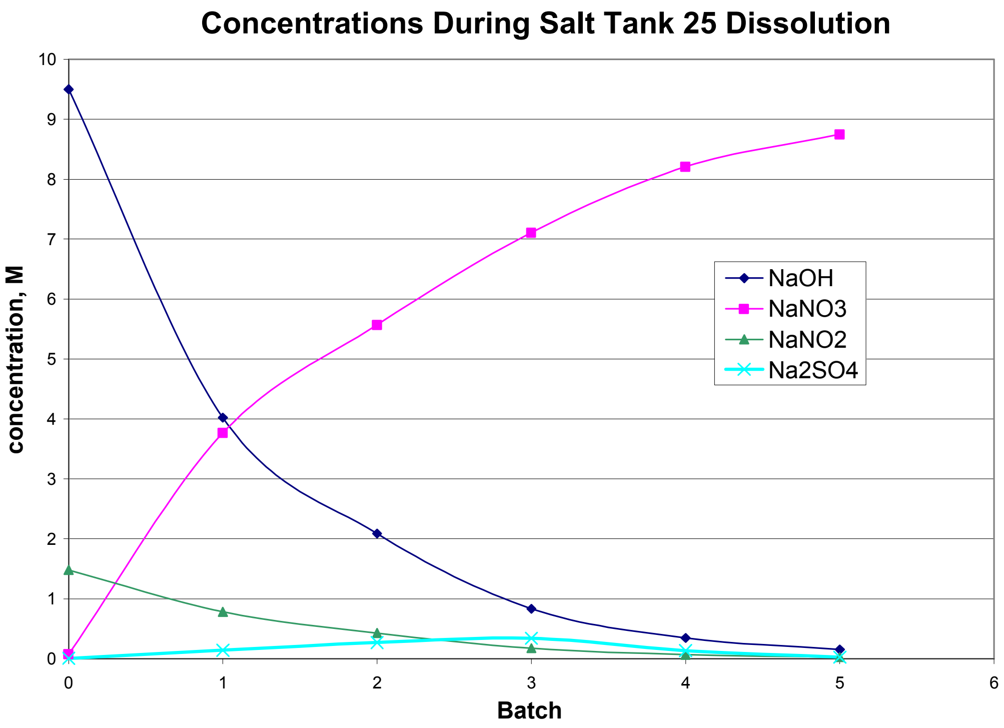

Figure 3 **Concentrations During Salt Tank 25 Dissolution**

2.4 Sizing the Hardware

SRS has two primary needs for caustic, to maintain salt tanks in corrosion control compliance during salt dissolution and to compensate for hydroxide that reacts with carbon dioxide to produce carbonate. To estimate the need for caustic it was assumed that the contents of one salt tank would be dissolved every four months. Assume that a salt tank contains one million gallons of salt that dissolves to form four million gallons of solution. Assume that the latter half of the salt solution volume, two million gallons, hydroxide molarity must be increased on average by 0.5 molar. That would require four million moles of hydroxide per four months or 12 million moles per year or 480 tonnes of NaOH per year. If purchased as 50 wt% solution the annual volume would be 170,000 gallons or 42 tanker trucks. All sodium added to tanks is eventually disposed of in Saltstone.

Hydroxide in waste tanks is constantly consumed by reaction with carbon dioxide. Hobbs [1987] measured that about 80% of the carbon dioxide in the purge air reacted with hydroxide. Typical purge air flow is about 300 cfm and air contains 360 ppm carbon dioxide on a molar basis. One mole of carbon dioxide reacts with two moles of hydroxide. Hydroxide consumption per waste tank is 100,000 moles per year. If caustic is being depleted in forty tanks the total rate of loss is 4 million moles per year. Therefore, the total for tank dissolution and carbon dioxide reaction for forty tanks is 16 million moles per year.

