LITERATURE REVIEW ON IMPACT OF GLYCOLATE ON THE 2H EVAPORATOR AND THE EFFLUENT TREATMENT FACILITY (ETF)

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LITERATURE REVIEW ON IMPACT OF GLYCOLATE ON THE 2H EVAPORATOR AND THE EFFLUENT TREATMENT FACILITY (ETF)

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CPC	Chemical Process Cell
DCM	dichloromethane
DF	decontamination factor
DWPF	Defense Waste Processing Facility
E&CPT	Environmental & Chemical Process Technology
EDTA	Ethylenediamine tetra acetic acid
PNNL	Pacific Northwest National Laboratory
ETF	Effluent Treatment facility
FTIR	Fourier Transform Infra-Red Spectroscopy
GA	glycolic acid
HEPA	high efficiency particulate filters
HLW	high-level waste
LLW	low level waste
MIBK	4-methylpentan-2-one
NPH	normal Paraffin hydrocarbons
OLI/ESP	OLI Environmental Simulation Package Software
RO	Reverse Osmosis
SPF	Saltstone Production Facility
SRNL	Savannah River National Laboratory
SRR	Savannah River Remediation
SRS	Savannah River Site
TBP	tributylphosphate
TDS	total dissolved solids
TOC	total organic carbon
TTQAP	Task Technical and Quality Assurance Plan
TTR	Technical Task Request
WAC	Waste Acceptance Criteria

SUMMARY

Glycolic acid (GA) is being studied as an alternate reductant in the Defense Waste Processing Facility (DWPF) feed preparation process. It will either be a total or partial replacement for the formic acid that is currently used.

A literature review has been conducted on the impact of glycolate on two post-DWPF downstream systems – the 2H Evaporator system and the Effluent Treatment Facility (ETF). The DWPF recycle stream serves as a portion of the feed to the 2H Evaporator. Glycolate enters the evaporator system from the glycolate in the recycle stream. The overhead (i.e., condensed phase) from the 2H Evaporator serves as a portion of the feed to the ETF.

The literature search revealed that virtually no impact is anticipated for the 2H Evaporator. Glycolate may help reduce scale formation in the evaporator due to its high complexing ability. The drawback of the solubilizing ability is the potential impact on the criticality analysis of the 2H Evaporator system. It is recommended that at least a theoretical evaluation to confirm the finding that no self-propagating violent reactions with nitrate/nitrites will occur should be performed. Similarly, identification of sources of ignition relevant to glycolate and/or update of the composite flammability analysis to reflect the effects from the glycolate additions for the 2H Evaporator system are in order. An evaluation of the 2H Evaporator criticality analysis is also needed.

A determination of the amount or fraction of the glycolate in the evaporator overhead is critical to more accurately assess its impact on the ETF. Hence, use of predictive models like OLI Environmental Simulation Package Software (OLI/ESP) and/or testing are recommended for the determination of the glycolate concentration in the overhead.

The impact on the ETF depends on the concentration of glycolate in the ETF feed. The impact is classified as minor for feed glycolate concentrations $\leq$ 33 mg/L or 0.44 mM.

The ETF unit operations that will have minor/major impacts are chlorination, pH adjustment, 1st mercury removal, organics removal, 2nd mercury removal, and ion exchange. For minor impacts, the general approach is to use historical process operations data/modeling software like OLI/ESP and/or monitoring/compiled process operations data to resolve any uncertainties with testing as a last resort. For major impacts (i.e., glycolate concentrations > 33 mg/L or 0.44 mM), testing is recommended.

No impact is envisaged for the following ETF unit operations regardless of the glycolate concentration – filtration, reverse osmosis, ion exchange resin regeneration, and evaporation.

1.0 INTRODUCTION

Studies are underway to use glycolic acid (GA) as an alternate reductant in the Defense Waste Processing Facility (DWPF) process flowsheet to totally or partially replace formic acid that is currently used.[1,2] Choi[3] in his modeling work on Melter Off-Gas Flammability Assessment for the DWPF Alternate Reductant Flowsheet Options indicated that over 50% of the glycolic acid in the DWPF feed exits the melter off-gas system as undissociated glycolate. This implies the condensed glycolate will be in the DWPF recycle stream that goes to the tank farm and eventually ends up as feed solution to the 2H Evaporator. The condensed vapor resulting from concentrating the feed solution with the 2H Evaporator goes to the Effluent Treatment Facility (ETF). The DWPF recycle stream is neutralized with sodium hydroxide prior to transfer to the tank farm, therefore sodium glycolate is the expected species present in the recycle stream.

The objective of this work is to conduct a literature review on the impact of glycolate on the 2H Evaporator system and the ETF. The work was performed according to the "Task Technical and Quality Assurance Plan (TTQAP) for Glycolic Acid Flowsheet Development".[4] The TTQAP was derived from a Technical Task Request (TTR).[5]

2.0 LITERATURE REVIEW

Literature information pertaining specifically to solutions with similar constituents as the evaporator feed solution or the ETF unit operations streams and also containing glycolate was almost non-existent. In other words, direct information was not found. Hence, most of the discussion that follows is based on indirectly related information.

The review is divided into two major portions – 2H Evaporator and the ETF. The evaporator feed solution is conservatively assumed to have a bounding glycolate concentration of 10,000 mg/L (0.133 M).[6]

2.1 2H EVAPORATOR

The function of the 2H Evaporator is to concentrate or reduce the volume of waste solutions by vaporizing the water in the feed solution. Volume reduction is about 30-40%. The resulting vapor (overhead) is condensed after passing through a de-entrainment unit (demister) and sent to the ETF. The demister removes entrained liquids and solids from the vapor. The non-condensable gases exiting the overhead condenser go through high efficiency particulate (HEPA) filters prior to venting to the atmosphere.[7-10] The evaporator feed solution typically comprises regular tank farm waste and the DWPF recycle stream. The feed solution is stored in Tank 43 (feed tank). The concentrated solution (or the bottoms) is stored in Tank 38 (drop tank).

The 2H Evaporator operates at atmospheric pressure and at a temperature of 110-120 $^{\circ}$C.[8,9] Table 1 provides the 2H Evaporator feed (Tank 43) composition data.[11] It gives the low and high values for a series of quarterly analyses that spans from January 4, 2008 to September 12, 2011. Note that the analysis is not comprehensive. It excluded analysis of a host of other constituents. Below are the other constituents that are expected to be in the Tank 43 evaporator feed. They are typical constituents in the DWPF recycle stream.[12-15] The concentrations are omitted since the feed concentration will be a blend of regular tank farm waste and the DWPF recycle stream.

Non-radioactive constituents:
NH_4^+, Al, As, B, Ba, Be, Ca, Cd, Ce, Cr, Cu, Fe, Gd, Hg, K, Li, Mg, Mn, Ni, P, Pb, S, Sb, Se, Si, Sn, Sr, Ti, V, Zn, Zr, and organics

Radioactive constituents:
Co-59, La-139, Rh-103, Pd, Ag, Alpha, Beta, H-3, C-14, Al-26, Ni-59, Ni-63, Co-60, Se-79, Sr-90, Nb-94, Tc-99, Ru-106, Sb-125, Sn-126, I-129, Cs-134, Cs-135, Cs-137, Pm-147, Sm-151, Eu-154, Eu-155, Ra-226, Th-230, Th-232, Np-237, Am-241, Am-243, and Cm-244.

Table 1. Composition of Some of the Constituents in the 2H Evaporator Feed Solution.

