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Ion Chromatography (IC) Analysis of Glycolate in Simulated Waste

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PREFACE OR ACKNOWLEDGEMENTS

Samples for this work were generated from bench-scale CPC runs. Kim Wyszynski prepared most of the samples with support from Jon Duval. David Best supported this work especially with the base addition studies.

EXECUTIVE SUMMARY

The Defense Waste Processing Facility (DWPF) is evaluating the use of glycolic acid as a mercury reductant instead of formic acid during the processing of radioactive waste in the chemical processing cell (CPC). Glycolic acid has been shown to possess improved handling and processing properties when compared to formic acid. An improved method of analysis for glycolic acid by ion chromatography (IC) was developed in support of the alternative reductant flowsheet and applied to simulated Slurry Reciept and Adjustment Tank (SRAT) product and Slurry Mix Evaporator (SME) product. The method, termed caustic quench (CQ), involves adjusting the pH of 10 g slurry samples with 2 g of 50% NaOH, diluting by with water to within the calibration curve, and analyzing the dilution by IC. The method was verified by comparing to an IC method where the samples were not pH adjusted, comparing to total organic carbon (TOC) analyses, and comparing to bench-scale chemical processing cell (CPC) off-gas data. A further comparison was made to a supernate method where supernate is analyzed by IC and calculated to a slurry basis. The glycolate method was confirmed at a second laboratory.

The CQ method was developed for acidic slurries with three benefits in mind. The first was to stop all oxidation reactions for archival purposes by changing the pH from mildly acidic in the SRAT and SME products to basic. Secondly, overwhelming the sample with base has the potential to convert organic acid chelated metal compounds to metal hydroxides. Our intent was to “free up” chelated organic acids for IC analysis by occupying metal binding sites with hydroxide. Finally, CQ adjusts the pH of the diluted sample to match the basic eluent of the IC analysis. Potassium hydroxide is the mobile phase for the IC analysis and samples should be similar in pH for optimal chromatography.

The following analytical findings are for alternate reductant flowsheet acidic slurry analyses of glycolate:

- CQ values were on average higher than water dilution values known to be biased low.
- CQ values for SME product, when put on a total carbon basis with formate, oxalate, and antifoam, compared well DWPF TOC results. The 10% error bars overlapped for all samples but one.
- CQ values for SRAT product, when put on a total carbon basis with formate, oxalate, and antifoam, were lower than DWPF TOC results by about 10%.
- Spike recoveries were >95% for glycolate in alternate reductant flowsheet slurry
- CQ values were higher by ~5% when compared to supernate analyses put on a slurry basis.
- CQ values reasonably matched offgas data. All 10% error bars overlapped.

Other analytes analyzed from acid slurry

- Nitrate values are acceptable with overlapping 10% error bars.
- Oxalate values were higher than water dilutions helping to close the bias with DWPF TOC. Further spike addition studies are suggested for oxalate
- Formate values are acceptable with overlapping 10% error bars.

Other points

- CQ increases the viscosity of the slurry which could cause sampling issues. Other protocols that limit sampling until the sample is diluted should be further evaluated.
- CQ is not suggested for supernate or condensate samples
- CQ should be evaluated with sludge
- CQ should be evaluated with formic acid/nitric acid flowsheet

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LIST OF ABBREVIATIONS

AD	Analytical Development
CPC	Chemical Process Cell
CQ	Caustic Quench
DWPF	Defense Waste Processing Facility
IC	Ion Chromatography
PSAL	Process Science Analytical Laboratory
RR	Round Robin
SME	Slurry Mix Evaporator
SRAT	Slurry Receipt and Adjustment Tank
SRNL	Savannah River National Laboratory

1.0 Introduction

Formic acid reduces mercury in the chemical processing cell (CPC) at the Defense Waste Processing Facility (DWPF) to elemental mercury for removal by steam stripping. Glycolic acid is under study as a potential replacement reductant [Pickenheim, 2009] with improved processing and storage properties. Formic acid concentration in the CPC is determined by ion chromatography where samples are diluted in water, separated on an ion exchange column using a hydroxide eluent, and analyzed by a conductivity detector. This data is used in conjunction with other analyses to balance oxidants and reductants in the melter feed for optimal vitrification [Jantzen, 2012]. The same analytical technique is used to quantify glycolate in studies supporting the use of glycolic acid instead of formic acid in the alternate reductive program.

1.1 2013 Round Robin Glycolate Study

Onsite analysis of glycolate was vetted in round robins (RR) studies between Analytical Development (AD) laboratory, DWPF laboratory, and Process Science Analytical Laboratory (PSAL) in anticipation of implementing the glycolate flowsheet at DWPF [Wiedenman, 2013]. Good agreement for glycolate was observed between the laboratories despite each laboratory using different anion columns. PSAL was unable to obtain consistent results with a capillary IC system as shown in the shaded cells of Table 1-1 but matched the glycolate values of DWPF and AD laboratory with their 4 mm column system in round robin 4. Table 1-2 summarizes the IC conditions of each laboratory. Table 1-1 summarizes the results of the two main analytes in the simulated waste samples from the last three round robins. The percent standard deviation for each analyte was 5 or below in each laboratory in round robin 3 and 4. Round robin 2 had known amounts of glycolate and nitrate in simulant supernate. The average of the results from each laboratory was within 10% of the theoretical values, which was considered acceptable.

Table 1-1. Inter-laboratory Glycolate Round Robin.

RR #	Laboratory/Simulant	Glycolate, mg/L (RSD %)	Nitrate, mg/L (RSD%)
2	AD/supernate standard	47800	53100
2 (capillary)	PSAL/supernate standard	48000	49600
2	DWPF/supernate standard	45900	50600
Average		47200 (3)	51100 (4)
Matrix Matched Theor.		48600	54600
3 (n=4)	AD/GF 40 sludge simulant	44000 (4)	47000 (1)
3 (capillary) (n=4)	PSAL/GF 40 sludge simulant	33000 (3)	51000 (4)
3 (n=4)	DWPF/GF 40 sludge simulant	43000 (5)	52000 (5)
3 (n=4)	AD/GN 34 sludge simulant	43000 (2)	45000 (2)
3 (capillary) (n=4)	PSAL/GN 34 sludge simulant	26000 (0)	45000 (0)
3 (n=4)	DWPF/GN 34 sludge simulant	42000 (2)	45000 (2)
4 (n=12)	AD/composite sludge	44000 (2)	66000 (1)
4 (n=12)	PSAL/composite sludge	43000 (2)	64000 (1)
4 (n=12)	DWPF/composite sludge	42000 (2)	68000 (1)
Average		43000 (2)	66000 (3)

n = number of times a sample was analyzed
%RSD is reported in glycolate and nitrate column in parentheses ().

Table 1-2. Ion Chromatography (IC) Instrument Settings by Laboratory.

