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# Glycolic Acid Physical Properties and Impurities Assessment

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June 8, 2017

SRNL-STI-2010-00314, Revision 2

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Savannah River National Laboratory™

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# EXECUTIVE SUMMARY

This document has been revised due to recent information that the glycolic acid used in Savannah River National Laboratory (SRNL) experiments contains both formaldehyde and methoxyacetic acid. These impurities were in the glycolic acid used in the testing included in this report and in subsequent testing using DuPont (now called Chemours) supplied Technical Grade 70 wt% glycolic acid. However, these impurities were not reported in earlier revisions. Additional data concerning the properties of glycolic acid have also been added to this report.

The Defense Waste Processing Facility (DWPF) is planning to implement a nitric-glycolic acid flowsheets to increase attainment to meet closure commitment dates during Sludge Batch 9. In fiscal year 2009, 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 0.033 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 $H_2$ and cause an adverse effect in the Slurry Receipt and Adjustment Tank (SRAT) or Slurry Mix Evaporator (SME) process. It has been cited that glycolic acid solutions that are depleted of $O_2$ 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. However, an irradiation test with a simulated SRAT product supernate containing glycolic acid in an oxygen depleted atmosphere found no evidence of polymerization.

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| | |
|---|---|
| ACTL | Aiken County Technology Laboratory |
| AD | Analytical Development |
| CPC | Chemical Process Cell |
| DWPF | Defense Waste Processing Facility |
| FTIR | Fourier Transformed Infrared |
| IC | Ion Chromatography |
| MAA | Methoxyacetic acid |
| PSAL | Process Science Analytical Laboratory |
| SRNL | Savannah River National Laboratory |
| SME | Slurry Mix Evaporator |
| SRAT | Sludge Receipt and Adjustment Tank |
| SRR | Savannah River Remediation, LLC |

## 1.0 Introduction

As part of the development of a nitric-glycolic 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 blends 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 study on the effects of radiation on glycolic acid was performed.

Additional review was requested because additional impurities were identified in the glycolic acid and to document the analysis of glycolic acid by SRNL laboratories. This work was requested by a Task Technical Request[1-2]. The additional review was requested via email as documented in Appendix C. This work was performed under the guidance of a Task Technical and Quality Assurance Plan.[3]

## 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 |

### 2.1 Sample Analysis

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). Water soluble slurry anions were determined by ion chromatography (IC) on weighted water dilutions by both PSAL and SRNL's Analytical Development (AD) Laboratory.

A flow curve for the glycolic acid was obtained using a Haake RS600 rheometer. The up and down curves were fit to a straight line to determine viscosity.

The surface tension of the blends was measured by PSAL 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:

$$\gamma = \frac{h\rho g r}{2},$$

where
$\gamma$ = the liquid air surface tension
$h$ = the height the liquid is lifted
$\rho$ = the density of the fluid
$g$ = the acceleration due to gravity
$r$ = the radius of the capillary

An irradiation test was conducted by adding ~30 mL of a simulated SRAT product supernate containing glycolic acid from Run GF-13 into a stainless steel vessel with two ports on the threaded lid.[4] The vessel was irradiated in the Co-60 gamma source at SRNL under a slow flow of argon gas for 24 hours. The dose rate of the Co-60 source was 2.678E+05 Rads/hr providing a total does to the sample of 6.4 Mrad. After irradiation, the vessel was opened and the sample visually examined. A small amount of rust colored spots were observed on the bottom of the vessel. The rust colored solids were sampled (using a cotton swab) and sent for analysis. A sample of the post irradiation SRAT product supernate was also obtained for analysis. The remainder of the post irradiation SRAT product supernate was transferred to a flask fitted with a water-cooled condenser and heated to boiling for one hour. After boiling, the SRAT product supernate was examined visually for the presence of solids and sampled for analysis. No visible changes were observed in the solution. A sample of the original SRAT product supernate, the irradiated SRAT product supernate, and the irradiated SRAT product supernate after boiling were sent for analysis by IC to determine the glycolate ion concentration.

### 2.2 Quality Assurance

Requirements for performing reviews of technical reports and the extent of review are established in Manual E7 Procedure 2.60[5]. SRNL documents the extent and type of review using the SRNL Technical Report Design Checklist[6].

## 3.0 Results and Discussion

This report has been revised to report the measured impurities in DuPont (now called Chemours) low sulfate Technical Grade Glycolic Acid Lot 03121306. This lot of glycolic acid was used for many of the experiments performed at SRNL. In addition, Chemours has issued a revised Certificate of Composition that reports two additional impurities: formaldehyde and methoxyacetic acid (MAA). This new information is included in an expanded discussion in Section 3.2.

