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Glycolic Acid Physical Properties, Impurities, and Radiation Effects Assessment

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EXECUTIVE SUMMARY

The DWPF is pursuing alternative reductants/flowsheets to increase attainment to meet closure commitment dates. In fiscal year 2009, SRNL evaluated several options and recommended the further assessment of the nitric/formic/glycolic acid flowsheet. SRNL is currently performing testing with this flowsheet to support the DWPF down-select of alternate reductants. As part of the evaluation, SRNL was requested to determine the physical properties of formic and glycolic acid blends.

Blends of formic acid in glycolic acid were prepared and their physical properties tested. Increasing amounts of glycolic acid led to increases in blend density, viscosity and surface tension as compared to the 90 wt% formic acid that is currently used at DWPF. These increases are small, however, and are not expected to present any difficulties in terms of processing.

The effect of sulfur impurities in technical grade glycolic acid was studied for its impact on DWPF glass quality. While the glycolic acid specification allows for more sulfate than the current formic acid specification, the ultimate impact is expected to be on the order of 0.03 wt% sulfur in glass. Note that lower sulfur content glycolic acid could likely be procured at some increased cost if deemed necessary.

A paper study on the effects of radiation on glycolic acid was performed. The analysis indicates that substitution of glycolic acid for formic acid would not increase the radiolytic production rate of H₂ and cause an adverse effect in the SRAT or SME process. It has been cited that glycolic acid solutions that are depleted of O₂ when subjected to large radiation doses produced considerable quantities of a non-diffusive polymeric material. Considering a constant air purge is maintained in the SRAT and the solution is continuously mixed, oxygen depletion seems unlikely, however, if this polymer is formed in the SRAT solution, the rheology of the solution may be affected and pumping of the solution may be hindered.

A series of tests to determine whether the polymer will be formed is currently being outlined. The first phase will be a simple experiment where a simulated SRAT supernatant containing the 80:20 blend of glycolic - formic acid could be irradiated in the Co-60 gamma source at SRNL to a very large dose resembling the dose received by the radioactive SRAT solution after several weeks. The resulting solution could then be heated to simulate refluxing in the SRAT process. Finally a radioactive demonstration of the SRAT process should be performed in the SRNL Shielded Cells to confirm successful execution of the glycolic - formic acid flowsheet.

TABLE OF CONTENTS

LIST OF TABLES	vi
LIST OF FIGURES	vi
1.0 Introduction	1
2.0 Experimental Procedure	1
3.0 Results and Discussion	2
3.1 Physical Property Measurements	2
3.2 Glycolic Acid Impurity Evaluation	3
3.3 Radiation Effects on Glycolic-Formic Acid Blend	4
4.0 Conclusions	6
5.0 References	7

LIST OF TABLES

Table 2-1. Glycolic-Formic Acid Blend Preparation	1
Table 3-1. Physical Properties of Glycolic-Formic Acid Blends	2
Table 3-2. Fractions of Radiolytic H Atoms Reacting with Formate, Nitrate and Nitrite in SB3 SRAT Solution.....	4
Table 3-3. Reactivities of H Atoms in a SRAT Solution with 80:20 Molar Blend of Glycolic:Formic Acids.....	5

LIST OF FIGURES

Figure 3-1. Effect of Formic Acid Concentration on Blend Viscosity.....	2
Figure 3-2. Effect of Formic Acid Concentration on Blend Density	3

LIST OF ABBREVIATIONS

ACTL	Aiken County Technology Laboratory
CPC	Chemical Process Cell
DWPF	Defense Waste Processing Facility
PSAL	Process Science Analytical Laboratory
SRNL	Savannah River National Laboratory
SRAT	Sludge Receipt and Adjustment Tank
SME	Slurry Mix Evaporator

1.0 Introduction

As part of the development of a glycolic-formic acid flowsheet for the Defense Waste Processing Facility (DWPF) Chemical Process Cell (CPC), Savannah River National Laboratory (SRNL) was requested to determine and assess the physical properties of the potential glycolic-formic acid blend to be implemented.¹ Five blends of glycolic and formic acids at varying concentrations were made and tested for density, surface tension and viscosity. Additionally, the impact of glycolic acid impurities on DWPF glass quality was assessed and a paper study on the effects of radiation on glycolic acid was performed. This work was performed under the guidance of a Task Technical and Quality Assurance Plan.²