Laboratory	AD	PSAL	DWPF
Instrument	ICS-3000	ICS-5000	ICS-3000
Column (4 mm)	AG-19/AS-19	AG-11HC/AS-11 HC	AG-11/AS-11
Flow Rate (mL/min)	1.0	1.0	1.5
Injection Loop (μL)	25	25	25
Cal. Standards (ppm)	1, 5, 10, 50	1, 5, 10, 20	1, 10, 20
Gradient Method	0-30 min. (5-25 mM KOH)	0-4 min. (0.5 mM KOH)	0-4 min. (0.5 mM KOH)
	30-48 min. (25 mM KOH)	4.1-25 min. (35 mM)	4.1-25min.(35 mM)
	48-50 min. (5 mM KOH)	25.1-27 min. (60 mM)	25.1-27 min. (60 mM)
	NA	27.1-32 min. (0.5 mM)	27.1-32 min. (0.5 mM)
Column Temp. (^oC)	35	35	ambient
CD Detector Temp. (^oC)	35	35	35

1.2 2015 Anion Improvement Study

As part of the alternate reductant program, it was observed that a number of CPC simulant glycolate analyses were often biased low in samples of high acid stoichiometry when compared to offgas data from bench scale CPC studies. Acid stoichiometry refers to the amount of nitric acid and glycolic acid added to a CPC run based on an acid calculation [Lambert, 2014] used to target REDOX values. Adding acid above the calculated amount is considered high acid stoichiometry. Table 1-3 summarizes the runs and Figure 1-1 illustrates the difference between the off-gas data and the IC data observed for SRAT product over nine bench-scale runs. The largest deviation was observed in the first five higher acid stoichiometry runs. These lower IC values impacted the ability to update the REDOX model [Zamecnik, 2015] and made the final oxidation state of the glass form difficult to predict. This report primarily covers improvements on the glycolate chromatography analysis to address the low bias in glycolate results observed with high acid stoichiometry samples. Further, oxalate values are consistently higher with CQ than water dilutions. These higher results helped close the bias between DWPF TOC values and calculated total carbon by IC. In addition, they are closer to the predicted values for oxalate by the off-gas data.

The offgas carbon balances were performed from measurements of the total offgas CO_2, the concentrations of carbon containing species in the feed (oxalate and carbonate), and the amount of glycolic acid added. During acid addition, carbonates are completely converted to CO_2. The overall generation of CO is negligible and can be ignored. The total CO_2 generated should be equal to the total carbonate plus the amount of glycolate oxidized to make CO_2 and any oxalate that is oxidized to CO_2. Possible reactions with the oxidant nitrous acid are shown below. Similar reactions can be written for the reduction of Mn^{4+} to Mn^{2+} or Fe^{3+} to Fe^{2+}. Note that these reactions can also be written for glycolate, formate, or oxalate anions.

Oxidation to 2 CO_2 per glycolate: $HOOC\text{-}CH_2OH + 6\ HNO_2 = 2\ CO_2 + 6\ NO + 5\ H_2O$ (0.0)

Oxidation to CO_2 and formic acid: $HOOC\text{-}CH_2OH + 4\ HNO_2 = HCOOH + CO_2 + 4\ NO + 3\ H_2O$ (0.0)

Oxidation to oxalic acid: $HOOC\text{-}CH_2OH + 4\ HNO_2 = HOOC\text{-}COOH + 4\ NO + 3\ H_2O$ (0.0)

Oxidation of oxalic acid to CO_2: $HOOC\text{-}COOH + 2\ HNO_2 = 2\ NO + 2\ CO_2 + 2\ H_2O$ (0.0)

During the Scaled CPC runs, it was found that a small amount of formic acid was usually formed, along with a small amount of oxalate. In earlier data (GN34-59), the amount of oxalate generated varied widely. Currently, it is not known what factors determine the glycolate to oxalate conversion. In runs with no noble metals, more formate was usually formed.

For purposes of the carbon material balance, the destruction of glycolate was assumed to be the total CO_2 generated minus CO_2 generated from Equation (0.0) plus formate generated from Equation (0.0) plus oxalate generated from Equation (0.0). The destruction of oxalate was assumed to be zero; there were some values for oxalate generation that were negative indicating destruction, but these values were generally small (<2% destruction).

The glycolate destruction from the offgas data gave different values than from the IC glycolate analyses. These two values for glycolate destruction are compared by calculating the glycolate concentration in the product that would correspond to the material balance using the offgas data. Then the data can be compared on a basis of the product compositions.

As Figure 1-1 shows, glycolate values by IC are lower than expected from the off-gas data. This observation is pronounced in high acid samples. Our concern was the acidic samples are neutralized by the IC mobile phase (KOH) upon injection leading to less than optimal chromatography. For instance, metal precipitation at the head of the IC column could lead to glycolate metal complexes that do not elute at the correct time and bias the glycolate value low. Additionally, the best peak shape for integration on a chromatographic is achieved by making the pH of the sample basic like the mobile phase.

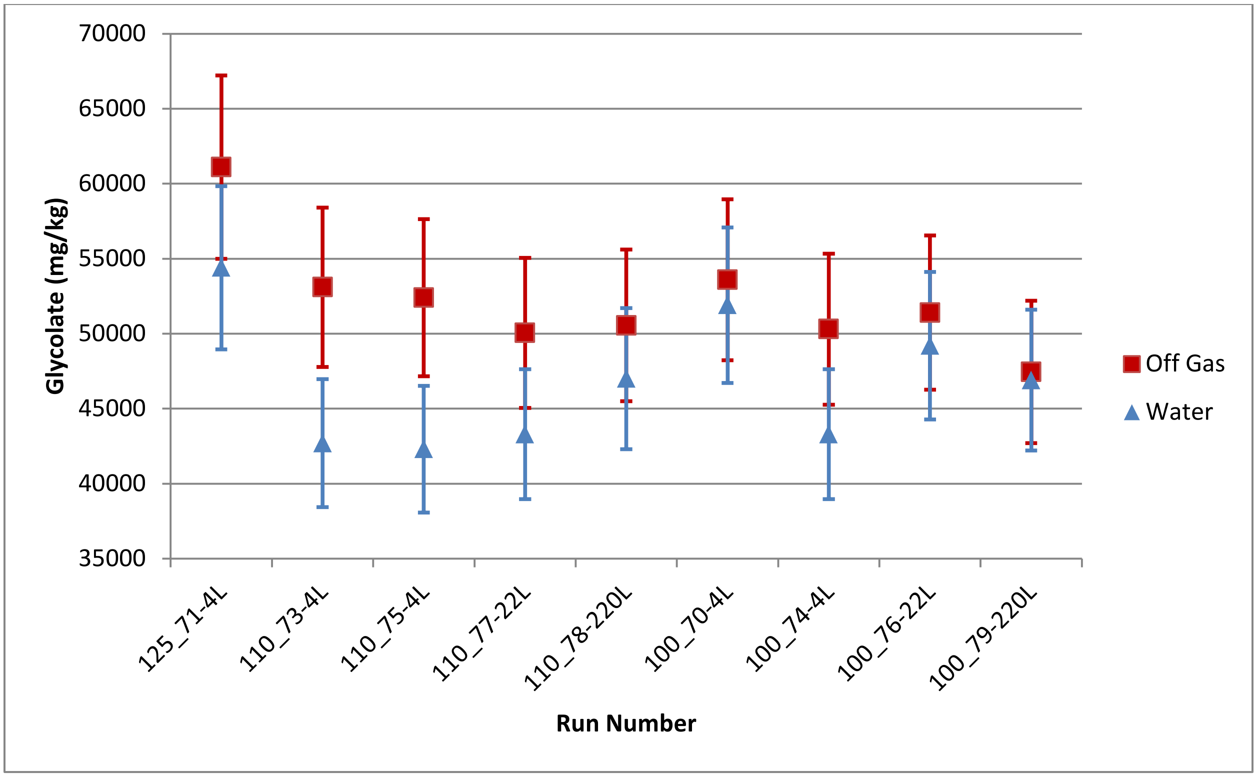

Figure 1-1. SRAT product water analysis versus CPC off-gas analysis.