Non-Radioactive Constituents	Low, mg/L (M)	High, mg/L (M)
Nitrate (NO_3^-)	3.66E+04 (5.91E-01)	7.43E+04 (1.20E+00)
Nitrite (NO_2^-)	4.55E+04 (9.89E-01)	9.02E+04 (1.96E+00)
Sulfate (SO_4^{2-})	< 1.14E+03 (< 1.19E-02)	2.27E+03 (2.36E-02)
Fluoride (F^-)	< 1.12E+02 (< 5.89E-03)	< 2.89E+03 (< 1.52E-01)
Oxalate ($C_2O_4^{2-}$)	< 1.14E+02 (< 1.30E-03)	2.82E+02 (3.20E-03)
Chloride (Cl^-)	< 1.12E+02 (< 3.15E-03)	1.52E+02 (4.30E-03)
Phosphate (PO_4^{3-})	< 5.51E+02 (< 5.80E-03)	3.42E+02 (3.60E-03)
Hydroxide (OH^-)	2.82E+04 (1.66E+00)	6.86E+04 (4.04E+00)
Specific Gravity	1.1400	1.3235
Radioactive Constituents	**Low**	**High**
Ba-137m, dpm/mL	5.52E+07	1.68E+08
Gross Gamma, dpm/mL	5.83E+07	1.78E+08
U-233, mg/L	< 2.04E-02	< 1.03E-01
U-234, mg/L	< 2.04E-02	< 1.03E-01
U-235, mg/L	2.09E-01	2.53E+02
U-236, mg/L	< 5.06E-02	< 1.58E-01
U-238, mg/L	3.62E+01	6.33E+01
U-235, wt%	< 9.10E-01	8.90E-01
U (total) mg/L	< 5.56E+01	2.55E+02
Pu-238, dpm/mL	1.64E+04	2.52E+06
Pu-239, mg/L	< 5.87E-03	3.26E-01
Pu-239/240, dpm/mL	< 8.09E+02	4.50E+04
Pu-241, dpm/mL	3.22E-05	2.71E+05

GA-glycolate equilibrium relationship indicates at pH > 5, it exists in the glycolate form.[16-18] Since the evaporator feed's pH is typically ≥ 13, it will be in the glycolate form. Even though it will be in glycolate form, the discussions deal with GA more than the glycolate. More information was found on GA than glycolate or glycolate salts.

2.1.1 Solubility

GA is very soluble in water.[19,20] As a result, it cannot be separated in solution by vacuum distillation.[20,21] The solubility of GA is ~2,440 g/kg H_2O (~71 wt%) at 25 °C.[22] Its hydrophilicity characteristics is exhibited by its low octanol-water partition coefficient (0.078 at 19 °C).[18,23,24] Note that no supporting data were provided by the authors on the statement that GA cannot be vacuum distilled.

Reference #19 provides aqueous solubility of the metal salts of glycolic acid. For example, the solubilities of sodium glycolate (20 °C), potassium glycolate (20 °C), magnesium

glycolate (28 ^{o}C), calcium glycolate (28 ^{o}C), lead glycolate (15 ^{o}C), and zinc glycolate (20 ^{o}C) are 40.9, 56.6, 7.7, 1.5, 20.6, and 3.3 wt% respectively.

The effect of the constituents in the evaporator feed on the solubility of GA or glycolate is not known. The closest information related to this was found in the work of Barney at the Hanford site between1994 to 1997. Barney[25,26] measured the solubility of glycolate and other organic compounds separately in Hanford high-level waste (HLW) tank supernate simulant solutions.

The overall objective of the solubility measurements was to obtain solubility data that will allow prediction of whether or not significant quantities of organics exist as solids in the HLW tanks. Knowledge of phase (liquid or solid) of the organic compounds is important to safety assessments of the waste tanks. This is because for tanks containing high concentrations of organic compounds there is a likelihood that the organics might react violently with nitrate or nitrite salts to produce heat and gaseous compounds. For this hazardous, self-propagating reaction to occur, the organic compounds and nitrate/nitrite salts must satisfy specified concentration and temperature limits. The stipulations are as follows based on a preliminary safety assessment criteria developed for the Hanford tanks.[27,28]

(i)   For a moisture content of 20 wt% or higher, no propagating reaction regardless of the total organic carbon (TOC) concentration.

(ii)   For a moisture content of 0 wt% (i.e., dry waste), no propagating reaction if TOC concentration < 4.5 wt%.

(iii) For a moisture content of between 0 and 20 wt%, no propagating reaction if TOC concentration is between 4.5 and 7.9 wt%. The 0 to 20 wt% moisture content range varies linearly with the 4.5 to 7.9 wt% TOC concentration range. In other words, within the range, high moisture levels accommodate high TOC levels.

(iv)   In addition to the above conditions, a temperature above 220 °C or an initiator of sufficient energy is required. The potential credible ignition sources identified included hot metal objects, rotary core upsets, burning gasoline spills from a ruptured vehicular fuel tank, and lightning.

The concentration of the tank supernate simulant was a 4.0 M sodium nitrate and 0.97 M sodium nitrite with sodium hydroxide concentrations ranging from 0.00003 M to 2.0 M. The temperature range of the measurements was 25 to 50 ^{o}C. Note that the above concentrations are broadly consistent with the 2H Evaporator feed concentration given in Table 1.

The solubility of sodium glycolate in the supernate simulant ranged from 4.4 to 5.8 M (or 106 to 140 g TOC/L). The solubility decreased with increasing sodium hydroxide concentration and increased with increasing temperature. The dissolution of sodium glycolate in the simulant solutions resulted in significant volume increases in these solutions. The volume increase, in turn, decreased the concentrations of the constituents (i.e., sodium nitrate, nitrite, and hydroxide) in the simulant solution. The volume increase (or the decrease in concentration) ranged from 25 to 36% going from 25 to 50 ^{o}C. Sodium glycolate did not

appear to form solids in the waste simulant solution and as a result passed the above preliminary safety assessment criteria.

In a follow up study, Barney[29] repeated the above work with a 2 M sodium nitrite supernate solution saturated with crystalline sodium nitrate, and sodium hydroxide concentrations ranging from 0.1 M to 2.0 M. The temperature range was the same as before. The sodium glycolate solubilities ranged from 3.6 to 4.2 M (or 86 to 101 g TOC /L). Note that the solubilities are less than the values (4.4 to 5.8 M) he obtained from the earlier work[25] for solutions not saturated with sodium nitrate. The solubilities decreased as the temperature was raised, especially at 50 ^{o}C. This was claimed to be due to the common ion effect of sodium for solutions containing high sodium nitrate concentrations. The solubilities slightly increased as sodium hydroxide concentrations increased.

Because the organics are not likely to exist as solids in the tanks, but only as aqueous solutions, self-propagating reactions with nitrates or nitrites were deemed unlikely by Barney. Note that the effect of temperature within the evaporator operating range (110-120 ^{o}C) is unknown but it looks like sodium nitrate will not be in the saturated condition in the evaporator. This is based on data on the sodium nitrate solubility in simulated Hanford waste at 100 ^{o}C.[30] The Hanford waste simulant solution is roughly similar to the 2H Evaporator feed solution except it did not contain silicate/silica. It is not clear the effect silicate/silica may have on the solubility of sodium nitrate.

A glycolate concentration of 10,000 mg/L (0.133 M) would be 17,000 mg/L after concentrating the solution 1.7X in the evaporator. This is equivalent to a TOC concentration of 5,400 mg/L (or 5.4 g/L). If one conservatively assumes the density of the concentrated solution in the evaporator to be 1 g/mL, then the wt% TOC for glycolate is 0.54.

Adding the TOC from other organics in the feed solution to the 0.54 wt% TOC will most likely be much less than 4.5 wt%.

For an initial water content of the feed solution of 70 wt% based on an assumed total dissolved solids (TDS) of 30 wt%, the water content after concentrating the solution 1.7X (i.e., volume reduction of 40%) will range between 45 to 58 wt% depending on the densities of the feed and concentrated solutions. The ranges of feed and concentrated solution densities used are 1.14 - 1.323 (see Table 1) and 1.2080 - 1.3450[11] g/mL respectively.