2.5 How the Technologies Would be Implemented

2.5.1 Electrochemical

The primary piece of hardware would be one or more stacks of electrochemical cells. SRNL has tested a commercial unit, the FM21 from Imperial Chemical Industries. Cell area is 0.21 m^2 and a stack can contain up to 60 cells. The cells are connected hydraulically in parallel. The cells in a stack are electrically connected in series so all of the current passes through each cell and the stack voltage is equal to the cell voltage drop, approximately 3.5 volts, multiplied by the number of cells in a stack. For a 60 cell stack the stack voltage is 210 volts. For a reasonable current density of 3500 A/m^2 the current is 735 A. Because of the voltage, the cell must be isolated electrically from tanks and other plant hardware. This requires that some of the piping be non-conducting and also that there be liquid breaks in the lines to and from the electrolyzer stack because the liquid waste is electrically conducting.

A sixty cell stack can generate about 2 million moles of hydroxide per year so eight stacks would be required to generate the demand listed in Section 3.4 of this report.

The cells may be configured in either divided or undivided configuration, either with or without membranes separating the anodes and cathodes. Divided mode tends to have higher electron efficiency because the membrane prevents molecules from being alternately reduced and oxidized at the cathode and anode and oxygen and flammable gases are separated. However divided mode tends to have higher voltage drop because of the voltage drop of the membrane and assembly and operation of the stack are more complicated.

Gases will be generated in the electrolyzer. The volumetric rate for a sixty cell stack is about 14 cfm. The cathode products are nitrogen, and smaller amounts of NO_x, ammonia and hydrogen. The anode generates oxygen. Offgas must be filtered and any ammonia or hydrogen flared. It may be possible to obtain a permit to release the NO_x to atmosphere.

2.5.2 Chemical Reduction

The primary piece of hardware is a reactor containing catalyst on a support. The catalyst is either a platinum group material or Raney nickel. If reaction times were minutes long the reactor could be continuous. If reaction times were hours long, which is more likely, the reactor must be batch. Off gas must be able to handle NO_x and excess reductant. The reductant would likely be hydrogen or ammonia.

2.5.3 Thermochemical

The primary piece of hardware is a reactor, possibly containing catalyst. The reactor and associated hardware must be strong enough to contain pressures as high as 300 atm and very corrosive conditions at temperatures as high as 525°C. The reactor would operate in batch mode. A significant length of time would be required to heat and pressurize the reactants and later to cool and de-pressurize the contents. Off-gas treatment would be required for reaction gases and excess reductant.

2.5.4 Calcining

This technology requires a plasma furnace. According to Navetta [2009], the Plasma Furnace technology would require agitated waste storage tanks, a plasma chamber, the plasma torch, a secondary chamber and an air pollution system.

2.6 Discussion of Rating Criteria

See Table 2 for criteria and scores.

2.6.1 Personnel exposure to radiation for installation, routine operation and maintenance.

The rating of Electrochemical in this category depends on where it is located. For hardware located outside a waste tank, this process was rated lower that the others. An electrolyzer stack may contain sixty cells and each layer of the stack has potential leak locations. Also, the stack has small passages that could clog. The other processes use reactors that have fewer locations that might leak and clog. For locating the electrolyzer inside a waste tank all technologies rank equally.

2.6.2 Non-radioactive safety issues.

Electrochemical was rated highest in this category because no chemicals or catalysts are added and the operation is at ambient temperature and pressure. Chemical reduction is conducted near ambient temperature and pressure, but involves reductants that are flammable and/or toxic, so was rated lower. Thermochemical involves reductants and much higher temperatures and pressures. Calcining involves even higher temperatures and subsequent steps to capture solid products and leach caustic from them.

2.6.3 Does the technology generate caustic and how much?

Electrochemical has been demonstrated to generate one mole of caustic for every mole of nitrate or nitrite decomposed to gas. This is less certain for Chemical Reduction and Thermochemical and even less certain for Calcining.

2.6.4 Does the technology handle nitrate and nitrite at concentrations encountered in actual waste?

Electrochemical has been demonstrated to work with simulants that approximate actual liquid waste. This is less certain for Chemical Reduction and Thermochemical. Calcining is reported to have slag formation problems with high concentrations of sodium.