Table 1-3. GN70 to GN79 CPC SRAT and SME products.

Run	Product	Sample #	Acid Stoichiometry (%)	Vessel Size, L
GN70	SRAT	S-1140	100	4
	SME	S-1146	100	4
GN71	SRAT	S-1268	125	4
	SME	S-1274	125	4
GN72	SRAT	S-1345	100	4
	SME	S-1351	100	4
GN73	SRAT	S-1425	110	4
	SME	S-1431	110	4
GN74	SRAT	S-1688	100	4
	SME	S-1694	100	4
GN75	SRAT	S-1770	110	4
	SME	S-1776	110	4
GN76	SRAT	S-1862	100	22
	SME	S-1869	100	22
GN77	SRAT	S-1975	110	22
	SME	S-1981	110	22
GN78	SRAT	S-2172	110	220
	SME	S-2180	110	220
GN79	SRAT	S-2394	100	220
	SME	S-2402	100	220

2.0 Experimental Procedure

Two sample preparation methods are described below. The original ion chromatography data generated for the alternate reductant program using the water dilution protocol. After literature review and initial scoping studies, Slurry Receipt and Adjustment Tank (SRAT) and Slurry Mix Evaporator (SME) GN70 to GN79 products [Newell, 2014] underwent preparation using the caustic quench protocol and IC analysis.

The CQ method was developed for acidic slurries with three benefits in mind. The first was to stop all oxidation reactions for archival purposes by changing the pH from mildly acidic in the SRAT and SME products to basic. Secondly, overwhelming the sample with base has the potential to convert organic acid chelated metal compounds to metal hydroxides. Our intent was to “free up” chelated organic acids for IC analysis by occupying metal binding sites with hydroxide. Finally, CQ adjusts the pH of the diluted sample to match the basic eluent of the IC analysis. Potassium hydroxide is the mobile phase for the IC analysis and samples should be similar in pH for optimal chromatography.

Samples are diluted to 500 for oxalate and formate and 5000 for nitrate and oxalate.

2.1 Water Dilution

Samples arrive in 125 mL HDPE bottles that are shaken by hand and about a 1 mL aliquot is removed using a pipette tip that has been cut to give a wide opening. The aliquot is added to a 125 mL HDPE bottle and the weight recorded. The bottle is filled to 100 g with water and the weight recorded. At this point, the density is considered one and the sample is diluted by volume. An outline of the steps is listed below.

- 1 gram of slurry sample in water to a total mass of 100 g.
- Filter
- Dilute for 500
    - 2 mL of the 100 g solution plus 8 mL of water
- Dilute for 5000
    - 0.2 mL of the 100 g solution plus 9.8 mL of water
- Analyze

2.2 Caustic Quench (CQ) followed by Dilution

Two grams of 50% NaOH are added to 10 grams of slurry sample. The container is shaken by hand and a 1 g aliquot is transferred to 100 grams water. An outline of the steps is listed below.

- 10 grams of slurry sample
- Add two grams of 50% NaOH
- 1 gram of CQ slurry sample in water to a total mass of 100 g.
- Filter
- Dilute for 500
    - 2 mL of the 100 g solution plus 8 mL of water
- Dilute for 5000
    - 0.2 mL of the 100 g solution plus 9.8 mL of water
- Analyze

2.3 Dilution with 0.1 M NaOH

The sample preparation follows the steps of water dilution. Below is an outline of the steps.

- 1 g slurry in 0.1 M NaOH to a total mass of 100 g
- Filter
- Dilute for 500
    - 2 mL of the 100 g solution plus 8 mL of water
- Dilute for 5000
    - 0.2 mL of the 100 g solution plus 9.8 mL of water
- Analyze

3.0 Results and Discussion

3.1 Instrument Standards and Error Bars

All samples were analyzed at PSAL using reference standards with expiration dates. Open and closing instrument standards for all of the analyses over a four month period are summarized in Table 3-1. For glycolate and nitrate, these standards showed a two sigma error of 10%. All error bars on graphed IC data are therefore set at 10%. Additionally when comparing to total organic carbon (TOC) analysis, the error bars for TOC were set at 10% in keeping with a recent report [Edwards, 2013].

Table 3-1. PSAL instrument opening Standards Summary

QC 10 mg/L	**Glycolate**	**Formate**	**Chloride**	**Nitrate**	**Sulfate**	**Oxalate**
95% confidence uncertainty	8.18%	10.1%	5.93%	9.20%	7.71%	10.7%

3.2 Multiple Analyses of SME GN78-S1980

Three bottles of SME product were each analyzed three times to determine if sampling issues were occurring. Table 3-2 summarizes the results. The percent relative standard deviation for nine samples was below 3% for both the glycolate and nitrate and considered acceptable. The method of shaking small HDPE bottles and removing an aliqout with a modified pippette tip showed no significant sampling issues.

Table 3-2. SME Product Analyses

SME Product	Glycolate, mg/kg (RSD%)	Nitrate, mg/kg (RSD%)
14-GN78-S2180 (A)	43400	52400
14-GN78-S2180 (B)	43900	52800
14-GN78-S2180 (C)	43200	52000
14-GN78-S2181 (A)	43300	52100
14-GN78-S2181 (B)	43200	51700
14-GN78-S2181 (C)	43800	51700
14-GN78-S2182 (A)	43000	51600
14-GN78-S2182 (B)	43600	51500
14-GN78-S2182 (C)	42600	51100
Average (%RSD)	43,300 (0.9)	51,900 (1.0)

3.3 Spike Addition

Glycolate was spiked at three levels into a gram of simulated waste (sample GN-79-2321) followed by the caustic quench protocol. This simulated waste sample was collected after nitric acid had been added to the process but prior to the addition of the glycolic acid reductant. Good recoveries were observed for glycolate at all three levels and the results are summarized in Table 3-3.

Table 3-3. Post Nitric Product Analyses

Sample ID	Comment	Glycolate, mg/kg	%recovery
14-GN79-2321	No glycolate spike	<1.00	NA
14-GN79-2321	Spiked 10 mg/kg	10.4	104
14-GN79-2321	Spiked 15 mg/kg	15.1	100
14-GN79-2321	Spiked 20 mg/kg	20.0	100

3.4 Water Dilution versus Caustic Quench (CQ)

Simulated waste samples of SRAT and SME product were analyzed using the water dilution and the CQ methods. The sample count was twenty samples from ten bench scale runs. High acid stoichiometry runs are identified as 110 or 125 in the sample label. In general, the water dilutions tended to yield lower glycolate values and this difference was most pronounced for the higher acid stoichiometries. For the SRAT products, all of the data points were within the error bars but CQ samples were higher than water dilutions by about 5% on average and were a closer match of the CPC off-gas data in section 3.7.

More deviation was observed with analyses of the SME product. Two of the high acid stoichiometry samples, 125 GN71 and 110 GN75, had higher glycolate values not within the error bars with the CQ protocol. In both cases the CQ values met what was expected for the run. For instance, the GN71 simulant was predicted to have a higher glycolate value than the lower acid stoichiometry runs such as GN76 and GN79 since the run started at a higher concentration. All of the runs varied primarily in how much acid was added and GN71 started with the highest glycolate addition. After processing these three simulants, GN71 should have the highest glycolate remaining in the SME product. Overall, seven of the ten water dilution analyses gave lower glycolate values.

The error bars of all nitrate values overlapped demonstrating either preparation protocol results in similar nitrate values. In the SRAT product, eight of the ten nitrate values were slightly higher than the caustic quench value. Four of the ten nitrate values were higher in the SME product for water dilution.