2.0 Experimental Procedure

Blends of formic acid in glycolic acid at 5, 10, 15, 20 and 25% on a molar basis were prepared for this study. Note that formic acid is supplied as a 90 wt% solution and glycolic acid as a 70 wt% solution. Table 2-1 shows the amounts of each acid required to make each blend. Additional 80:20 blend was prepared for use in later flowsheet studies. Formic acid alone was also tested as a standard for comparison.

Table 2-1. Glycolic-Formic Acid Blend Preparation

Mol% Formic Acid	90 wt. % Formic Acid Required (g)	70 wt.% Glycolic Acid Required (g)
5	6.07	245
10	12.29	235
15	19.10	230
20	105.87	900
25	33.72	215

The densities of the acid blends were measured at 25°C by using an Anton-Parr instrument at the Aiken County Technology Laboratory (ACTL) Process Science Analytical Laboratory (PSAL). The viscosity of the blends were measured at 25°C with a Haake RS600 rheometer using a Newtonian fluid model, that is the measured shear stress is plotted against the applied shear rate resulting in a straight line with a slope that is the apparent viscosity of the material in centipoises (cP). The surface tension of the blends was measured using the capillary rise method where the end of a capillary tube is inserted into the liquid and the height the solution reaches in the capillary is measured. The surface tension of the liquid is calculated by the following equation:

$$\gamma = \frac{h\rho gr}{2},$$

where

γ = the liquid air surface tension

h = the height the liquid is lifted

ρ = the density of the fluid

g = the acceleration due to gravity

r = the radius of the capillary

3.0 Results and Discussion

3.1 Physical Property Measurements

The physical properties of the five prepared acid blends and neat formic acid as a standard were measured as detailed in Section 2.0. These properties as measured are reported in Table 3.1 and Figures 3.1 and 3.2 below. Neat glycolic acid was not measured; however its properties are reported per the vendor specification sheet.

Table 3-1. Physical Properties of Glycolic-Formic Acid Blends

Formic Acid (Mole Percent)	Viscosity (cP)	Density (g/mL)	Surface Tension (dyne/cm)
5%	7.38	1.2581	68.85
10%	6.92	1.2572	58.50
15%	6.91	1.2576	55.90
20%	6.42	1.2567	52.55
25%	6.14	1.2540	55.60
Neat Acids			
90 wt.% Formic Acid	1.5	1.1997	40.30
70 wt. % Glycolic Acid	8.6	1.27	n/a