2.6.5 Maturity of technology

In general, Chemical Reduction, Thermochemical and Calcining are mature technologies. However, for the specific application of converting nitrate and nitrite in tank waste to hydroxide, Electrochemical is the most mature technology.

2.6.6 Estimated annual cost of operation

The primary components of annual operating cost are labor, depreciation, materials and utilities. Labor was estimated to be the same in each case. Electrochemical requires no chemicals or other supplies, but has a higher electrical cost than Chemical Reduction. Chemical Reduction and Thermochemical require chemical reductants such as hydrogen. Thermochemical and Calcining have high and very high energy costs, respectively.

2.6.7 Capitol cost.

Chemical reduction is judged to require the smallest investment because the reactor will be low temperature and pressure and not involve materials more expensive than stainless steel. Electrochemical is more expensive because more plates and seals are need. Thermochemical and Calcining are expected to require exotic materials to prevent corrosion and wear at high temperatures.

2.6.8 Selectivity to nitrogen as decomposition product

For Electrochemical there is favorable data on product selectivity to nitrogen. There is less data for the competing techniques.

2.6.9 Impact of introduced species

Electrochemical and Calcining would not intentionally introduce any new species, however, there might be some dissolution of electrode in the electrolyzers or degradation of hot surfaces in the calciner.

2.6.10 Selectivity for destruction of nitrate vs. nitrite

None of the processes considered has any significant selectivity to destroying nitrate instead of nitrite.

2.6.11 Cost of deactivation and demolition

It is expected to be more expensive to deactivate Electrochemical and Calcining than the other two technologies. Electrochemical has many crevices and calcining creates solid than can accumulate in various locations.

3.0 Conclusions

As shown in Table 2 the rating process concluded the ranking of the technologies from most promising to least promising is Electrochemical, Chemical Reduction, Thermochemical and Calcining. The primary reasons for ranking Electrochemical first are that it is the most mature technology, it is operated at ambient conditions and nitrate and nitrite are converted to gases and hydroxide. The technologies that offer the most flexibility in location for implementation are Electrochemical and Chemical Reduction. Potentially both of those technologies may be inserted inside waste tanks.

4.0 Recommendations

The purpose of this report was to document a literature survey of nitrate destruction technologies and also to document the process whereby the primary and secondary technologies were selected. The two selected technologies are Electrochemical and Chemical Reduction. The next phase of study involves development of flowsheets for those technologies and then preparation of a draft design for hardware or a conceptual facility to implement the Electrochemical technology. The flowsheet and design report, SRNL-STI-2011-00097-"Design of In-tank Nitrate Electrolyzer", is in development and will contain recommendations for additional experimental and calculational work that will be necessary should the selected process be pursued at the conclusion of this research.

5.0 References

Aliexpress. “Palladium nitrate 10102-05-3 Pd(NO3)2.” http://www.aliexpress.com/product-gs/302229300-Palladium-nitrate-10102-05-3-Pd-NO3-2-wholesalers.html. (Accessed May 28th, 2010)

AZoMaterials. “Stainless Steel-Grade 316-Properties, Fabrication and Applications” http://www.azom.com/details.asp?articleid=863. (Accessed June 1, 2010)

Bostick, D.T.; Arnold, W.D.; Burgess, M.W.; Davidson, D.J; Wilson, J.H.; Bostick, W. D.; Dillow, T.A.; Abotsi, G.; Taylor, P. A.; McTaggart, D.R.; Osborne, S.C. and Kent, T.E. “FY 1995 Separation Studies for Liquid Low-Level Waste Treatment at Oak Ridge National Laboratory.” ORNL/TM-13101. 1996.

Burket, P.R.; Daniel W. E.; Jantzen, C.M.; Nash, C.A.; Crawford, C.L.; Williams, M.R. and Barnes, A.B. “Steam Reforming Technology Demonstration for the Destruction of Organics on Actual DOE Savannah River Site Tank 48H Waste-9138” SRNL-L3100-2009-00048. 2009.