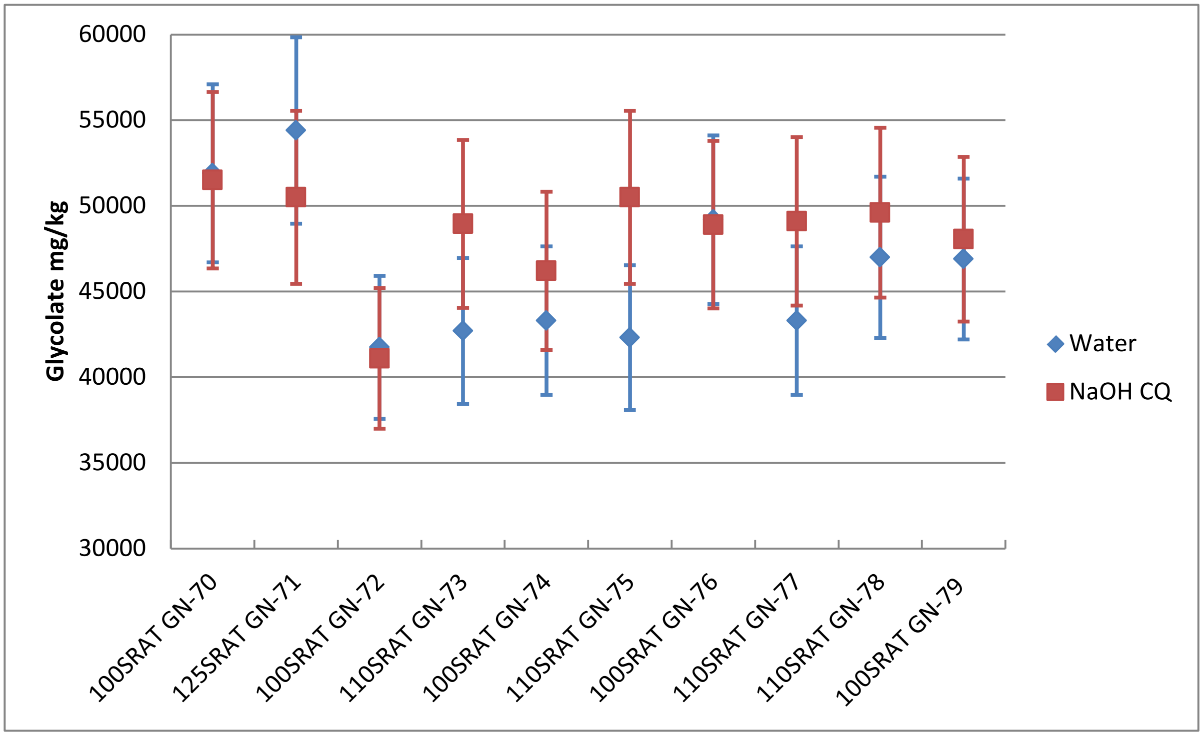

Figure 3-1. Water dilution versus caustic quench for glycolate in SRAT product.

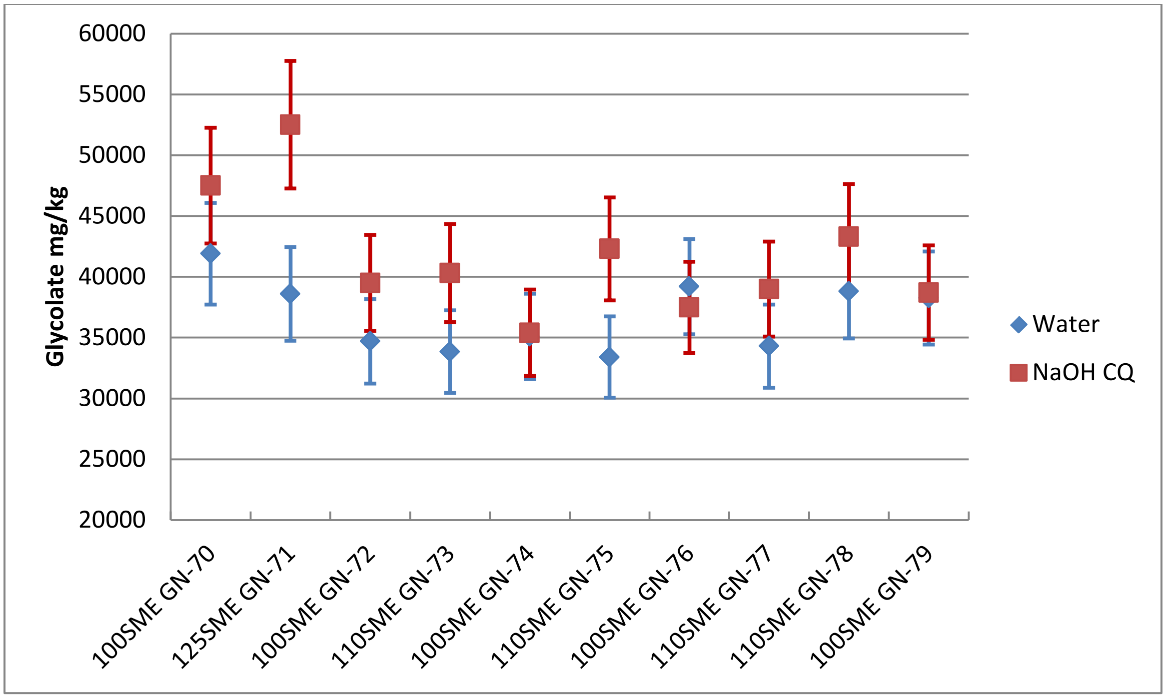

Figure 3-2. Water dilution versus caustic quench for glycolate SME product.