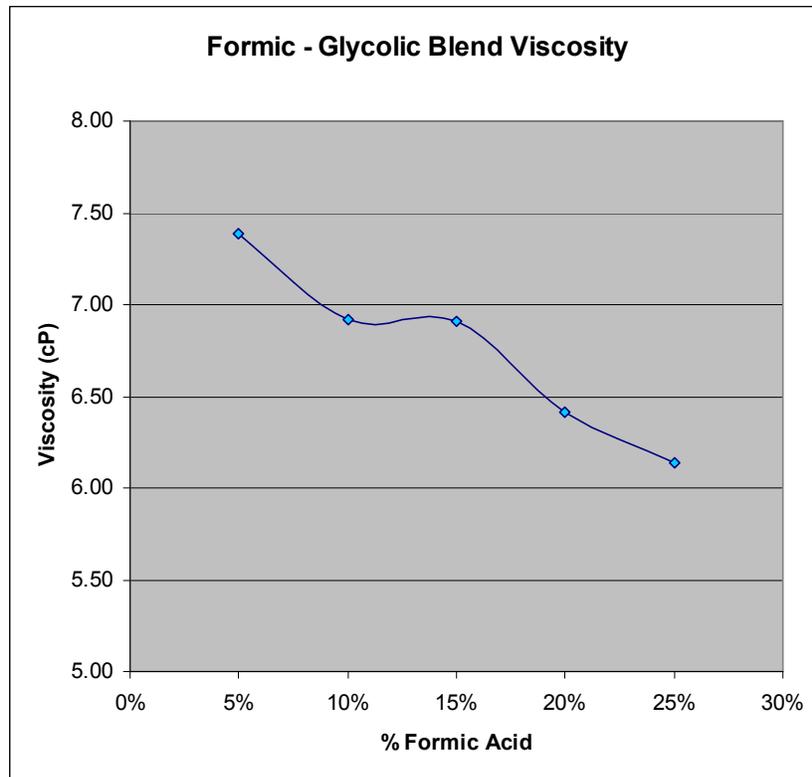


Figure 3-1. Effect of Formic Acid Concentration on Blend Viscosity

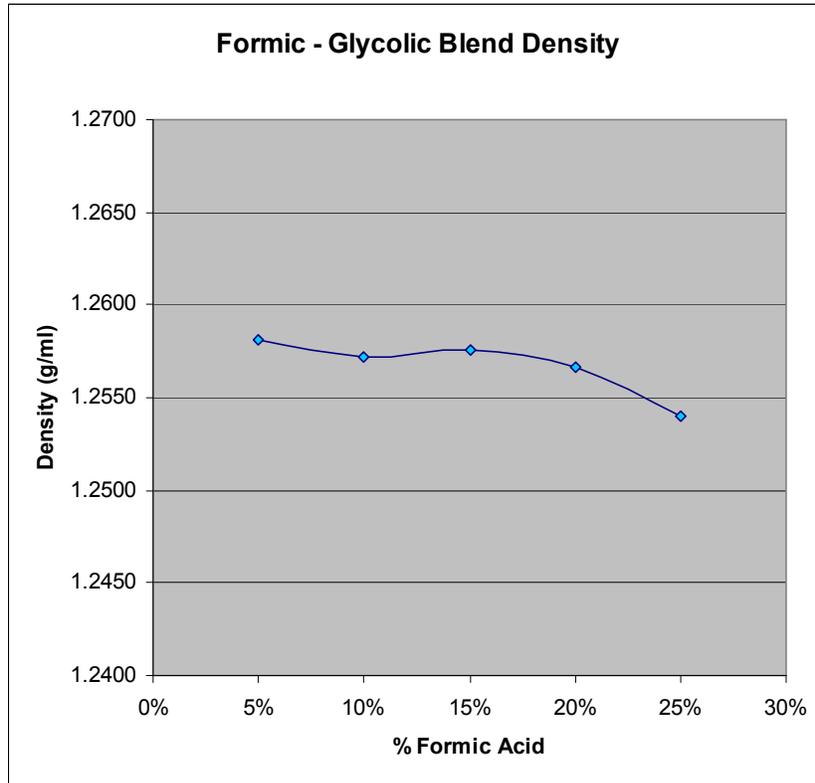


Figure 3-2. Effect of Formic Acid Concentration on Blend Density

As expected, the inclusion of larger amounts of formic acid leads to decreases in viscosity, density and surface tension. The glycolic-formic blends are more viscous than the 90 wt.% formic acid that is currently being used but should not present any difficulties in terms of transport. While a more viscous fluid will decrease pump efficiency, viscosity corrections are generally considered negligible for fluids below 40 cP.

3.2 Glycolic Acid Impurity Evaluation

Technical grade glycolic acid can contain sulfates as impurities. Typical analysis is 300-500 ppm but the specification allows for up to 800 ppm. The maximum allowable sulfate in the currently used formic acid is 100 ppm. An 80:20 molar blend of glycolic and formic acids would therefore contain up to 709 ppm sulfate. The amount of acid added varies based on sludge chemistry and concentration, but a conservatively high acid blend requirement would be about 15 wt% of the starting sludge mass. For a nominal batch of 1000 grams of SRAT receipt material at 20 wt% total solids and 13 wt% calcined solids, this would correspond to 150 grams of glycolic/formic acid blend. This hypothetical SRAT/SME batch would yield about 367 grams of glass. The 150 grams of acid would contribute 0.106 grams of sulfate at the upper limit of 709 ppm. The 0.106 grams of sulfate contained in (divided by) 367 grams of glass equates to 0.03 wt% sulfate in glass contributed by the acid. Note that a lower sulfate content glycolic acid could likely be obtained at some cost if deemed necessary.