Caime, Jon and Hoeffner, Steve. “Nitrate to Ammonia and Ceramic (NAC) Bench Scale Stabilization Studies.” DOE/MC/32113 – 5269. 1996.

Chai, D., Hartsough, D., Genders, D., Phase III Final Repor “Electrochemical Processing of Hanford and SRS Waste Simulants using ICI FM21-SP Pilot Scale Flow Cell”, Electrosynthesis Co., Inc. 1995.

Cheng, H.; Scott, K. and Christensen P. A. “Paired Electrolysis in a Solid Polymer Electrode Reactor—Simultaneous Reduction of Nitrate and Oxidation of Ammonia.” Chemical Engineering Journal. 109 (2005) 257-268.

Cole, Clifford, “CSTF Corrosion Control Program”, WSRC-TR-2002-00327, 2002.

Cox, John, L; Hallen, Richard T. and Lilga Michael A. “Thermochemical Nitrate Destruction” Environmental Science Technology. 28 (1994) 423-428.

D’Arino, Marco; Pinna, Francesco; Strukul, Giorgio; “Nitrate and Nitrite Hydrogenation with Pd and Pt/SnO_2 Catalysts: the Effect of the Support Porosity and the Role of Carbon Dioxide in the Control of Selectivity” Applied Catalysis B: Environmental. 53 (2004) 161-168.

Deganello, F.; Liotta, L.F.; Macaluso, A.; Venezia, A.M. and Deganello, G. “Catalytic Reduction of Nitrates and Nitrites in Water Solution on Pumice-Supported Pd-Cu Catalysts” Applied Catalysis B: Environmental. 24 (2000) 265-273.

Department of Energy. “Technical Report on Hydroxylamine Nitrate” DOE/ EH-0555. February 1998.

Duarte, H. A., Jha, K. and Weidner, J. W., “Electrochemical Reduction of Nitrates and Nitrites in Alkaline Media in the Presence of Hexavalent Chromium”, J. of Appl. Electrochemistry, v. 28, 811-817, 1998.

Engineering Toolbox. "Solids and Metals-Specific Gravities." http://www.engineeringtoolbox.com/specific-gravity-solids-metals-d_293.html. (Accessed June 1, 2010)

E-Stainless Steel. "US 304/316 Stainless Steel Surcharge & Monthly History" http://www.estainlesssteel.com/usstainlesssurcharges.shtml. (Accessed May 28, 2010)

Fanning, James C. "The Chemical Reduction of Nitrate in Aqueous Solution" Coordination Chemistry Reviews. 199 (2000) 159-179.

Faculty of Chemical Technology. "Strontium" http://www.ktf-split.hr/periodni/en/sr.html. (Created January 4th, 2003)

Gillam, J.M. and Larsen D.D. "Sludge Batch 5 Summary and Projected Blend Compositions, Post Tank 51 to Tank 40 Transfer." LWO-LWP-2008-00008. 2008.

Hoang, Tri T. "Stabilization/Solidification Processes for Mixed Waste." EPA 402-R-96-014. June 1996.

Hobbs, D.T. "Summary Technical Report on the Electrochemical Treatment of Alkaline Nuclear Wastes" WRSC-TR-94-0287. 1994.

Hobbs, D. T. and R. M. Wallace, "Hydroxide Depletion in Waste Storage Tanks by Reaction with Carbon Dioxide", DPST-85-00846, 1985.

Hobbs, D. T., "Absorption of Carbon Dioxide in Waste Tanks", DPST-87-00535, 1987

Hobbs, D. T. and D. Lambert, "Strategic Research: In-Tank Generation of Corrosion Inhibitors", WSRC-2002-00115, 2002.

Hoffman, E. N.; Zapp, P. E.; Wiersma, B. J. and Subramanian, K. H. "Inhibiting Localized Corrosion in Mild Carbon Steel" SRNL-STI-2008-00391. 2008.

Jantzen, C.M.; "Mineralization of Radioactive Wastes by Fluidized Bed Steam Reforming (FBSR): Comparisons to Vitreous Waste Forms, and Pertinent Durability Testing" WSRC-STI-2008-00268. 2008.