Revision 0 and revision 1 of this report were written when the nitric-glycolic acid flowsheet used an 80% glycolic, 20% formic acid molar blend for the reducing acid. Since it has been shown that added formic acid is not needed for reducing mercury[7], later experiments were all completed with 100% glycolic acid as the reducing acid. The irradiation testing was not repeated as the composition of the SRAT product does not differ appreciably with these changes.

### 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. Neat glycolic acid was not measured; however its properties are reported per the vendor specification sheet. Other glycolic acid data is reported in Appendix B.

**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 |

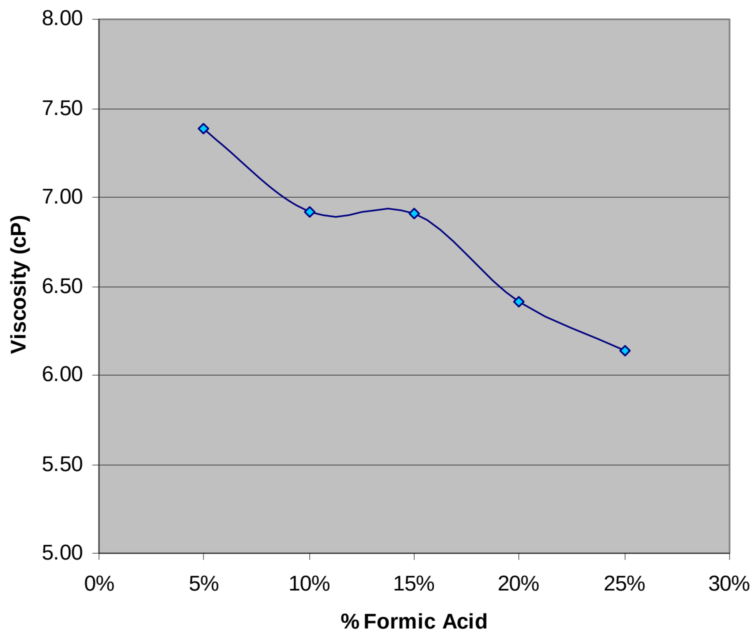


**Figure 3-1. Effect of Formic Acid Concentration on Blend Viscosity**

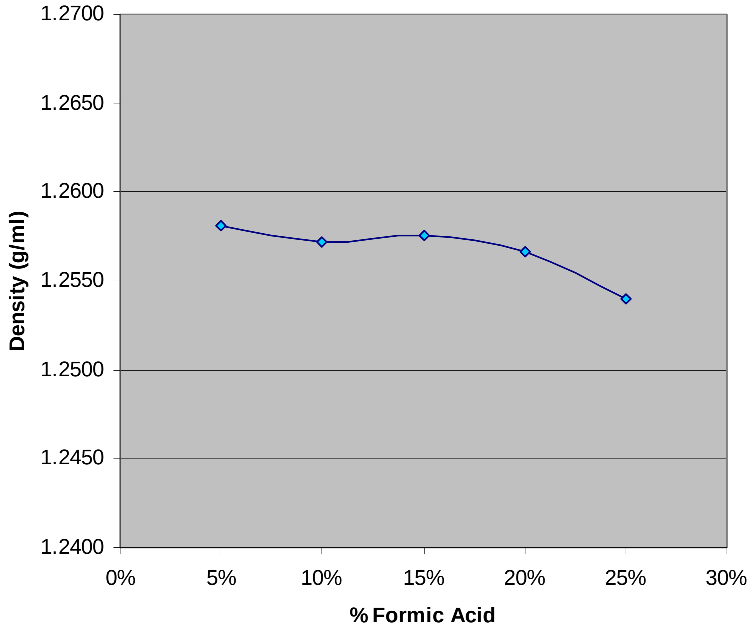


**Figure 3-2. Effect of Formic Acid Concentration on Blend Density**

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.

Communication with DuPont after the issuing of the above report led to the discovery of DuPont data relating density and glycolic acid concentration at 50ºC. This data was developed by titrating the acids, measuring the density and relating acid concentration to molarity. The data was used to calculate the concentration of the pure glycolic acid wt % and the resulting concentration of the glycolic/formic acid. Based on this data, the as purchased glycolic acid concentration was 71.1 wt% versus the 70 wt % assumed throughout the first 20 tests[3]. The data is summarized in Table 3-2. Additional data reported by DuPont in summarizing the properties are attached in Appendix A.