Even for a worse-case scenario of an initial water content of 60 wt% (i.e., 40 wt% TDS), the water content for a 1.7X concentrated solution will be between 27 and 44 wt%.

The above estimations indicate self-propagating reactions with nitrates or nitrites are unlikely to occur in the 2H Evaporator because of low TOC (< 4.5 wt%) and temperature < 220 ^{o}C. Note also that the initial concentration of glycolate (0.133 M) in the feed is much lower than the solubility values reported by Barney even though the two systems (solutions) are not the same. It may be worthwhile to do a similar safety assessment for the 2H Evaporator system and also look for glycolate-related ignition sources.

2.1.2 Complex Formation

GA or glycolate has the ability to complex virtually all multivalent metals and make them soluble.[19,21,24,31-37] As a result it has wide applications in the following areas.

(i)   Household and Institutional Cleaning: Hard water salts (magnesium, calcium), soap scum and iron oxide.

(ii)   Stainless Steel Boiler and Process Equipment Cleaning: Calcium carbonate and iron oxide mill scale including iron oxides, calcium salts, magnesium salts, silica, silt, nickel oxides and copper oxides.

(iii)   Dairy Cleaning: Milkstone, casein and other deposits from dairy processing equipment.

(iv)   Food Processing Equipment Cleaning: Meat, poultry and egg products processing equipment

(v)   Concrete Removal from Tools, Equipment and Vehicles: Metal oxide salts.

(vi)   Masonry Surface Cleaning: Bricks and concrete in general, and trace metal stains in white bricks.

(vii)   Paper Maker Felt Cleaning or Conditioning: Aluminum salts and other hard water salts.

(viii)   Cooling Tower and Heat Exchanger Cleaning: Hard water scale from all types of heat-exchanger equipment.

(ix)   Water Well Cleaning: Accumulated iron and carbonate deposits in water wells.

Examples of the complex formation are discussed below. Note that they span the broad pH region and also varying concentrations. Most are at a temperature of 20 - 25 $^{\circ}$C. The main techniques used to detect the complexes are potentiometry, spectroscopy, and distribution between two phases.

Stable metal-glycolate complex formations even in the high pH region are well documented in the literature dating back to the 1950s. Sonesson[38] formed glycolate complexes with ten rare-earth metals. The rare-earth metals were La, Ce, Pr, Nd, Sm, Gd, Dy, Ho, Er, and Yb. Note that these elements are all in the lanthanide family.

Powell and Suzuki[39] measured the stability constants or (formation constants) of the complex species formed between tripositive rare-earth cations (La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, and Y) and the glyoxylate $[(HO)_2CHCOO^-]$ anion and compared with the data with the glycolate $(HOCH_2COO^-)$ and acetate (CH_3COO^-) counterparts. They found the rare-earth glycolate species to be the most stable followed by the corresponding glyoxylate species and the corresponding acetate species in that order. In the case of Y, the formation constants for all three species were between the corresponding values for Tb and Dy.

Uranyl-glycolate complex was also formed by Ahrland[40]. May et al.[41] used near infra-red spectroscopy to detect Np(IV)-glycolate complexes in solution. Complexation of trivalent actinide (Cm) and lanthanide (Eu) ions by GA especially at high pH was studied by Stumpf et al.[42] Toraishi et al.[42] investigated the complex formation of tetravalent thorium and various trivalent lanthanides (Sm, Eu, Dy, Er, and Lu) by glycolate at high pH.

Farkas[44] studied for his doctoral thesis the complexation at high pH between glycolate and different lanthanide (III) ions (Sm, Eu, Dy, Er, and Lu) and identified various ternary polynuclear complexes. Hnatejko et al.[45] formed trivalent lanthanide (Eu, Tb, and Gd) complexes with GA in the pH range of 0.5 to 7. Riri et al.[46] formed Gd (III)-glycolate complex in the pH range of 5.5 and 7.5 using an Indirect Photometry Detection technique.

Lu and Iglesia[47] detected soluble glycolate complexes with Y (III) and Zr (IV) using infrared spectroscopy at pH between 5 and 11. They indicated $Y(OH)_3$ and $Zr(OH)_4$ precipitate in the absence of glycolate. Wang et al.[48] used sodium glycolate to dissolve antimony(III) acetate.

Examples of transition metal-glycolate complexation were also found in the literature. Gil[49] used multinuclear magnetic resonance spectroscopy to study the complexes that form between V(V), Mo(VI), W(V1), and U(V1) and glycolic acid in the pH range of 2.5 to 7.5. Justino, et al.[50] also used nuclear magnetic resonance spectroscopy to investigate V(V) complexation with GA in the pH range of 3.3 to 5.7. Cuin and Massabni[51] formed Mo(VI) glycolate complex with GA.

Naujalis and Padarauskas[52] used the complexing ability of glycolate to develop a new capillary electrophoretic method for the selective and sensitive determination of common divalent metal ions (Fe, Co, Ni, Cu, and Zn). Slowey[53] formed glycolate complexs with Pb, Zn, and Cu and measured their stability constants. Jachuta et al.[54] utilized the metal complexing ability of glycolic acid to remove Cd(II) and Pb(II) from solution with several ion exchange resins via the formation of Cd(II) and Pb(II) complexes.

Ohshima et al.[20] formed Al-glycolate complexes in their study of Al(III)-catalyzed conversion of glyoxal to glycolic acid.

Portanova et al.[55] performed a critical evaluation of the stability constants for different aliphatic 2-hydroxycarboxylic acid complexes in aqueous solutions with metal ions published between 1960 and 1994. The metal ions evaluated was numerous (51 total). It included just about all the elements mentioned above and Pu, Hf, Hg, In, and Am.

The discussion so far has centered on low temperatures between 20 to 25 ^{o}C because glycolate complexation data for high temperatures are scanty at best. Deberdt et al.[56] studied the complexation of La with the acetate ion using both solubility and potentiometric measurements in the temperature and pH range ranges of 25 - 80 ^{o}C and 5-9.5 respectively. The solubility of $La(OH)_3$ in acetate-bearing solutions were significantly higher than their corresponding values in acetate-free solutions. This indicated the presence of La-acetate complexes. The stability of the complexes increased with increasing temperature. Even though this is for acetate, acetate is in the same carboxylic acid family as glycolic acid. Hence, it is most likely glycolates will behave in a similar manner.

Deberdt et al.[57] also investigated the stability of aqueous complexes formed by Gd(III) and Yb(III) aqueous species with the acetate ion at 25 to 80 ^{o}C using potentiometric measurements. Again, the data showed increasing stability of the metal-acetate complexes

with increasing temperature. Wood et al.[58] used potentiometric method to study the Nd-acetate and Nd-chloride complexes in the 25 to 225 ^{o}C temperature range. The stabilities of both complexes increased with temperature. However, the acetate complexes were more stable than the corresponding chloride complexes.