Jeong, Y.H; Park, J.Y.; Kim, H.G.; Busby, J. T.; Garter, E.; Atzmon, E.; Wos, G.S.; Comstock, R.J.; Chu, Y.S; Gomes da Silva, M.; Yilhazbayhan A. and Motta A. T. "Corrosion of Zirconium Based Fuel Cladding Alloys in Supercritical Water" Proceedings of the 12th International Conference on Environmental Degradation of Materials in Nuclear Power System – Water Reactors TMS (The Minerals, Metals & Materials Society). 2005

Katsounaros, I.; Dortsiou, M. and Kyriacou, G. "Electrochemical Reduction of Nitrate and Nitrite in Simulated Liquid Nuclear Wastes." Journal of Hazardous Materials. 171 (2009) 323-327.

Li, Miao; Feng, Chuanping; Zhang, Zhenya; Lei, Ziaohui; Chen, Rongzhi; Yang, Yinan and Sugiura, Norio. "Simultaneous Reduction of Nitrate and Oxidation of By-Products Using Electrochemical Method" Journal of Hazardous Materials 171 (2009) 724-730.

Marshall, D. W.; Soelberg, N.R. and Shaber, K.M. “THOR Bench-Scale Steam Reforming Demonstration” INEEL/EXT-03-00437. 2003.

Marshall, D. W. and Soelberg, N.R. “TWR Bench-Scale Steam Reforming Demonstration” INEEL/EXT-03-00436. 2003.

Martino, C and Poirier, M, “Mixing Evaluation for Tank 21H Salt Batch Preparation”, SRNL-TR-2010000235, 2010

Mason, J. Bradley; McKibbin, John; Ryan, Kevin; and Schmoker, Duane. "Steam Reforming Technology for Denitration and Immobilization of DOE Tank Wastes" WM ‘-3 Conference, 2003, Tucson, AZ.

Mattus, A. J.; Lee, D. D.; Dillow, T. A.; Farr, L. L.; Loghry, S.L; Pitt, W.W. and Gibson, M.R. " A Low-Temperature Process for the Denitration of Hanford Single-Shell Tank, Nitrate-Based Waste Utilizing the Nitrate to Ammonia and Ceramic (NAC) Process” ORNL/TM-12245. 1994.

Mattus, A. J.; Walker, Jr. , J. F.; Youngblood, E. L.; Farr, L. L.; Lee, D. D.; Dillow, T. A.; Tiegs, T. N. "A Low-Temperature Process for the Denitration of Hanford Single-Shell Tank, Nitrate-Based Waste Utilizing the Nitrate to Ammonia and Ceramic (NAC) or Nitrate to Ammonia and Glass (NAG) Process: Phase II Report" ORNL/TM-12631. 1994.

Mattus, A. J.; “Technological and Economic Update on the Nitrate to Ammonia and Ceramic Process” ORNL/CP-95756. 1998.

MTI. “Metals.” http://www.mtialbany.com/metals.php. (Accessed June 1, 2010)

Navetta, Michael S., “Evaluation of Nitrate and Nitrite Destruction/Separation Technologies”, RSC Corporation, WSRC-OS-97-00008, 1997.

Periodic Table of the Elements. “Niobium” http://periodic.lanl.gov/elements/41.html. (Accessed May 28, 2010)

Pike, J. A., “Flowsheet and Physical Property Estimation for SRS Tank 25 Salt Dissolution”, CBU-PIT-2005-00081, Rev. 1, February 11, 2008

Pintar, Albin; Batista, Jurka; Levec, Janaz and Kajiuchi, Toshio. “Kinetics of the Catalytic Liquid-Phase Hydrogenation of Aqueous Nitrate Solutions” Applied Catalysis B: Environmental. 11 (1996) 81-98.

Pintar, Albin; Batista, Jurka and Levec, Janaz. “Hardness and Salt Effects on Catalytic Hydrogenation of Aqueous Nitrate Solutions” J. Catalysis. 72 (1998) 174.

Plodinec, M.J. “Vitrification of Tank 15 Waste” DPST-80-00272. 1980.