**Table 3-2. Glycolic Acid Determination Using Density Measurement**

| Density, g/ml @50 ºC | Wt% Glycolic |
|---|---|
| 1.196373 | 60.7346 |
| 1.222427 | 67.3276 |
| 1.229959 | 69.0459 |
| 1.238992 | 71.2213 |
| 1.253999 | 75.3670 |
| 1.274718 | 80.2045 |
| 1.288263 | 83.4646 |

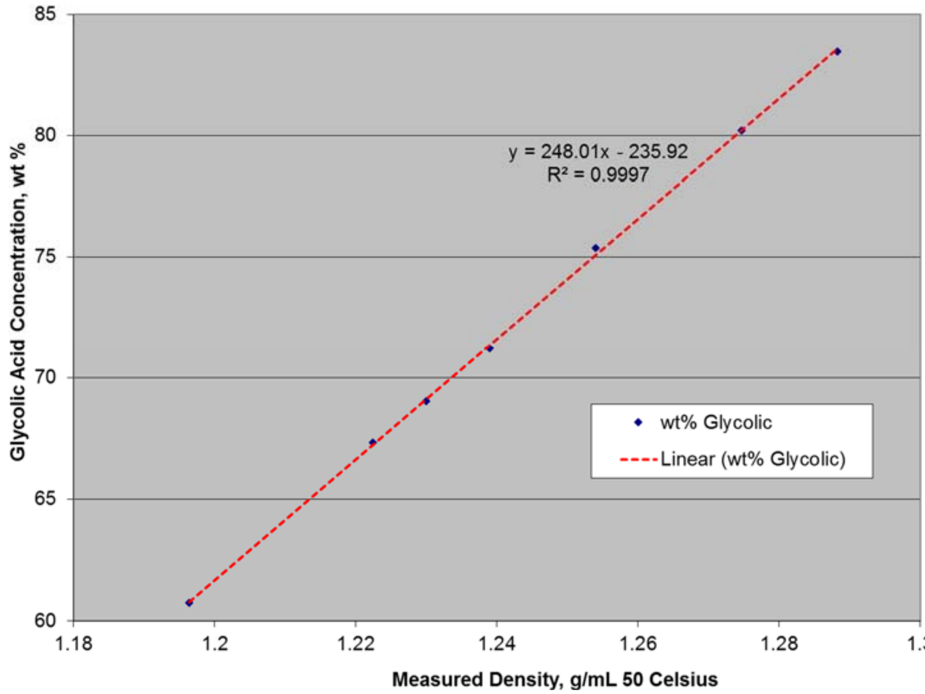


**Figure 3-3 Graph of wt % Glycolic Acid versus Density, g/mL @ 25 ˚C**

3.2 Glycolic Acid Impurity Evaluation

A shipment of 70 wt% Technical Grade glycolic acid was received from Chemours in March 2013 (Lot 03121306). This lot was produced with low concentrations of sulfate impurity. This glycolic acid has been used in all SRNL experiments since receipt, including 32 experiments with simulants and the Sludge Batch (SB) 9 actual waste demonstration in the shielded cells (SC-18). Documentation shipped with the glycolic acid stated the "impurities of the glycolic acid shall not exceed the limits" defined in Table 3-3 below: Note there was no mention of formaldehyde or MAA.

**Table 3-3. Reported Impurities in 70 wt% Low Sulfate Technical Grade Glycolic Acid Solution (Received March 2013)**

| Impurity | Limit (mg/kg max) |
|---|---|
| Aluminum | 10 |
| Calcium | 20 |
| Iron | 5 |
| Potassium | 20 |
| Magnesium | 20 |
| Sodium | 40 |
| Chloride | 100 |
| Sulfate | 100 |
| Nitrite | 100 |

Results from analysis of the 70 wt % low-sulfate Technical Grade glycolic acid by PSAL are reported in Table 3-4. Based on these analyses, the glycolic acid will meet the procurement specifications except for chloride and phosphate. Both chloride and phosphate samples were excessively diluted, so the detection limit from the analysis was higher than the purchase specification value. The glycolic acid likely would have met the purchase specification limit had a lower dilution (lower detection limit) been used in analysis.

The formate concentration was reported as <79 mg/kg by PSAL and 802 mg/kg or 0.08 wt % by AD. Both were significantly lower than the value reported by Chemours (0.13 wt % formic acid or 1,600 mg/L formate). Note that the glycolate concentration was reported 64.4 wt% and 72.0 wt% by PSAL and AD, respectively. Both results were within 10% of the specification. AD also noted that formate was off the calibration curve[8] and the peak at 27.331 minutes is likely diglycolic acid and not oxalate (Figure 3-4).