Prapaipong and Shock[59] developed models to predict stability constants for many metal-organic ligand complex systems for the temperature range of 0 to 150 ^{o}C. The metals included all the rare-earth elements, some actinides [Th(IV), Cm(III), Bk(III), Cf(III), UO2(II), Am(III)]; some transition metals [Zn(II), Cu(II),Ag(I), Cd(II), Fe(II), Fe(III), Cr(III), Ni(II), Co(II), Mn(II)]; and others like [Al(III), Sr(II), Pb(II), Mg(III), Ca(II), Ba(II), Na(I), K(I), Li(I)]. The organic ligands included glycolate, acetate, oxalate, malonate, nitrolotriacetate,diglycolate, etc. The model results for La-acetate, Gd-acetate, Nd-acetate, and Yb-acetate complexes agreed quite well with the values measured by Deberdt et al.[56], Deberdt et al.[57], and Wood et al. [58]

The foregoing discussion provides enough substantiation to the complex forming ability of glycolate. This implies there is a good chance most of the metal constituents (see   Table 1 and page 2) in the evaporator feed will complex with the glycolate. The fact that stability constants increase with increasing temperature bode well for the evaporator system. The benefit in all of the above may be a minimization of scale formation in the evaporator. On the flip side, the potential increase in the solubility of Pu, Fe, etc. may affect the critically assumptions for the 2H Evaporator. Note that the downstream impact of the potential increase in the solubility of Pu on the evaporator concentrate (bottoms) product is not part of the scope of this literature review.

2.1.3 Polymerization

Even though the compound will be in the glycolate form (e.g., sodium glycolate) instead of the acidic form, the discussion below uses GA. It assumes that glycolide polymer can be formed using glycolate (e.g., sodium glycolate) as the starting compound instead of the acid counterpart. Note that only one paper provided polymerization information with sodium glycolate as the starting material.[60]

There are several synthesis pathways to polymerize glycolic acid to polyglycolide. The ones that are somewhat close to the 2H Evaporator operating conditions are outlined below.

The first is via a polycondensation reaction of glycolic acid. It involves heating glycolic acid at atmospheric pressure and a temperature of about 175-185 °C until distillation of water ceases. It is followed by reducing the pressure to 150 mm Hg for about two hours while still maintaining the temperature at about 175-185 °C to yield low molecular weight polyglycolide.[61-63]

As mentioned earlier, the 2H Evaporator typically reduces the feed volume to about two-thirds of its original volume and also operates at atmospheric pressure.[8,9] Hence, this reaction is most likely not to occur.

The second is via ring-opening catalytic polymerization reaction of low molecular weight polyglycolide. It involves reacting a catalyst (initiator) and the low molecular weight polyglycolide at a temperature of 195 ^{o}C for about two hours at reduced pressure (12-15 mm Hg) under a nitrogen environment. It is followed by raising the temperature to 230 ^{o}C for about 30 minutes. Various catalysts are used. They include antimony compounds (antimony trioxide, antimony trihalides), zinc compounds (zinc lactate), and tin compounds (stannous octoate - tin(II) 2-ethylhexanoate, or tin alkoxides), aluminum isopropoxide, calcium, acetylacetonate, and several lanthanide alkoxides (e.g., yttrium isopropoxide).[61-67]

Murugan et al.[68] in 2008 used clay as a catalyst to produce polyglycolides. Again, the 2H Evaporator operation conditions (i.e., temperature of 110-120 ^{o}C, atmospheric pressure, and non-inert atmosphere) do not favor the second polymerization synthesis pathway.

Polyglycolide is unstable or degrades in water (hydrolysis) back to the starting compound (i.e., glycolic acid).[61,66,69-72] Hence, if polymerization were to occur, it will not be sustainable because the content in the 2H Evaporator is an aqueous solution.

2.1.4 Radiation

Large radiation doses in an oxygen-deficient atmosphere may polymerize glycolic acid solutions.[2] This is somewhat in line with polymerizations mentioned above if one considers the fact that the radiation is essentially a heating source. Again, its occurrence is unlikely based on the reasons (evaporation at atmospheric pressure, degradation by water, etc.) mentioned earlier.

2.1.5 Volatilization

No information was found on the Henry's law constant or vapor pressure for metal glycolate solutions (e.g., sodium glycolate). Henry's law constant for GA at essentially ambient temperature was found from a few sources: Ip et al.[73] - 4.46x10^{-5} atm-L/mole (35 ^{o}C), DuPont document[22] - 8.5x10^{-5} atm-L/mole (no temperature was given but from the text ambient temperature may be a good guess).

Vapor pressure for GA solutions at essentially room temperature was found from a few sources. Table 2 provides the values found. The first two are vapor pressure of the GA component while the remaining seems to be the vapor pressure of the entire solution.

Note that all the above Henry's law constants and vapor pressures are very low. Even though data at high temperatures suitable for the evaporator operating conditions were not found, the anticipation is that the Henry's law constants and vapor pressures at high temperatures (110-120 ^{o}C) will also be relatively low. This is based on the high solubility of GA and sodium glycolate, their non-volatility characteristics, and more importantly the fact that GA cannot be distilled even under high vacuum.[20,21,28,31-37]

Also, based on Barney's (Hanford site) solubility studies, solubility increases with temperature at least to 50 ^{o}C for non-saturated sodium nitrate system.[25,26] Hence, the amount of glycolate that will be in the evaporator overhead and go to the ETF will be small especially when the evaporator's demister is taken into consideration. This will be revisited

in Section 2.2 in terms of estimating a value for the fraction of glycolate that goes to the overhead.

Table 2. Vapor Pressure of GA Solutions.

Manufacturer	Glycolic Acid (GA) Concentration	Vapor Pressure - Temperature
DuPont[74]	70 wt%, high purity	4.05×10^{-6} atm (3.08×10^{-3} mm Hg) - 25 °C
DuPont[75]	70wt%, technical solution	1.68×10^{-5} atm (1.28×10^{-2} mm Hg) - 25 °C
Merck[76]	70 wt% ,special quality	2.71×10^{-2} atm (2.067×10^{1} mm Hg) - 25 °C
Spectrum Laboratory Products, Inc.[77]	70 wt%	2.27×10^{-2} atm (1.73×10^{1} mm Hg) - 20°C
SolvChem, Inc.[78]	70 wt%	1.45×10^{-2} atm (1.10×10^{1} mm Hg) - 20 °C
Pharmco Laboratories, Inc.[79]	70 wt%	vapor pressure = vapor is water
CETCO – Drilling Products Group[80]	70 wt%	vapor pressure = vapor is water
Sciencelab.com, Inc.[81]	70 wt%	2.27×10^{-2} atm (1.73×10^{1} mm Hg) - 20°C

Lambert et al.[1] performed Chemical Process Cell (CPC) simulation testing using glycolic acid as the alternate reductant. The CPC is part of the DWPF process flowsheet that culminates in the production of glass. The CPC is essentially an evaporation operation. However, its operating conditions are not equivalent to that of the 2H Evaporator. Table 3 lists the major characteristics of the two operations.

The CPC test results indicated glycolate gets into the CPC overhead (condensate) despite its low volatility characteristic and the claim that it cannot be vacuum distilled. The concentration of glycolate in the CPC condensate ranged from 60 to 180 mg/L. Because the two operations are different, the CPC condensate data cannot necessarily be used to infer one way or the other as to whether glycolate will be in the 2H Evaporator overhead let alone the amount.

Table 3. Key Features of the CPC and the 2H Evaporator Operations.

	CPC	**2H Evaporator**
Temperature	100 - 102 $^{\circ}$C	110 - 120 $^{\circ}$C
Pressure	1 atmosphere	~1 atmosphere
Feed Chemistry/Composition	pH is acidic, etc.	pH is alkaline, etc.
Boiling Comparison*	The boiling point of water at 1 atm is 100 $^{\circ}$C. Implies the CPC is 2 $^{\circ}$C above its boiling point.	The boiling point of water at 1 atm is 100 $^{\circ}$C. Implies the 2H Evaporator is 10 - 20 $^{\circ}$C above its boiling point.
	Boiling may be a little more intense in the 2H Evaporator than the CPC.	

*The feed material/solutions will have boiling point elevations because they are not pure water. Water, whose boing point is known, is used to heighten the difference.

2.1.6 Reaction of Glycolate with Evaporator Feed Constituents

Two compounds that may be of concern are tributylphosphate (TBP) and normal paraffin hydrocarbons (NPH).