PTE. “Caesium.” http://www.periodni.com/en/cs.html. (Created 2010).

Reigel, M.M. and Bibler, N.E; "Results for the First Quarter 2010 Tank 50 WAC Slurry Sample: Chemical and Radionuclide Contaminant Results” SRNL-STI-2010-00210. 2010.

Reyter, David; Belanger, Daniel and Roue, Lionel. “Study of the Electroreduction of Nitrate on Copper in Alkaline Solution” Electrochimica Acta. 53 (2008) 5977-5984.

Reyter, David; Belanger, Daniel and Roue, Lionel. “Nitrate Removal by a Paired Electrolysis on Copper and Ti/IrO_2 Coupled Electrodes – Influence of the Anode/Cathode Surface Area Ratio” Water Research. 44 (2010) 1918-1926.

Sabzali, A.; Gholami, M.; Yazdanbakhsh, A.R.; Khodadadi, A.; Musavi, B. and Mirzaee, R. “Chemical Denitrification of Nitrate from Groundwater Via Sulfamic Acid and Zinc Metal” Iranian Journal of Environmental Health Science. Vol 3. No. 3 (2006) 141-146.

Science Lab. “Palladium Chloride” http://www.sciencelab.com/page/S/PVAR/10423/SLP1378. (Accessed May 28, 2010)

Soelberg, N.R; Marshall, D.W.; Bates, S. O. and Taylor, D.D. “Phase 2 THOR Steam Reforming Tests for Sodium-Bearing Waste Treatment” INEEL/EXT-04-01493. 2004.

Steimke, J. L., Hobbs, D. T., Fowley, M. D. and Steeper, T. J., “Results from Tests of TFL Electrochemical Reactor”, WSRC-TR-97-0196, 1997.

Steimke, J. L. and Steeper, T. J., “Design of In-Tank Nitrate Electrolyzer”, SRNL-STI-2011-00097, 2011.

Taylor, P. A. "Evaluation of Nitrate Destruction Methods" DOE/MWIP-10. 1993.

Turbosystems Engineering. “Overview of Supercritical Water Oxidation” http://www.turbosynthesis.com/summitresearch/sumscw1.htm. (Accessed June 1, 2010)

WSWS. “Five Workers Killed in Pennsylvania Chemical Blast” http://www.wsws.org/articles/1999/feb1999/penn-f24.shtml. (Created February 24, 1999)

Table 2 List of Rating Criteria and Scores

			Score (1 - 5)			
	Criteria	**Weighting Factor (1 - 10)**	**Electro-Chemical**	**Chemical Reduction**	**Thermo-Chemical**	**Calcining**
1	Personnel exposure to radiation for installation, routine operation and maintenance.	10	4 in tank 3 outside tank	4	4	4
2	Non-radioactive safety issues	10	4	4	2	2
3	Does the technology generate caustic and how many moles of caustic is generated per mole of nitrate plus nitrite decomposed	10	5	3	3	1
4	Whether the technology can handle nitrate and nitrite at the concentrations encountered in waste	10	5	3	3	3
5	Maturity of technology	7	4	2	2	2
6	Estimated annual cost of operation (labor, depreciation, materials, utilities)	7	4	3	2	2
7	Capital cost	6	4	5	2	2
8	Selectivity to nitrogen as decomposition product, i.e. risk of flammable gas mixtures	5	4	3	3	1
9	Impact of introduced species	5	4	2	2	4
10	Selectivity for destruction of nitrate vs. nitrite	5	4	4	3	3
11	Cost of deactivation and demolition	3	2	5	5	2
	Total Score		326 in tank 316 outside tank	265	215	186

Distribution:

A. B. Barnes, 999-W
D. A. Crowley, 773-43A
S. D. Fink, 773-A
B. J. Giddings, 786-5A
C. C. Herman, 999-W
S. L. Marra, 773-A
A. M. Murray, 773-A
F. M. Pennebaker, 773-42A
J. H. Scogin, 773-A
W. R. Wilmarth, 773-A