**Table 3-4. Measured Impurities in 70 wt% Low Sulfate Glycolic Acid Solution (Received March 2013)**

| Lab ID | PSAL | AD[8] | Units | Meets Procurement Spec? |
|---|---|---|---|---|
| Aluminum | 3.71 | 3.89 | mg/kg | Yes |
| Barium | 0.248 | NR | mg/kg | NA |
| Calcium | 13.9 | 2.05 | mg/kg | NA |
| Chromium | 0.041 | 0.185 | mg/kg | Yes |
| Iron | 2.08 | 1.99 | mg/kg | NA |
| Potassium | 13.0 | NR | mg/kg | NA |
| Magnesium | 10.0 | 9.63 | mg/kg | NA |
| Sodium | 27.0 | 33.0 | mg/kg | NA |
| Nickel | 0.345 | NR | mg/kg | NA |
| Sulfur | 2.01 | NR | mg/kg | NA |
| Silicon | 0.238 | NR | mg/kg | NA |
| Titanium | 0.454 | NR | mg/kg | NA |
| Glycolate | 644,000 | 720,000 | mg/kg | Yes |
| Fluoride | <79 | NR | mg/kg | NA |
| Chloride | <79 | NR | mg/kg | Yes |
| Nitrite | <79 | NR | mg/kg | NA |
| Sulfate | <79 | NR | mg/kg | Yes |
| Oxalate | <79 | NR | mg/kg | NA |
| Formate | <79 | NR | mg/kg | Yes |
| Phosphate | <79 | NR | mg/kg | No* |
| Density@20˚C | 1.2667 | NR | g/mL | NA |
| Density@50˚C | 1.2409 | NR | g/mL | NA |

NR = Not Requested
NA = Not Applicable (not in purchase specification)
* Detection limit too high to prove whether specification was met

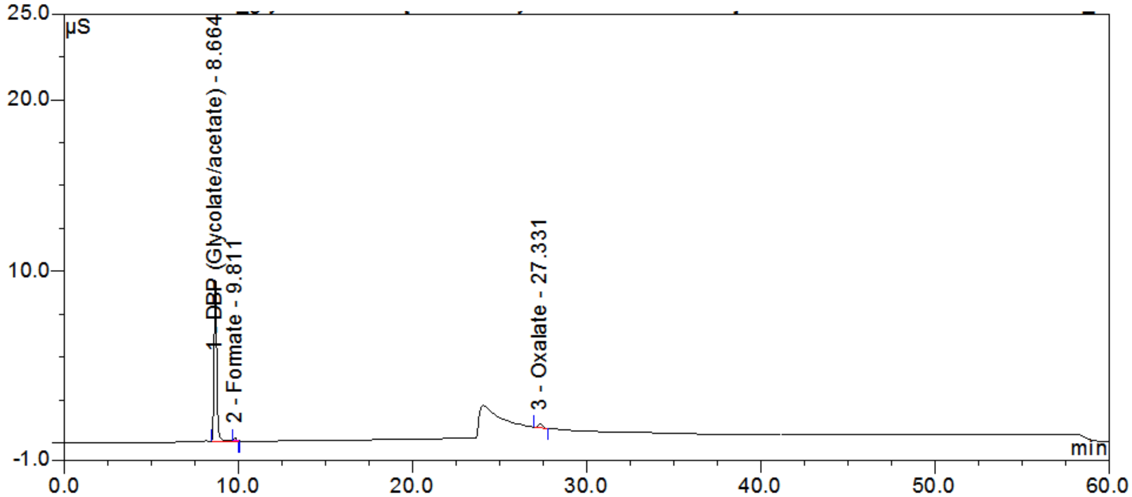


**Figure 3-4 Ion Chromatogram for 70 wt % Technical Grade Glycolic Acid**

The impurities in Technical Grade glycolic acid were revised in March 2017 by Chemours.[9] The list of impurities from the Certificate of Composition is summarized in Table 3-5 and attached in Attachment B. The new impurities that were identified included MAA and formaldehyde. In addition, the sulfate in the Technical Grade glycolic acid exceeds the Savannah River Remediation (SRR) procurement specification.[10]