May et al.[41] studied solvent extraction of Np(IV) using 30% tributylphosphate in odorless kerosene as the organic phase and various organic ligands in 0.7 M HNO_3 as the aqueous phase. One of the ligands was glycolic acid. No adverse reaction was reported regarding the interaction of glycolate with TBP or kerosene (an NPH). The temperature of the tests was not given but it looks like they were conducted at ambient conditions. Even though the interaction occurred at ambient conditions, no unusual reaction is expected to occur at the evaporation operating temperatures (110-120 $^{\circ}$C).

Datta and Kumar's[82] study dealt with the extraction of GA from aqueous solution with two different extractants [tri-n-butyl phosphate (TBP) and tri-n-octylamine (TOA)] dissolved in a wide range of diluents [n-hexane, decane-1-ol, n-hexane + decane-1-ol (1:1 v/v), 4-methylpentan-2-one (MIBK), benzene, and dichloromethane (DCM)] at 25 $^{\circ}$C. Note that hexane and decane-1-ol are not strictly NPH, they are in the non-polar solvent family. Again, no unusual reactions were reported and no unusual reaction is anticipated at high temperatures.

Pagel and Schwab[83] similarly extracted glycolic acid using TBP in the temperature range of 20 to 35 $^{\circ}$C.

2.1.7 Thermal Decomposition of Glycolate

No direct information was found. Stock and Pederson[84] mentioned it is quite possible glycolate may degrade thermally to other compounds like formate and oxalate.

Also, glycolate can be decomposed by persulfate, hypochlorite and hydrogen peroxide in alkaline solutions with heating.[85] The amount of oxidant needed increases when $NaNO_2$ is

present in solution. Decomposition of glycolate by persulfate was slow at room temperature but fairly fast at 90 ^{o}C. The products of the reaction were not given but the authors mentioned complete oxidation to CO_2 and H_2O may not have occurred.

Persulfates, under various conditions, are known to react with reductants either directly or after decomposition to sulfate radicals.[85,86] The sulfate radicals oxidize water and hydroxide to OH radicals in alkaline solution. There are no persulfates in the evaporator feed. It is unknown or unclear whether sulfate radicals could be produced. It seems the products from the reaction if any will be lower molecular weight organics or CO_2 and water.

Ozone is planned to be used in the tank farm in the Enhanced Chemical Cleaning process. Reaction between ozone and glycolate is expected to be similar to that of persulfate, hypochlorite and hydrogen peroxide.

Ashby et al.[87] studied thermal degradation mechanisms of organics in Hanford waste simulants. The tests used the range of simulant compositions and operating conditions shown below.

Glycolate: 0.1 - 0.21 M
Aluminate: 1 - 1.54 M
Nitrite: 1.12 - 2.24 M
Carbonate: 0.24 M.
Nitrate: 2.59 M
Hydroxide: 2 M

Temperature: 60 - 120 ^{o}C
Pressure: atmospheric
Headspace above the solution: air or argon

Formate and oxalate are formed from the glycolate decomposition reaction. The gases produced included hydrogen, nitrogen, nitrous oxide and methane. The reaction was approximately first order with respect to glycolate concentration. The rate of the reaction increased with increasing temperature.

Table 4 is summary of the results in terms of the percent of glycolate that was consumed in the decomposition reaction at various times for all the test runs at 120 ^{o}C. Note that with the exception of the 1.25-hour values, all the data are based on experimentally measured values. See footnote of the Table.

Reactions under argon or inert atmosphere are faster than those under air atmosphere. The 2H Evaporator operates at atmospheric pressure (air headspace) and at a temperature of 110-120 ^{o}C with a residence time of 1.25 hours. The percent of glycolate consumed or reacted in 1.25 hours is low for both air and argon headspaces. The amount of glycolate at the start of the reaction remains virtually unchanged at 1.25 hours into the reaction. Even though the 120-degree reaction temperature is the same as the 2H Evaporator temperature, glycolate

decomposition requires significantly more time to achieve substantial conversion of the glycolate to formate and oxalate.

Table 4. Percent Glycolate Consumed at Various Reaction Times at 120 ^{o}C.

Air Headspace	
Time, hours	**Percent Reacted**
1.25	0.05 – 0.09*
100	5 - 8
200	7 - 14
300	11 - 20
Argon Headspace	
Time, hours	**Percent Reacted**
1.25	0.8 – 1.4*
25	1.2 - 18
100	32 - 61
200	63 - 88

* Values were calculated using the first-order rate constants at 120 ^{o}C provided by the authors.

2.2 EFFLUENT TREATMENT FACILITY

The Effluent Treatment Facility (ETF) treats wastewater from the F and H Tank farms. The wastes are primarily from four sources - evaporator overheads, potentially contaminated surface water, contaminated cooling water, and miscellaneous very low level waste (LLW) streams. The bulk of the treated wastewater is discharged to a site outfall (Upper Three Runs Creek). The concentrated stream (i.e., reject stream) from the ETF's evaporator goes to the Saltstone Production Facility (SPF).[88,89]

The ETF comprises the following major unit operations: Chlorination, pH adjustment, filtration, 1st mercury removal, organic removal, reverse osmosis (RO), 2nd mercury removal, ion exchange, ion exchange resin regeneration, and evaporation.[89-93]

Figure 1 is a simplified schematic of the ETF process. Detailed flowsheets are provided in references #91 to 93. Table 5 and Table 6 provide evaporator overhead composition data for the 2F, 2H, and 3H Evaporators.[94-97] They give the low and high values for a set of analyses between 2007 and 2010. These overhead streams serve as feed to the ETF. Table 7 is the radioactive counterpart of Table 5 and Table 6. The list of constituents or components is consistent with the F/H treatment project Waste Acceptance Criteria (WAC).[98]
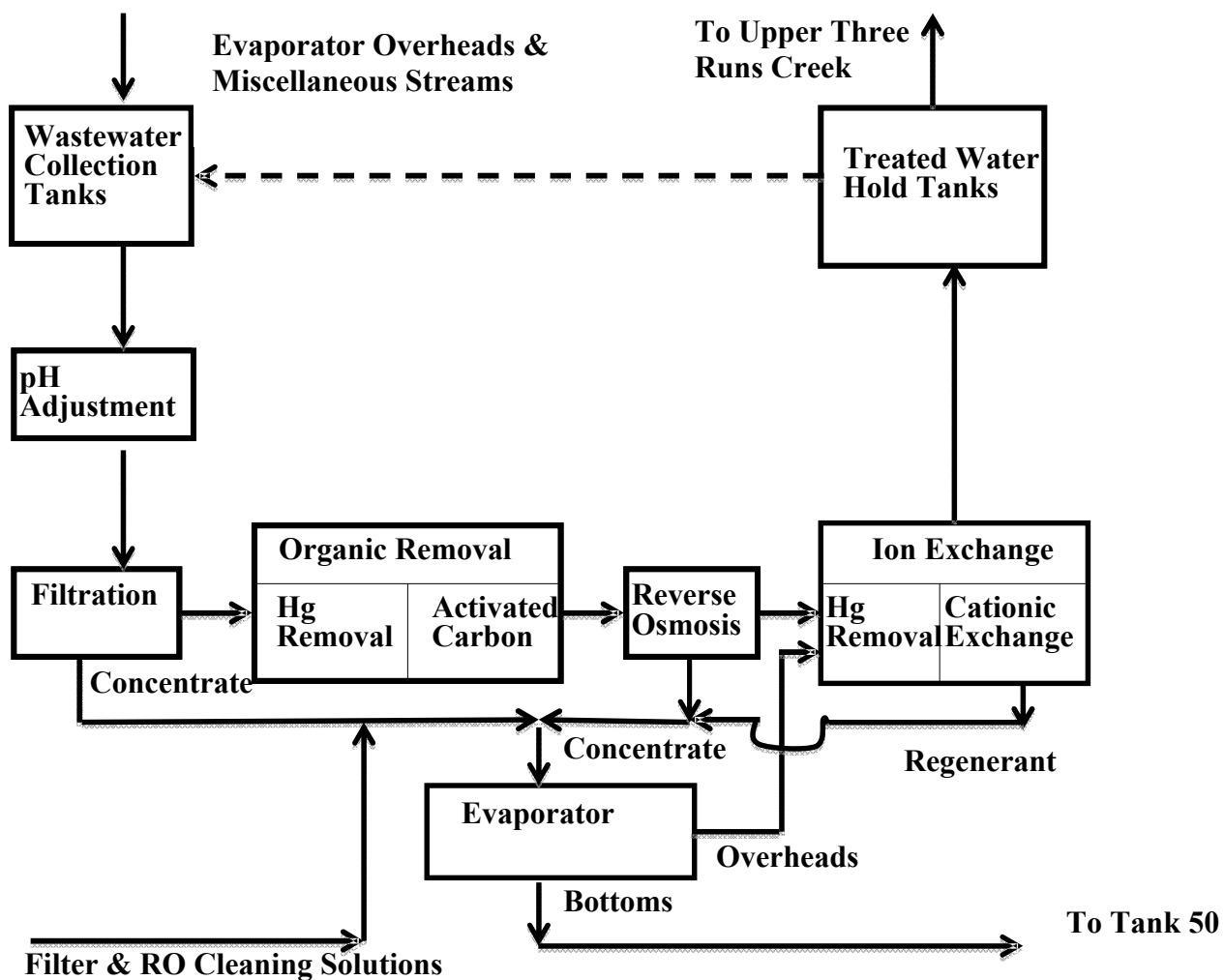
Figure 1. Schematic ETF process flowsheet.