3.3 Radiation Effects on Glycolic-Formic Acid Blend

The effect of radiation on the 80:20 molar blend of glycolic-formic acid in the SRAT solution is two-fold. One is the effect of glycolic additions on the radiolytic production of H₂ from the SRAT solution during processing in the DWPF. The other is the effect of organic products from the radiolytic decomposition of the glycolic acid on the SRAT solution.

The radiolytic formation of hydrogen was evaluated by comparison of known rate constants for the radiolytic reactions producing H₂. Hydrogen atoms from the radiolysis of water (the main component in the SRAT solution) are produced and can react with both formic and glycolic acids or their formate and glycolate ions to produce H₂. The hydrogen atoms can also react with nitrate or nitrite ions in the solutions. The reactions with nitrate or nitrite do not produce H₂. Consequently there is a competition that affects the rate of production of H₂. The rate of radiolytic hydrogen production from formic acid and formate ion in the SRAT solution of Sludge Batch 3 (SB3) has been measured and agrees well with predictions made for the SB3 solution based on its radionuclide composition.³ The predictions were based on the known rate constants for the reactions of hydrogen atoms with formate and the nitrate/nitrite ions. This analysis can be extended to a glycolic-formic acid flowsheet.

Rate constants for the reactions of hydrogen atoms with formic and glycolic acids and their corresponding anions have been measured and are published in the radiation chemistry literature.⁴ The rate constant for the reaction with glycolic acid to produce H₂ is about 39 times higher than the reaction with formic acid; however, based on the acid dissociation constants for glycolic and formic acids (1.5E-04 and 1.8E-04 respectively), essentially both acids are completely dissociated into glycolate and formate ions in the SRAT solution. It is therefore the reactivity of the ions with hydrogen atoms that is of more concern.

The rate constant for the reaction of glycolate ions with hydrogen atoms is 4.6E+07 L mol⁻¹ sec⁻¹. This is 4.6 times smaller than the rate constant for the reaction of formate ions (2.1E+08 L mol⁻¹ sec⁻¹). The reactivity of each anion with the hydrogen atoms is the product of its rate constant and its molarity in the SRAT solution. The fractions of hydrogen atoms reacting with each of the four anions can then be calculated from their respective reactivities. This methodology was used in Reference 3 to determine the fraction of radiolytic hydrogen atoms reacting with the formate in the SB3 SRAT solution. In that solution it was calculated that 94% of the radiolytic hydrogen atoms react with formate to produce H₂. The remaining 6% react with nitrate and nitrite and don't produce H₂. Results of the calculations are presented in Table 3-2.

Table 3-2. Fractions of Radiolytic H Atoms Reacting with Formate, Nitrate and Nitrite in SB3 SRAT Solution

Anion	Rate Constant L/ mol·s	Concentration, mole/L	Reactivity, s ⁻¹	Fraction Reacting with each Anion
Formate	2.1E08	0.98	2.1E08	0.94
Nitrate	1.4E06	0.51	7.1E05	0.003
Nitrite	7.1E08	0.08	1.4E07	0.06

The effect on hydrogen atom reactivities of substituting glycolic acid for some of the formic acid in the SB3 SRAT to form an 80:20 molar glycolic to formic blend is shown in Table 3-3.