**Table 3-5. Chemours Certificate of Composition for Technical Grade Glycolic Acid**

| Component | CAS # | Typical | Typical Range | Sales Spec |
|---|---|---|---|---|
| Glycolic Acid | 79-14-1 | 68.4 wt % | 67.0-69.0 wt % | 70-72 wt %** |
| Formic Acid | 64-18-6 | 0.4 wt % | 0.1-0.9 wt % | ≤1 wt % |
| Sulfates | NA | 267 mg/kg | 46-525 mg/kg | ≤800 mg/kg |
| Methoxyacetic acid | 625-45-6 | 0.51 wt % | 0.31-0.92 wt % | <1 wt %* |
| Formaldehyde | 50-00-0 | 553 mg/kg | 214-983 mg/kg | <1000 mg/kg* |
| Water | 7732-18-5 | Balance | Balance | |

* Internal value that is not shown on sales specification or certificate of analysis unless requested
** Sales specification is Total Acid reported as Glycolic Acid

**Table 3-6. Specification for Procurement of 70 wt% Glycolic Acid Solution**

| Impurity | Limit | |
|---|---|---|
| Formic Acid | 10,000 mg/kg | 1 wt% |
| Sulfate | 150 mg/kg | 0.015 wt% |
| Chloride | 100 mg/kg | 0.01 wt% |
| Formaldehyde | 100 mg/kg | 0.01 wt% |
| Phosphate | 10 mg/kg | 0.001 wt% |
| Aluminum | 10 mg/kg | 0.001 wt% |
| Chromium | 10 mg/kg | 0.001 wt% |

Technical Grade glycolic acid can contain sulfates as impurities. Typical analysis is 46-525 mg/kg but the sales specification allows for up to 800 mg/kg. The maximum allowable sulfate in the currently used formic acid is 100 mg/kg. 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 1,000 grams of SRAT receipt material at 20 wt% total solids and 13 wt% calcined solids, this would correspond to 150 grams of glycolic acid. This hypothetical SRAT/SME batch at 36% waste loading would yield about 367 grams of glass. The 150 grams of acid would contribute 0.120 grams of sulfate at the upper limit of 800 mg/kg. The 0.120 grams of sulfate contained in (divided by) 367 grams of glass equates to 0.033 wt% sulfate in glass contributed by the acid. As a result of the higher than desired sulfate in glass, the procurement specification limit for sulfate is 150 mg/kg, which Chemours can produce in a batch specifically made for DWPF.

Technical Grade glycolic acid also contains formaldehyde, a reactant used to produce glycolic acid. The current procurement specification lists formaldehyde as <100 mg/kg. A typical range is 214-983 mg/kg with a sales specification of <1,000 mg/kg. Unless Chemours is able to produce Technical Grade glycolic acid to meet the formaldehyde procurement specification, it is recommended to increase the procurement specification limit to 1,000 mg/kg for formaldehyde and to establish the procurement specification limit of 10,000 mg/kg for the MAA. A request to report the concentration of formaldehyde and MAA should be included in the certificate of analysis for each batch.

The list in Table 3-5 and Table 3-6 might not include all of the impurities in fresh glycolic acid and in glycolic acid after storage. It is recommended that fresh glycolic acid and the 2013 lot of glycolic acid should both be analyzed for impurities. SRNL does not have the equipment and methods to analyze the samples for some of the small organic molecules that might be present. Chemours or an independent lab such as Intertek in Allentown, PA have experience in analyzing for impurities in glycolic acid.

Although MAA and formaldehyde cannot be detected in liquid samples, they could be detected by the offgas equipment used in SRNL experiments. A Fourier Transformed Infrared (FTIR) analyzer is used to detect a variety of organic species remaining in the vapor after the condensers. The FTIR spectra from a large number of these experiments have been examined for residual peaks unaccounted for in the current analysis "recipe". The FTIR analysis software allows for "recipes" of analytes to be examined and subtracted from observed spectra. Based on spectral residuals once all known species are removed, no peaks remain that would correlate to MAA or formaldehyde above detection limit in the offgas (typically 10 parts per million, molar basis) for the instrumentation. The lack of formaldehyde and MAA measured after the condensers is expected for a few reasons. These compounds are water soluble and if they enter the offgas they would be condensed in the aqueous condensate.

## 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 $H_2$ 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 $H_2$. 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 $H_2$. The hydrogen atoms can also react with nitrate or nitrite ions in the solutions. The reactions with nitrate or nitrite do not produce $H_2$. Consequently there is a competition that affects the rate of production of $H_2$. The rate of radiolytic hydrogen production from formic acid and formate ion in the SRAT solution of SB3 has been measured and agrees well with predictions made for the SB3 solution based on its radionuclide composition.[11] 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.[12] The rate constant for the reaction with glycolic acid to produce $H_2$ 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.