Table 5. Composition of Anions and Metals in 2F, 2H & 3H Evaporator Overheads.

Species	2F, 2H & 3H Evaporator Overheads	
	Low, mg/L	High, mg/L
Ammonia (NH_4^+)	< 5.00E+00	2.30E+01
Nitrate (NO_3^-)	< 1.00E+00	1.20E+01
Nitrite (NO_2^-)	< 1.00E+00	9.00E+00
Sulfate (SO_4^{2-})	< 1.00E+00	3.40E+01
Carbonate (CO_3^{2-})	< 6.25E+00	8.50E+01
Fluoride (F^-)	< 1.00E+00	< 5.00E+00
Oxalate ($C_2O_4^{2-}$)	< 1.00E+00	2.00E+00
Chloride (Cl^-)	< 1.00E+00	1.80E+01
Phosphate (PO_4^{3-})	< 2.50E+00	< 5.00E+00
Silver (Ag)	< 1.34E-02	< 2.91E-01
Aluminum (Al)	< 4.72E-02	< 1.02E+00
Arsenic (As)	< 2.75E-02	< 2.75E-02
Boron (B)	< 2.91E-02	< 2.51E-01
Barium (Ba)	< 8.48E-03	< 1.03E-01
Beryllium (Be)	< 1.53E-03	< 4.E-02
Calcium (Ca)	< 1.73E-02	1.04E+00
Cadmium (Cd)	< 6.76E-03	< 3.80E-02
Chromium (Cr)	< 1.11E-02	< 1.03E-01
Copper (Cu)	< 4.99E-03	< 1.65E-01
Iron (Fe)	< 1.72E-02	3.36E-01
Mercury (Hg)	1.00E-02	3.72E+00
Potassium (K)	< 1.50E-01	5.91E-01
Magnesium (Mg)	< 2.15E-03	9.26E-02
Manganese (Mn)	< 3.13E-03	< 2.21E-02
Sodium (Na)	< 3.30E-01	2.73E+00
Nickel (Ni)	< 1.78E-02	< 2.81E-01
Lead (Pb)	< 5.97E-02	< 1.04E-01
Antimony (Sb)	< 1.25E-01	< 1.58E+00
Selenium (Se)	< 5.50E-02	< 5.50E-02
Silicon (Si)	< 2.91E-02	1.92E+01
Zinc (Zn)	< 1.04E-02	< 1.03E+00

Table 6. Composition of Organics in 2F, 2H & 3H Evaporator Overheads.

Species	2F, 2H & 3H Evaporator Overheads	
	Low, mg/L	High, mg/L
EDTA	< 5.0E+00	< 5.0E+00
Phenol	< 1.00E-01	1.00E-01
Benzene	< 5.00E-03	< 2.50E-01
PCBs	< 2.00E-02	1.0E-01
Tetraphenylborate (TPB)	< 1.00E+00	< 5.00E+00
Tetrachloroethylene (TCE)/Perchloroethylene (PCE)	< 5.00E-03	< 2.50E-01
Trichloroethylene (TCE)	< 5.00E-03	< 2.50E-01
Tributyl Phosphate (TBP)	< 1.00E-01	< 1.00E-01
Isopropanol	< 5.00E-02	< 1.00E-01
n-Butanol	5.3E-03	5.60E-02
Toluene	< 5.0E-03	< 1.70E+00
Other Volatile Organics	< 5.0E-03	5.0E-03
Dimethylmercury	8.9E-01	8.9E-01
Total Organic Carbon (TOC)	< 1.25E+00	2.50E+01
Total Suspended Solids (TSS)	< 0.01 wt %	0.02 wt %
pH (no units)	3.83	9.67
Specific gravity (no units)	0.99	0.99

Table 7. Composition of Radioactive Constituents in 2F, 2H & 3H Evaporator Overheads.

Species	2F, 2H & 3H Evaporator Overheads	
	Low, dpm/mL	High, dpm/mL
H-3	6.33E+02	1.31E+05
Cs-134	< 3.59E-01	< 4.62E-01
Cs-137	3.51E+01	6.20E+02
Alpha	< 9.90E-01	7.29E+00
Beta/Gamma	< 2.35E+01	5.89E+02
C-14	< 5.71E+00	< 9.66E+00
Ni-59	< 1.19E+02	< 2.11 E+02
Ni-63	< 2.21E+00	< 2.29E+01
Co-60	< 1.06E-01	< 8.27E+00
Sr-90/Y-90	< 1.20E+01	8.51E+01
Tc-99	< 4.16E+00	< 1.20E+02
Ru-106/Rh-106	< 1.20E+00	< 9.66E+01
Sn-126	< 2.77E-01	< 2.84E+01
Sb-125	< 5.67E-01	< 2.08E+01
I-129	< 1.42E-01	< 7.21E-01
Eu-154	< 1.85E-01	< 9.31E+00
U-233	< 2.00E-01	< 4.84E+00
U-235	< 4.80E-06	< 2.53E-01
Np-237	< 1.10E-03	< 5.24E-02
Pu-241	< 8.32E+00	< 2.87E+01

Table 8 shows the maximum overhead/feed ratio for nitrate and nitrite for the 2H Evaporator. They are based on the same data used to compile Table 1, Table 5, Table 6, and Table 7. The maximum ratios were calculated by dividing the 2H Evaporator overhead high value by the respective 2H Evaporator feed low value. The ratio is an indication of the fraction of the evaporator feed that goes into the overhead stream. The ratio is essentially the reciprocal of the decontamination factor (DF).

Table 8. Maximum Overhead/Feed Ratio for Selected 2H Evaporator Components

Component	2H Evaporator Feed		2H Evaporator Overhead		Maximum Overhead/Feed Ratio	Solubility* at 20 ^{o}C
	Low, mg/L	High, mg/L	Low, mg/L	High, mg/L		g/g H$_2$O (wt%)
Nitrate (NO$_3$⁻)	3.66E+04	7.43E+04	< 2.50E+00	1.20E+01	3.28E-04	87.6 (46.7)
Nitrite (NO$_2$⁻)	4.55E+04	9.02E+04	< 2.50E+00	9.00E+00	1.98E-04	80.8 (44.7)

* Sodium salt of the anion.