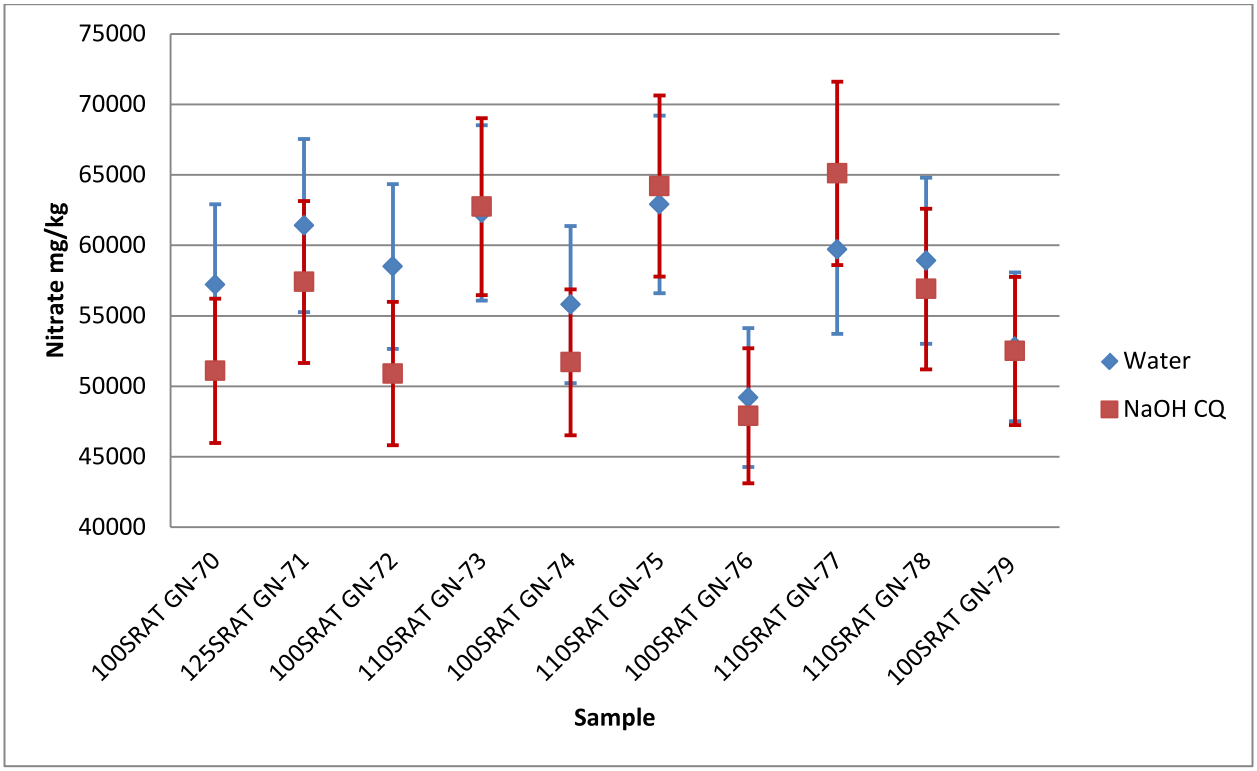

Figure 3-3. Water dilution and caustic quench for nitrate in SRAT product.

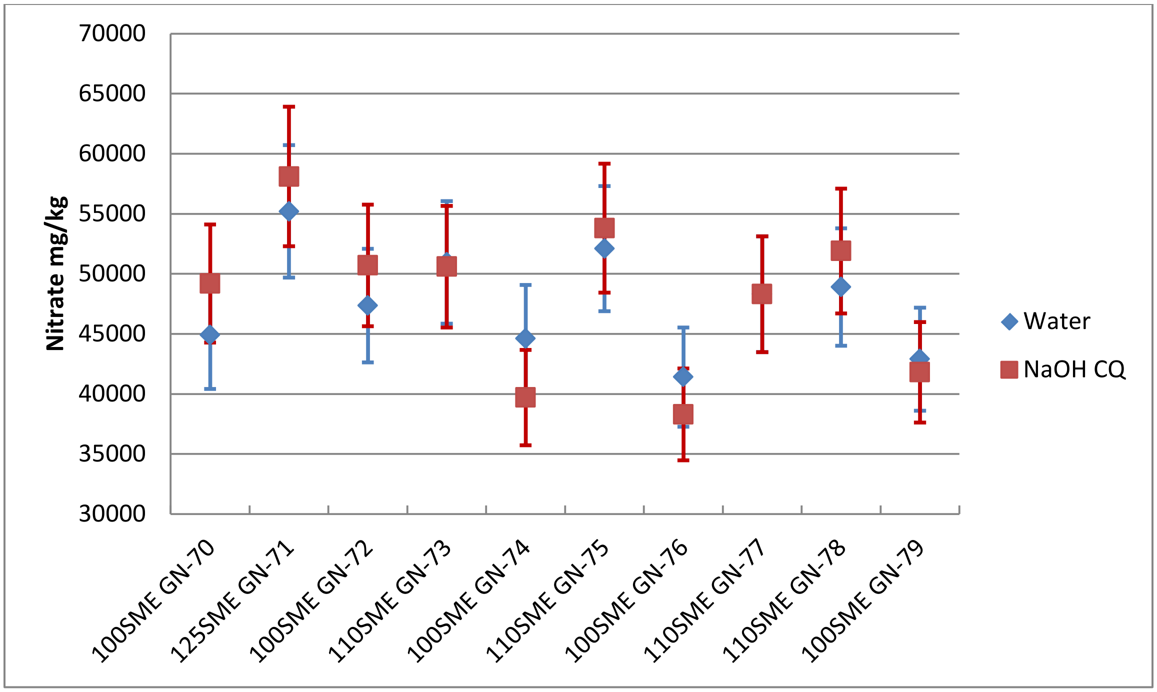

Figure 3-4. Water dilution and caustic quench for nitrate in SME product.

Oxalate concentrations were higher by CQ and nearer the values expected based on DWPF TOC and off-gas data. Spike addition of 5000 mg/kg oxalate into sample GN70-S1141 containing 3440 mg/kg of oxalate gave 4180 mg/kg or 84% recovery. Follow on work is suggested to add oxalate at 3 levels into a post nitric sample.

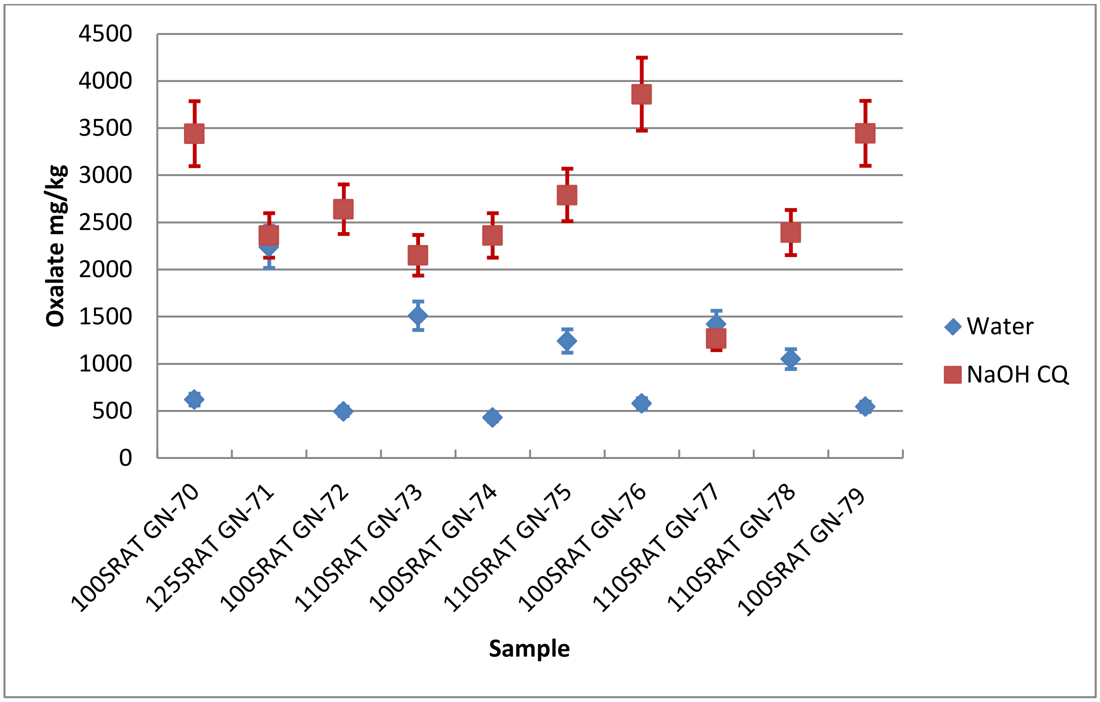

Figure 3-5. Water dilution and caustic quench for Oxalate in SRAT product.