**Table 3-7. 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 | 2.1E+08 | 0.98 | 2.1E+08 | 0.94 |
| Nitrate | 1.4E+06 | 0.51 | 7.1E+05 | 0.003 |
| Nitrite | 7.1E+08 | 0.08 | 1.4E+07 | 0.06 |

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 $H_2$. The remaining 6% react with nitrate and nitrite and don't produce $H_2$. Results of the calculations are presented in Table 3-8.

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 3-8.

**Table 3-8. 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 | 4.6E+07 | 0.78 | 3.6E+07 | 0.39 |
| Formate | 2.1E+08 | 0.20 | 4.2E+07 | 0.46 |
| Nitrate | 1.4E+06 | 0.51 | 7.1E+05 | 0.008 |
| Nitrite | 7.1E+08 | 0.08 | 1.4E+07 | 0.14 |

In Table 3-8 it can be seen that in this case 85% instead of 94% of the H atoms would react with the organic anions to produce $H_2$. This would slightly <u>lower</u> the total radiolytic rate of $H_2$ production. Consequently the analysis indicates that substitution of glycolic acid for formic acid would not increase the radiolytic production rate of $H_2$ 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 $H_2$ 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.[13] 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/100eV[14]) 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 $O_2$ then subjected to large radiation doses (1.5 to 15 Mrad used in study) produced considerable quantities of a non-diffusive polymeric material.[15-16] 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 $-C_6O_7H_{10}-$ and had molecular weights greater than 5000 g/mol.[16] 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 $O_2$.[17] In the SRAT, this $O_2$ can only be replenished by the diffusion of atmospheric air into the solution. Consequently, 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.

### 3.4 Radiation Effects on Simulated SRAT Product Supernate

An irradiation test was completed to determine whether a SRAT product supernate containing glycolic acid will form polymers. The SRAT supernate from Run GF-13[4], a simulated SRAT supernatant, was irradiated in the Co-60 gamma source at SRNL under a slow flow of argon gas to a dose of 6.4 Mrad (approximately the dose received by the radioactive SRAT solution after 5 weeks based on a SB composition). No visible changes were observed in the SRAT product supernate after irradiation (Figure 3-5). However, a small amount of dark colored solids was observed on the bottom of the vessel. The solids on the bottom of the vessel appeared to be spots of rust and were sampled using a cotton swab. The elemental analysis of the solids found Fe, Mn, and Na to be the major components consistent with either precipitation of these elements from solution or resulting from steel corrosion products. The solids also contained minor amounts of Al, Ca, Cr and Ni. The irradiated SRAT product supernate was heated to reflux for 1 hour, and again, no visible changes occurred to the solution. Analysis of samples of the original SRAT product supernate, the irradiated SRAT product supernate, and the irradiated SRAT product supernate after boiling for 1 hour showed no significant change in the glycolate concentration (Table 3-9). No evidence for the formation of organic polymers was found.

**Table 3-9. Anion Analysis of the SRAT Product Supernate Samples**

| Anion * | Orig. SRAT Product Supernate (mg/L) | Irradiated SRAT Product Supernate (mg/L) | Irradiated and Boiled SRAT Product Supernate (mg/L) |
|---|---|---|---|
| Glycolate | 3.40E+04 | 4.02E+04 | 3.77E+04 |
| Formate | 1.33E+03 | 1.05E+03 | <1.0E+03 |
| Nitrate | 8.86E+04 | 1.14E+05 | 1.07E+05 |
| Nitrite | <9.9E+02 | <9.8E+02 | <1.0E+03 |
| Oxalate | 4.48E+03 | 3.88E+03 | 4.20E+03 |
| Sulfate | 5.22E+03 | 7.05E+03 | 6.83E+03 |
| Phosphate | <9.9E+02 | <9.8E+02 | <1.0E+03 |
| Chloride | 1.54E+03 | 2.17E+03 | 2.06E+03 |
| Fluoride | <9.9E+02 | <9.8E+02 | <1.0E+03 |

* Anion analysis by ion chromatography. All results are the average of duplicate measurements.