The solubility of the sodium salt of the anions is also given in the last column. As mentioned earlier, the solubility of sodium glycolate at 20 ^{o}C is 69.1 g/g H$_2$0 (or 40.9 wt%). Since sodium glycolate, sodium nitrate and sodium nitrite are all highly soluble compounds, these ratios can be used to estimate the amount of sodium glycolate that will be in the overhead.

Using a glycolate feed evaporator concentration of 10,000 mg/L and the two ratios gives concentration of glycolate in the overhead to be 3.27 and 1.98 mg/L for the nitrate and nitrite respectively. Multiplying the above by 10 conservatively makes the overhead glycolate concentration 33 mg/L or 0.44 mM and 20 mg/L or 0.27 mM respectively.

Note that this is a crude estimate based solely on solubility analogy. A better estimate can only be obtained with vapor pressure and/or Henry's law constant data at the evaporator operating temperatures. For the discussions below the glycolate concentration in the ETF feed will be assumed to be 33 mg/L or 0.44 mM.

Now the unit operations listed above will be discussed in terms of the findings in the literature regarding the impact of glycolate. With a few exceptions (e.g., evaporator and RO), the operating conditions of the ETF unit operations are generally ambient temperature and a pH of 6-8. Hence, unless stated otherwise, assume the temperature and pH of all the unit operations below are as stated above. Again, based on the information provided in Section 2.1, the GA will be in glycolate form. Most of the information on the discussions below is from reference #89.

2.2.1 Chlorination

Sodium hypochlorite (NaOCl) is used on an as-needed basis to prevent fouling from biological growth. Hypochlorite reacts with aqueous ammonia in the waste to form chloramines (NH_2Cl). The residual concentration of hypochlorite following the reaction is given as 1 mg/L (0.02 mM).

Based on the information provided in Subsection 2.1.7, hypochlorite can decompose glycolate. The reaction is expected to be slow at ambient temperatures. The products of the reaction were not given but it is quite possible chlorine gas may be formed. It does not look like there will be any impact because it is essentially not different from the hypochlorite-bisulfite reaction that currently takes place in the system. Depending on the levels of the residual hypochlorite, bisulfite is added on an as-needed basis to eliminate the residual hypochlorite downstream after the filtration step. Bisulfite and glycolate are both reductants.

In addition to the hypochlorite-glycolate reaction, glycolate may react with chloramine to produce chlorine and ammonia. Reducing agents like sodium metabisulfite are used to remove chloramine from solution.[97] What is unknown is the rate of the two reactions i.e., the hypochlorite-glycolate reaction and the chloramine-glycolate reaction. They may, however, lead to a depletion of the hypochlorite needed for the biocidal reaction. Use of historical process operations data and modeling software like OLI Environmental Simulation Package Software (OLI/ESP), and testing as a last recourse may be needed to resolve this. The consumption of hypochlorite and the chloramine by glycolate may be beneficial in that it may eliminate the downstream bisulfite (HSO_3^-) addition. The key parameter in all the above is the concentration of glycolate in the waste stream.

2.2.2 pH Adjustment

The pH of the waste stream is adjusted to 6-8 with either 2 wt% NaOH or 2 wt% HNO_3 to form precipitates of sparingly soluble compounds like Fe, Al, Si, U, Cm, Pu, Am, etc. to allow them to be removed in the next step. In other words, it reduces the solubility of the compounds of the metals. As mentioned in the Evaporator Section (Section 2.1), glycolate tends to form soluble complexes with multivalent metals. Hence, the solubility levels may be impacted. The extent of the impact is unknown. Appropriate modeling software e.g., OLI/ESP may be needed to predict the solubilities of the compounds anticipated to form. If modeling is not successful then testing will be needed.

2.2.3 Filtration

Norton ceramic cross-flow filters are used. No glycolate impact is anticipated.

2.2.4 1st Mercury Removal

Rohm and Haas Duolite GT-73 ion exchange resin is used. Mercury removal is necessary to prevent its adsorption onto the downstream activated carbon adsorption step. Otherwise the activated carbon would be a mixed waste. The Duolite GT-73 ion exchange resin is a polystyrene/divinylbenzene weak acid cation exchange resin with thiol functional groups with high selectivity for mercury. No direct information was found on the effect of glycolate on mercury sorption by the Duolite GT-73 ion exchange resin.

One paper that is a little close is the work by Jachuta et al.[56] They investigated how GA influence the removal of heavy-metal ions [Cd(II) anf Pb(II)] from waters and wastewaters by ion exchange resins via its complexing ability. The ion exchangers studied included chelating resins: Purolite S-930, Purolite S-940, Purolite S-950, Diaion CR-20, and Wofatit MC-50; and the cationic resins: Purolite C-104, Lewatit CNP-80, and Lewatit SP-112. They claimed using Fourier Transform Infra-Red Spectroscopy (FTIR) that GA generally enhance the sorption of Cd and Pb onto the resins through complexation.

Another related study is the work of Hassan et al.[100] performed at SRNL. They used a proprietary polymeric organic cation exchange resin (SuperLig 644) to remove cesium from several Hanford site waste tank radioactive supernate solutions (AN-103, AZ-102, and AN-102) and AN-105 supernate simulant solution. All the above solutions contained relatively large amounts of organic complexants. The TOC ranged from 0.0266 to 1.88 M. The AN-105 simulant solution had a TOC concentration of 0.066 M (or 66 mM) which comprised the following organic compounds: sodium formate (0.02 M), sodium oxalate (0.003 M), and glycolate (0.01 M or 10 mM).

The breakdown of the organic constituents in the radioactive wastes was not given but the authors mentioned they included organic complexants, like formate, glycolate, acetate, gluconate, oxalate, citrate, ethylenediaminetetraacetate, and iminodiacetate.

The AN-102 waste solution with the highest TOC concentration had relatively low cesium sorption distribution coefficients even though the compositions of the three radioactive wastes had wide variations of other constituents. They reported the complexants were not expected to affect the sorption of cesium but it was quite possible they may have fouled the resin and subsequently limited access to the active sites.

Note that the concentrations of the organics are high in comparison with the estimated glycolate concentration in the ETF stream. It is hard to infer from the two papers how glycolate fouling will affect the sorption of Hg onto Duolite GT-73 ion exchange resin. However, it seems if the glycolate concentration is low (i.e., on the order of ≤ 0.44 mM), then probably the fouling effect will be minimal at best because it is likely some of the initial glycolate will be consumed in the prior steps (e.g., chlorination).

Again, knowing the concentration of the glycolate or having a high confidence in an estimated value is the key. This makes determining the amount of glycolate in the evaporator overheads (by OLI/ESP or testing) more critical. To summarize, monitoring/compiling data during process operations may suffice if the concentration of the glycolate is low (≤ 0.44 mM). On the other hand, testing is needed if the glycolate concentration is high (> 0.44 mM).

2.2.5 Organics Removal

Activated carbon is used to remove TBP, NPH and other non-ionized organics to help reduce RO fouling downstream.

Hypochlorite is decomposed to chlorine upon contacting the activated carbon. Similarly, chloramine is decomposed to chloride and either NH_3/NH_4^+ or N_2 upon contacting the

activated carbon. Again, it is possible glycolate will consume both the hypochlorite and chloramine prior to this step.