Table 3-3. Reactivities of H Atoms in a SRAT Solution with 80:20 Molar Blend of Glycolic:Formic Acids

Anion	Rate Constant L/ mol-s	Concentration, mol/L	Reactivity, s ⁻¹	Fraction Reacting with each Anion
Glycolate	4.6E07	0.78	3.6E07	0.39
Formate	2.1E08	0.20	4.2E07	0.46
Nitrate	1.4E06	0.51	7.1E05	0.008
Nitrite	7.1E08	0.08	1.4E07	0.14

In Table 3-3 it can be seen that in this case 85% instead of 94% of the H atoms would react with the organic anions to produce H₂. This would slightly lower the total radiolytic rate of H₂ production. Consequently the analysis indicates that substitution of glycolic acid for formic acid would not increase the radiolytic production rate of H₂ and cause an adverse effect in the SRAT or SME process. Because the reactivity of glycolate is less than that of formate, considering the effect of nitrite destruction during the SRAT still leads to the conclusion that the net effect is a lower total rate of H₂ generation as compared to a formic only flowsheet.

The possible formation of organic compounds from radiolytic decomposition of glycolic acid was also assessed. These compounds are formed primarily by the reactions of hydrogen atoms and hydroxyl radicals (OH) (another reactive intermediate from radiolysis of water) on the glycolate anion. Products from the low dose gamma radiolysis of oxygen saturated aqueous solutions are carbon dioxide (1.9), along with formic (1.6), glyoxylic (2.8) and tartaric (0.04) acids and smaller amounts of oxalic acid and formaldehyde.⁵ The numbers in parentheses are the number of molecules of each product formed per 100 eV of radiation absorbed. The calculation of the 100 eV yields of the number of carbon atoms in the products indicates that the number of glycolic acid molecules decomposed is 4.5 molecules/100 eV. This yield is very close to that measured for the decomposition of water by gamma radiolysis (4.1 molecules/100eV⁶) using oxygenated solutions of formic acid. This agreement suggests that reactions for the decomposition of the glycolic acid to form a polymer are not occurring. If a polymer were produced, the G value for the disappearance of glycolic acid would be greater. However, it has been cited that glycolic acid solutions that are depleted of O₂ then subjected to large radiation doses produced considerable quantities of a non-diffusive polymeric material.^{8,9} This polymer is yellowish white to yellow and soluble in water. The polymer could be converted by heating in a mineral acid to a polymer that was insoluble in water and dilute base. The repeating unit in the polymer was identified as -C₆O₇H₁₀- and had molecular weights greater than 5000 g/mol⁹ The possibility of this occurring in the SRAT solutions has to be considered even though the SRAT solution contains dissolved air. It has been shown that in the radiolysis of water containing organic solutes, oxygen can be depleted at large radiation doses by reactions with the organic radicals with the O₂.¹⁰ In the SRAT, this O₂ can only be replenished by the diffusion of atmospheric air into the solution. Consequently, in the DWPF the radioactive SRAT solutions may become oxygen depleted and the polymer may form at large radiation doses. Considering a constant air purge is maintained in the SRAT and the solution is continuously mixed, oxygen depletion seems unlikely, however, if

this polymer is formed in the SRAT solution, the rheology of the solution may be affected and pumping of the solution may be hindered.

A series of tests to determine whether the polymer will be formed is currently being outlined. The first phase will be a simple experiment where a simulated SRAT supernatant containing the 80:20 blend of glycolic - formic acid could be irradiated in the Co-60 gamma source at SRNL to a very large dose resembling the dose received by the radioactive SRAT solution after several weeks. The resulting solution could then be heated to simulate refluxing in the SRAT process. Finally a radioactive demonstration of the SRAT process should be performed in the SRNL Shielded Cells to confirm successful execution of the glycolic - formic acid flowsheet.

4.0 Conclusions

The physical properties of glycolic acid were studied as they relate to DWPF processing. In summary, there are no immediate concerns from a physical property standpoint in implementing a glycolic acid flowsheet. From this study, the following conclusions can be drawn:

- Adding more glycolic acid will increase the density, viscosity, and surface tension of the glycolic/formic acid blend. This is not expected to present any difficulties in pumping of the material.
- Changing to a glycolic acid flowsheet may increase the sulfate level in glass by up to 0.03 wt%.
- Introducing glycolic acid to high radiation doses may cause some polymerization of the acid in an oxygen depleted atmosphere. The rheology of the SRAT and SME products may thus increase by some amount. The effect is expected to be minor.

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