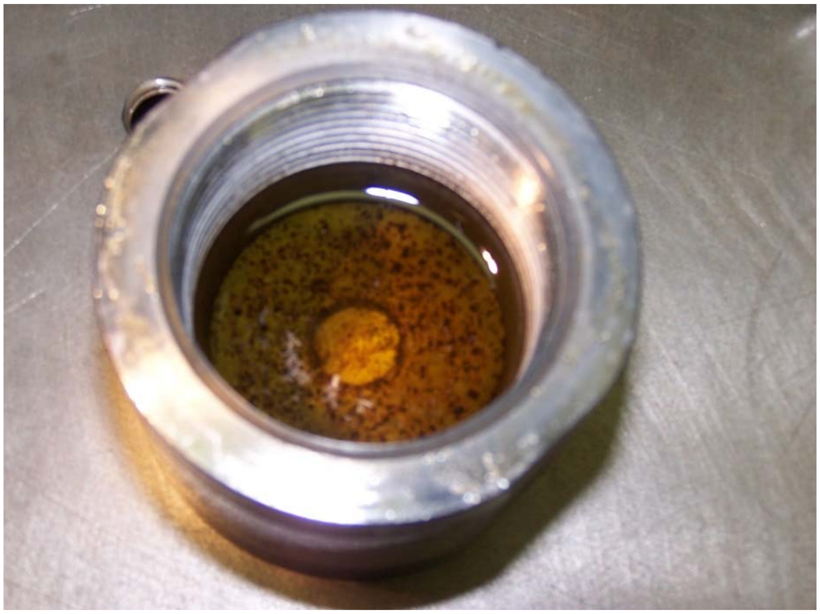

**Figure 3-5. GF-13 Post SRAT Supernate after Irradiation**

## 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 0.033 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, but the effect is expected to be minor. However, an irradiation test with a simulated SRAT product supernate containing glycolic acid in an oxygen depleted atmosphere did not find evidence of polymerization.

- Formaldehyde and MAA are impurities in the glycolic acid.

## 5.0 Recommendations

Analysis of fresh glycolic acid, glycolic acid to simulate a year of storage, and the 2013 lot of glycolic acid should be completed to determine impurities. SRNL/AD does not have the equipment and methods to analyze the samples for some of the small organic molecules that might be present. Both Chemours and an independent lab such as Intertek in Allentown, PA has experience in analyzing for impurities in glycolic acid.

Technical Grade glycolic acid also contains formaldehyde, a reactant used to produce glycolic acid. Unless Chemours is able to produce Technical Grade glycolic acid to meet the SRR formaldehyde procurement specification, it is recommended to increase the procurement specification limit to 1,000 mg/kg for formaldehyde and to establish the procurement specification limit of 10,000 mg/kg for the MAA. A request to report the concentration of formaldehyde and MAA should be included in the certificate of analysis for each batch.

## 6.0 References


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## Appendix A. DuPont Glycolic Acid Technical Product Attributes

The Glycolic Acid Technical Product Attributes from DuPont are included in Appendix A.

# DuPont™ Glycolic Acid

## TECHNICAL PRODUCT ATTRIBUTES

### Chemical and Physical Stability

Glycolic Acid 70% technical solution and DuPont™ Glypure® 70% solution are chemically stable when stored at normal temperatures. The solution products are physically stable if they are stored at temperatures above 10°C (50°F). At colder temperatures, Glycolic Acid crystals can form. The crystals can be put back into solution by warming the container with stirring. This does not affect chemical quality. DuPont personnel can provide detailed procedures for reconstituting precipitated Glycolic Acid.

The Glypure® 99% crystalline grade of Glycolic Acid is chemically stable to 50°C (122°F). Above this temperature, polymerization begins to occur. DuPont guarantees the specification chemical quality of its Glycolic Acid products for two years, provided the container has not been opened. DuPont will help customers determine if the quality of their Glycolic Acid is still viable.

### Properties of Equilibrium

| Glycolic Acid 70% Technical Solution | | |
|---|---|---|
| Concentration of Glycolic Acid Solution, % | % Free Acid at 25°C (77°F) | Precipitation Point, °C (°F) |
| 0.0 | 0.0 | 0 (32) |
| 10.0 | 10.0 | –2 (28) |
| 20.0 | 19.9 | –5 (23) |
| 30.0 | 29.6 | –9 (16) |
| 40.0 | 39.0 | –14 (7) |
| 50.0 | 47.7 | –19 (–2) |
| 60.0 | 56.2 | –5 (23) |
| 70.0 | 63.6 | 9.5 (49) |
| 80.0 | 69.0 | 22 (72) |
| 90.0 | 71.8 | 32 (90) |
| 100.0 | 68.0 | 37 (99) |