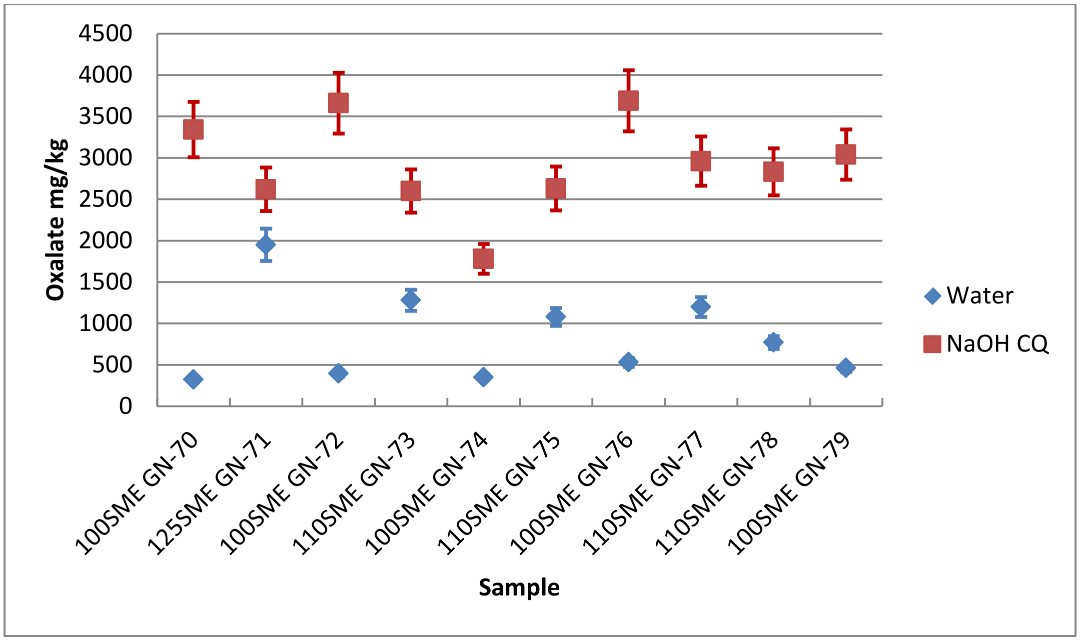

Figure 3-6. Water dilution and caustic quench for Oxalate in SME product.

3.5 Caustic Quench IC versus DWPF TOC

Glycolate and other carbon containing species were converted to a carbon basis and compared to total organic carbon values measured by the DWPF laboratory. For the calculation, less than values were used as is and antifoam was considered to be 500 mg/kg in each sample. For example, <100 mg/kg formate was used as 100 mg/kg formate. Table 3-4 summarizes the carbon values that are plotted in Figure 3-7. All but two high acid stoichiometry samples, 110 GN77 and 110 GN 78, had overlapping error bars. Overall, the results for SRAT product by IC caustic quench were lower than DWPF TOC values by about 10%. This difference could be due to low bias glycolate, formate, and/or oxalate IC values in SRAT samples although glycolate values reasonably match the off-gas data for the CPC in section 3.7. CQ does give improved results that more closely match the TOC over the water dilution protocol.

Table 3-4. SRAT Carbon Amounts

	DWPF TOC	CQ Sum of acids and antifoam	Water Sum of acids and antifoam
Samples	mg/kg C	mg/kg C	mg/kg C
100SRAT GN-70	18900	17700	16800
125SRAT GN-71	20200	17000	18000
100SRAT GN-72	16600	14100	13600
110SRAT GN-73	18300	16400	14200
100SRAT GN-74	17500	15600	14100
110SRAT GN-75	18700	17100	14000
100SRAT GN-76	18300	17000	16100
110SRAT GN-77	19700	16200	14300
110SRAT GN-78	20900	16600	15400
100SRAT GN-79	19700	16400	15300

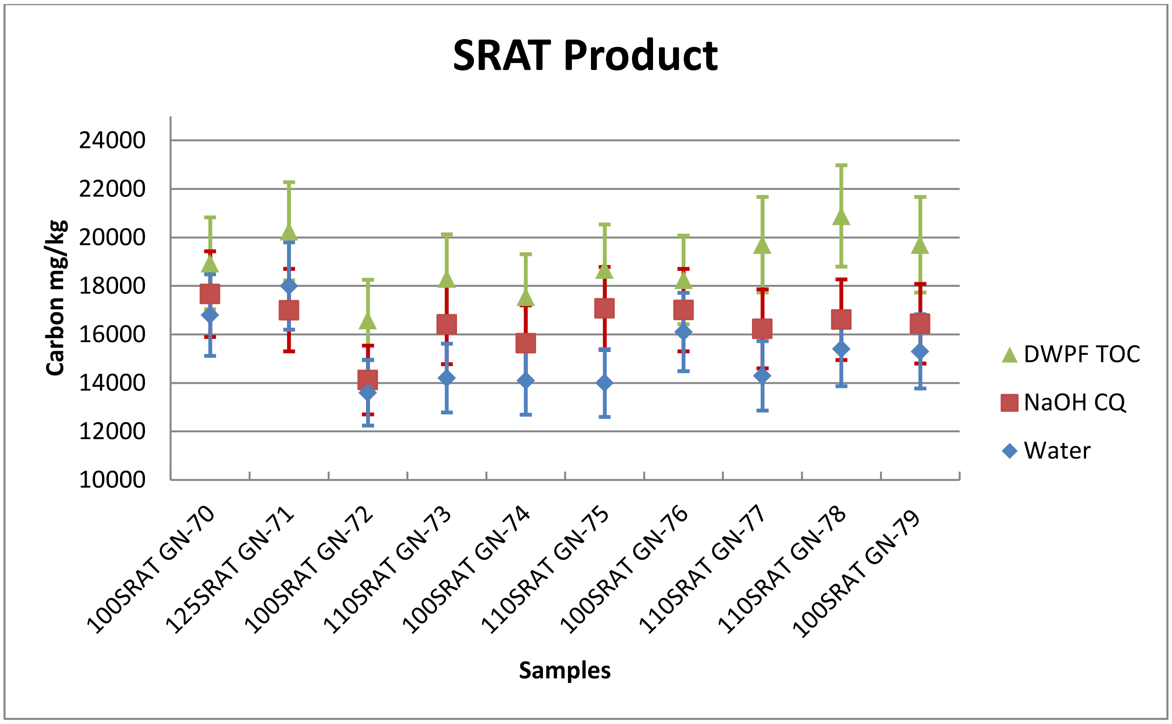

Figure 3-7. IC caustic quench versus DWPF TOC for SRAT Product.

Better overlap of CQ and DWPF TOC values was observed with the SME product where the percent difference for all but GN71 ranged from 1 to 10%. The water dilution values were lower on average by about 12%. One case of deviation was 125SRAT-GN71 TOC analysis. This sample had the highest acid stoichiometry and a concentration of glycolate higher than the low acid stoichiometry runs (labeled 100). In this case, the TOC value is lower than expected from the acid stoichiometry.