Glycolate in the pH range of 6-8 is generally not expected to be adsorbed onto activated carbon. However, Soni et al.[101] used bagasse fly ash to successfully remove GA from solution. The GA concentration ranged from 0.2 to 1.2 mol/L. This indicates the pHs of the solutions were very low. The composition of the fly ash was as follows: moisture (14.39%), volatile matter (9.80%), ash (53.22%), fixed carbon (23.59%). It is unclear if the sorption of the glycolate is due to the carbon in the bagasse. If true, sorption of glycolate may imply competition with the other organics which, in turn, may mean inadequate removal of the other organics or shorter resin replacement time. Testing may be needed to resolve this if the concentration of the glycolate is high. Otherwise, monitoring/compiled process operations data may be adequate.

2.2.6 Reverse Osmosis (RO)

FILMTEC™ High Rejection Seawater RO membrane is used. The membrane type is polyamide thin-film composite. The presence of free chlorine and other oxidizing agents can cause premature membrane failure.

GA or glycolate is a reducing agent and therefore is not expected to have any adverse impact on the membrane material. Todtheide et al.[102] used a polyamide reverse osmosis membrane to concentrate several carboxylic acid solutions including GA. Note that the pH of the solution was reduced from 6-8 to 5.5 with HNO_3 to increase solubility of the metal salts and decrease fouling. It is quite possible the glycolate in the stream may make the pH adjustment unnecessary.

2.2.7 2nd Mercury Removal

Rohm and Haas Duolite GT-73 ion exchange resin is used. The feed to the 2nd mercury removal system is a combination of the RO permeate and the ETF evaporator overheads (see Figure 1). The pH of the combined stream is 6-9. Mercury removal is necessary prior to releasing the treated waste to the environment (Upper Three Runs Creek). Note that the deductions made on the 1st mercury removal also hold here.

2.2.8 Ion Exchange

Cs and Sr removal from the effluent from the 2nd mercury removal system is necessary prior to releasing the treated waste to the environment. Mitsubishi Diaion HPK-25 macroporous sulfonic acid resin is used. The pH of the feed to the ion exchange system is 6-9.

The uncertainties made regarding resin fouling in the 1st mercury removal step also apply here. Note that any glycolate leaving the ion exchange unit will go to the outfall. Glycolate is not specified in the WAC.[98] However, GA is biodegradable. DuPont[22,31-37] reports that 89.6% degrades in the environment in 7 days.

2.2.9 Ion Exchange Resin Regeneration

The ion exchange resin in the previous step is regenerated (i.e, cesium and strontium removal from the resin) to allow it to be reused using 2M $NaNO_3$.

The details are as follows.

(i)   Pre-regeneration water wash or rinse. The water wash effluent goes to the waste water collection tanks.
(ii)   Regeneration with recycled (used) $NaNO_3$. The cesium- and strontium-laden regenerant solution is sent to the evaporation step.
(iii)   Continuation of the regeneration with an equal volume of fresh $NaNO_3$. The regenerant solution (with any residual cesium and strontium) is sent to the recycled (used) $NaNO_3$ tank.
(iv)   Post-regeneration water rinse. The water rinse effluent goes to the evaporation step.
(v)   Continuation of the post-regeneration water rinse at 2.5X flow rate. The water rinse effluent goes to the waste water collection tanks.

No impact is expected.

2.2.10 Evaporation

The evaporator concentrates the combined streams listed below from total TDS concentration of 16,000 mg/L (~1.5 wt%) to 360,000 mg/L (30 wt%). This is about 22.5X concentration or a DF of 4,600.

(i)   RO concentrate
(ii)   Filtration concentrate
(iii)   Part of the regeneration effluent
(iv)   Part of the post-regeneration water rinse effluent
(v)   Filter cleaning solution
(vi)   RO cleaning solution
(vii)   pH adjustment solution

The pH of the combined evaporator feed stream is 5-6. The operating temperature is 138 ^{o}C. The overheads from the evaporator go to the 2nd mercury removal system while the bottoms go to Tank 50 and eventually to the SPF. The earlier discussion on the 2H Evaporator (Section 2.1) also pertains here except the concentration of the glycolate in the ETF evaporator feed will be relatively lower.

3.0 CONCLUSIONS

3.1 2H EVAPORATOR

Even though direct information was virtually non-existent on evaporation of glycolate solution at 110-120 ^{o}C, it seems glycolate-containing feed solution poses no adverse impact to the 2H Evaporator system in terms of self-propagating violent reactions with nitrate/nitrites, reaction with other constituents in the feed solution, polymerization, thermal decomposition and radiation.

If anything at all, the complexing ability of glycolate should be beneficial in minimizing or preventing scale formation in the evaporator. The downside to the solubilizing power of glycolate may be its effect on the criticality analysis of the 2H Evaporator system.

The sticking point or unknown is the amount of glycolate that will be in the evaporator overhead (i.e., the condensed stream that serves as feed to the ETF). Again, despite lack of suitable data (e.g., Henry's law constant at high temperatures), a crude estimate based on solubility analogy with other soluble compounds ($NaNO_3$ and $NaNO_2$) in the feed indicates the fraction of glycolate in the overhead will be relatively small (concentration of 33 mg/L or 0.44 mM). Note that the amount of glycolate in the overhead has no bearing on the potential impacts being addressed here but rather on the downstream process i.e., the ETF process. High confidence in the value of the concentration of glycolate in the overhead stream is key to assessing the potential impacts on the ETF system.

3.2 EFFLUENT TREATMENT FACILITY

The review indicates determination of the potential impacts on the ETF system's unit operations depends on the concentration of glycolate in the ETF feed stream. The lack of directly relevant data on the glycolate concentration in the feed stream led to a crude estimate of the glycolate concentration.

The limited direct literature information on the ETF process suggests (based on an estimated maximum feed glycolate concentration of 33 mg/L or 0.44 mM) that there may be minor potential effects on the following ETF unit operations – Chlorination, pH adjustment, 1st mercury removal, organics removal, 2nd mercury removal, and ion exchange. However, if the glycolate concentration in the ETF feed turns out to be much higher than the above value, then the impacts may be more substantial.

No impact is expected on the following ETF unit operations – filtration, reverse osmosis, ion exchange resin regeneration, and evaporation.

4.0 RECOMMENDATIONS

4.1 2H EVAPORATOR

(i)   Use appropriate modeling software like OLI/ESP to get a better estimate on the amount of glycolate that transfers to the evaporator overhead.

(ii) Conduct evaporation tests if the confidence in the value obtained in (i) is not high.

(iii) Confirm (at least via theoretical evaluation) that no self-propagating violent reactions with nitrate/nitrites are expected.

(iv) Identify sources of ignition that pertain to glycolate for the 2H Evaporator system and/or update the composite flammability analysis for the 2H Evaporator to include the effects from glycolate additions.

(v)   Evaluate the 2H Evaporator system's criticality analysis. This includes performing tests to investigate whether a glycolate containing evaporator feed will dissolve solid Pu, U, Fe, and aluminosilicate, etc. compounds.

4.2 EFFLUENT TREATMENT FACILITY

(i)   Chlorination: For both low ($\leq$ 33 mg/L or 0.44 mM) and high (> 33 mg/L or 0.44 mM) glycolate concentrations, use historical process operations data and modeling software like OLI/ESP to resolve the uncertainties and testing as a last resort.

(ii) pH Adjustment: For both low and high glycolate concentrations, use appropriate modeling software e.g., OLI/ESP to predict the solubilities of the compounds anticipated to form and testing as a last resort.

(iii) 1st Mercury Removal: For low glycolate concentrations, monitoring/compiling data during process operations may be adequate. Perform testing for high glycolate concentrations.

(iv) Organics Removal: Same as 1st mercury removal.

(v)   2nd Mercury Removal: Same as 1st mercury removal.

(vi) Ion Exchange: Same as 1st mercury removal.

5.0 REFERENCES

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