### Physical Properties

| Glycolic Acid 70% Technical Solution | |
|---|---|
| Weight, lb/gal at 15.6°C/60°F<br>kg/L at 15.6°C/60°F | 10.6<br>1.27 |
| Density, g/mL at 15.6°C (60°F) | 1.27 |
| Coefficient of Thermal Expansion at 15.6–60°C<br>at 60–140°F | 0.00047<br>0.00026 |
| Viscosity, MPa/s at 15.6°C (60°F)<br>at 43.3°C (110°F) | 11.28<br>3.49 |
| Heat Capacity, Btu/lb-ft at 25°C (77°F) | 0.579 |
| Heat of Solution, kJ/mol | –11.55 |
| Enthalpy, Btu/lb-ft at 25°C (77°F) | –464.4 |
| Heat of Combustion, kcal/mol | 166.6 |
| Boiling Point, °C (°F) | 112 (234) |
| Precipitation Point, °C (°F) | 10 (50) |
| pH at 25°C (77°F) | 0.1 |
| Dissociation Constant at 25°C (77°F) | $1.5 \times 10^{-4}$ |
| Heat of Neutralization, kcal/mol | –52.02 |
| Biological Oxygen Demand (BOD) at 5 days (standard diluted sewage) | 0.175 |
| 7-day Biodegradability, % | 89.6 |
| Volatile Organic Compound (VOC), at 101°C (213°F), 45 min | 99.6 (water) |

DUPONT
*The miracles of science™*

## Appendix B. Chemours Glycolic Acid 70 Certificate of Composition

The Glycolic Acid Certificate of Composition from Chemours is included in Appendix B.

The Chemours Company
1007 Market Street
PO Box 2047
Wilmington, DE 19899

302-773-1000 t
chemours.com

March 28, 2017

## RE: GLYCOLIC ACID 70 CERTIFICATE OF COMPOSITION

**Dear Regulatory Specialist:**

We, The Chemours Company hereby certify that our Glycolic Acid family of products are of wholly synthetic manufacture, and made on dedicated equipment.

We certify that Glycolic Acid 70 has the following composition.

| Component | CAS # | Typical | Typical Range | Sales Spec |
|---|---|---|---|---|
| Glycolic Acid | 79-14-1 | 68.4 Wt.% | 67.0- 69.0 Wt.% | 70-72 Wt.** |
| Formic Acid | 64-18-6 | 0.4 Wt.% | 0.1-0.9 Wt.% | ≤ 1 Wt.% |
| Sulfates | n/a | 267 ppm | 46-525 ppm | ≤ 800 ppm |
| Methoxyacetic Acid | 625-45-6 | 0.51 Wt.% | 0.31-0.92 Wt.% | < 1%* |
| Formaldehyde | 50-00-0 | 553 ppm | 214-983 ppm | < 1000 ppm* |
| Water | 7732-18-5 | Balance | Balance | |

*internal value that is not shown on sales specification or COA unless requested
** Sales specification is Total Acid reported as Glycolic Acid

Do not hesitate to contact us should you require further information.

Sincerely,

Robert Durante
Principal Investigator & Global Product Steward,
The Chemours Company
(302) 695-4338

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## Appendix C. Email Authorization of Task

**Re: Glycolic Acid Impurities**

Bill Holtzscheiter to: Dan Lambert 05/09/2017 10:49 AM

Cc: Spencer Isom, Victoria Kmiec... Hide Details

From: Bill Holtzscheiter/SRR/Srs Sort List...

To: Dan Lambert/SRNL/Srs@Srs

Cc: Spencer Isom/SRR/Srs@SRS, Victoria Kmiec/SRR/Srs@SRS, Thomas Colleran/SRR/Srs@Srs,

---

Dan,

Spencer and I have discussed this and agree that you should finish the report revision that you have been working so we can see the impact you report from the currently known/suspected impurities. But it certainly helps us if the process the vendor uses to reduce the sulfate to meet our spec also takes care of the methoxyacetic acid. From the perspective of finalizing a spec, we need the samples analyzed so, even though you are finishing the report and adding the recommendation, we know we are going to accept your recommendation and need to get started on getting the analysis completed. It would be great if we don't have to consider degradation products, but if we do, we need to start the process so we get it finished and can proceed with glycolic acid procurement.

I looked back at the existing TTR and this analysis is certainly within the existing TTR scope, so we don't need another TTR. I think we just need to allocate funding to cover the analyses and transport of samples to the vendor.

Bill Holtzscheiter
Flowsheet Engineering
Office: 803-208-2409
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