Table 3-5. SME Carbon Amounts

	DWPF TOC	CQ Sum of acids and antifoam	Water Sum of acids and antifoam
Sample	mg/kg C	mg/kg C	mg/kg C
100SME GN-70	15800	16400	13600
125SME GN-71	11300	17700	13000
100SME GN-72	13700	14000	11400
110SME GN-73	16000	13800	11300
100SME GN-74	12200	12000	11500
110SME GN-75	15100	14400	11100
100SME GN-76	14300	13500	13000
110SME GN-77	15700	13400	11400
110SME GN-78	15100	14800	12700
100SME GN-79	15100	13400	12600

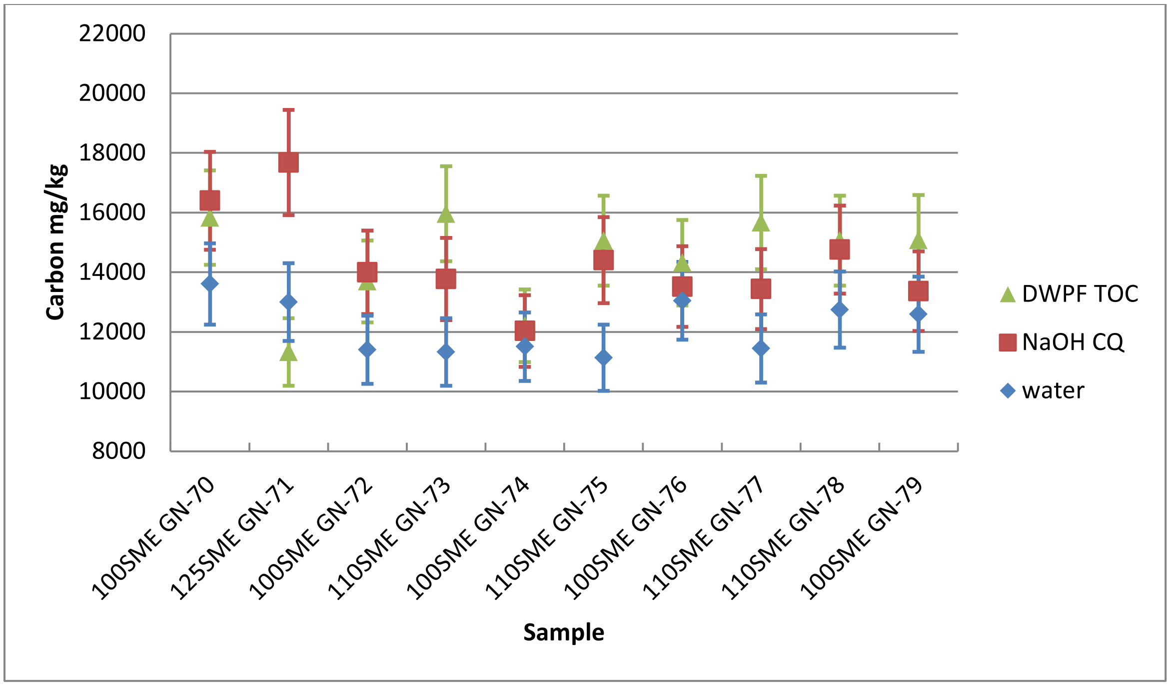

Figure 3-8. CQ versus Water versus DWPF TOC for SME product

3.6 DWPF TOC versus IC supernate versus IC CQ

Two IC preparation methods, CQ and supernate analysis, were used to determine glycolate and other carbon species and the results were compared after conversion to a carbon basis. Historically, the filtration of the sludge samples and analysis of the supernate after water dilution has given higher glycolate values (adjusted back to a slurry basis using four measurements) than water dilution of the sludge samples and analysis. For these runs, the supernate values tended to be lower than CQ values but within error bars for all but GN75. The data sets for CQ and supernate analyses, Table 3-6 and 3-7, are plotted in Figure 3-9 and Figure 3-10. As mentioned earlier, CQ IC analyses match the TOC analyses for the SME product better than the SRAT product. The TOC value for the high stoichiometry acid run GN71 in the SME product on Figure 3-10 is lower than expected and seems biased low. The supernate analysis relies on diluting acid samples with water once the solids have been removed. A glycolate value from this method that is lower than the CQ analysis is not unexpected and trends similar to with the water dilution of slurries seen earlier.

Table 3-6. SRAT Carbon Amounts

	DWPF TOC	CQ Sum of acids and antifoam	Supernate sum of acids and antifoam
Samples	mg/kg C	mg/kg C	mg/kg C
100SRAT GN-70	18900	17700	16800
125SRAT GN-71	20200	17000	18300
100SRAT GN-72	16600	14100	13400
110SRAT GN-73	18300	16100	14400
100SRAT GN-74	17500	15600	13800
110SRAT GN-75	18700	17100	13900
100SRAT GN-76	18300	17000	16900
110SRAT GN-77	19700	16200	14900
110SRAT GN-78	20900	16600	17100
100SRAT GN-79	19700	16400	15300

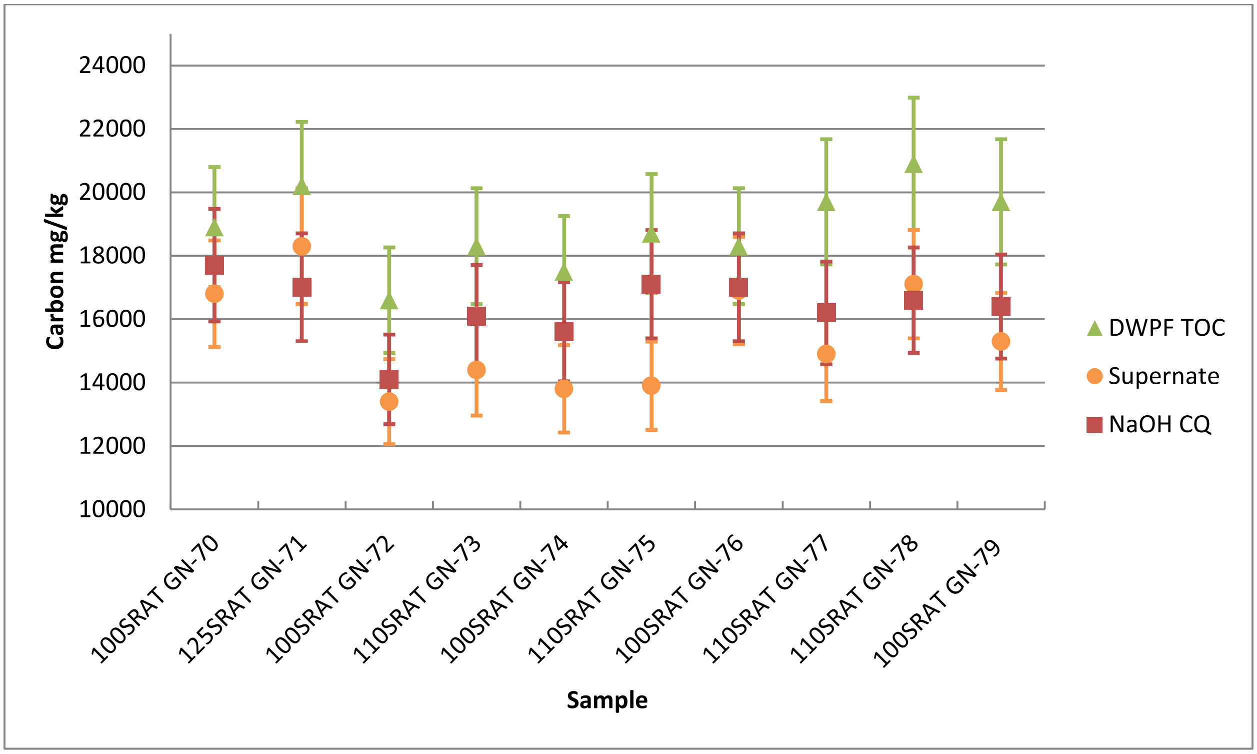

Figure 3-9. SRAT product IC QC versus IC supernate versus DWPF TOC.

Table 3-7. SME Carbon Amounts

	DWPF TOC	CQ Sum of acids and antifoam	Supernate sum of acids and antifoam
Sample	mg/kg C	mg/kg C	mg/kg C
100SME GN-70	15800	16400	14800
125SME GN-71	11300	17700	14900
100SME GN-72	13700	14000	11400
110SME GN-73	16000	13800	11400
100SME GN-74	12200	12000	11400
110SME GN-75	15100	14400	11100
100SME GN-76	14300	13500	13400
110SME GN-77	15700	13400	12300
110SME GN-78	15100	14800	13400
100SME GN-79	15100	13400	12000

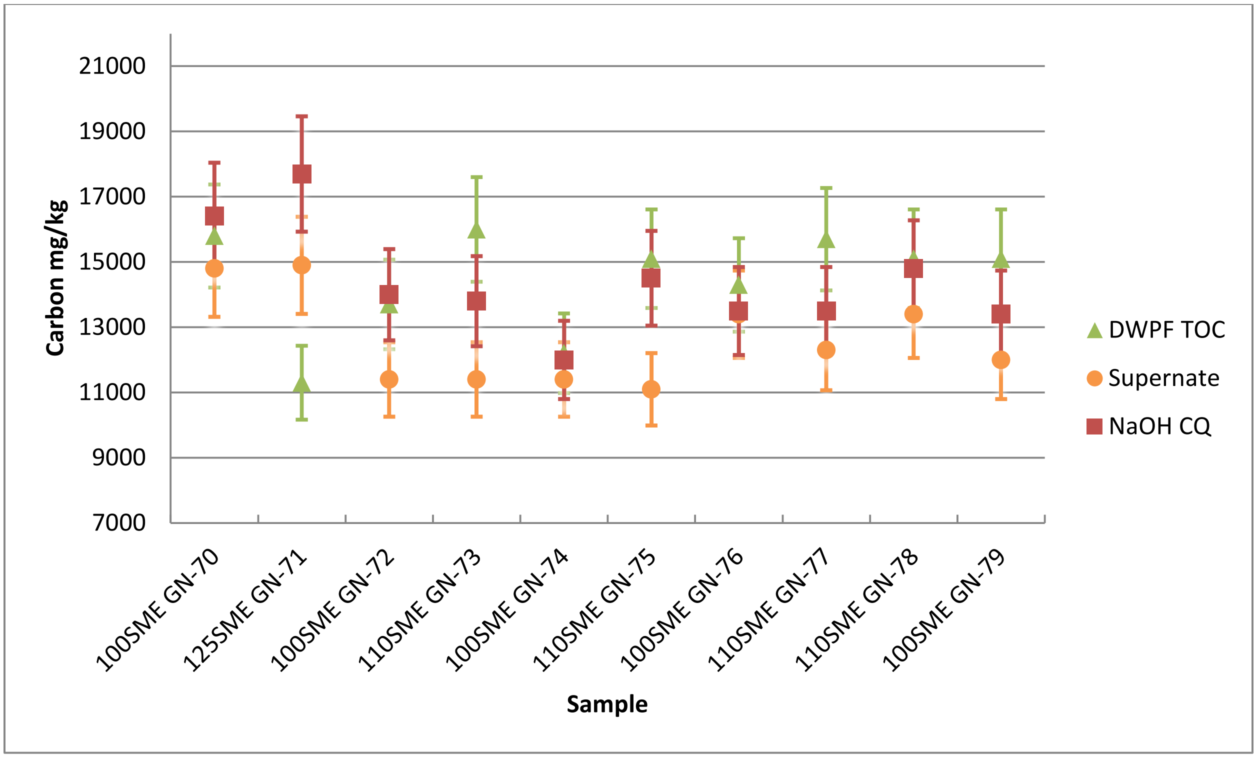

Figure 3-10. SME product IC caustic quench versus IC supernate versus IC caustic quench

3.7 Caustic Quench versus Water versus Off-gas analyses

The off-gas from SRAT bench scales runs was analyzed using inline instrumentation for hydrogen, carbon dioxide, carbon monoxide, nitrogen, nitrous oxide, nitrogen oxide, and oxygen analysis [Newell, 2014]. Figure 3-11 shows the off-gas data converted to glycolate concentration for bench-scale SRAT runs. Water dilution and CQ IC data for glycolate are also graphed to demonstrate the improvement by the CQ method. The CQ values follow the off-gas values more closely while the water dilution values are lower for most runs. The CQ value for 125_71-4L was taken from a CQ analysis done with 3 g of NaOH. The original analysis was considered low and no sample remained for reanalysis. The TOC numbers have been added to this graph as a reference since the total carbon was converted to a glycolate value and the other carbon species are not subtracted out. All other methods should be near or below the TOC values.

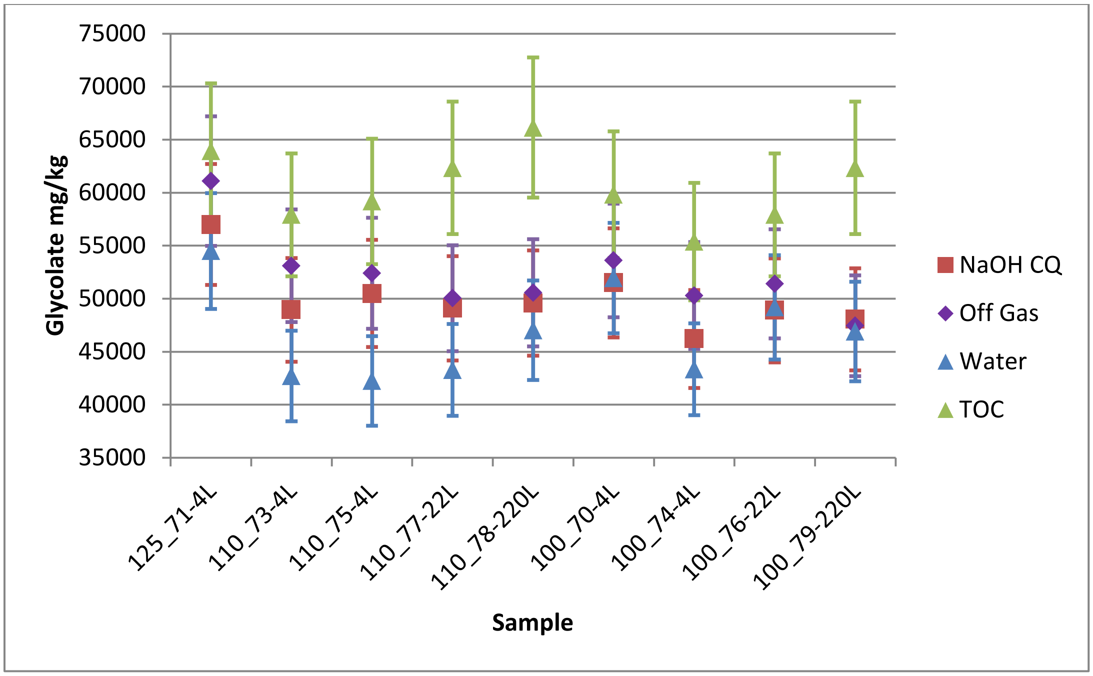

Figure 3-11. SRAT Product

3.8 Caustic Quench with Dilute Base

Samples of GN78-S2180 SME product were prepared using CQ and diluting slurry with 0.1 M NaOH. This might be a simpler preparation method for use in DWPF. The results are summarized in Table 3-8. About 9% lower values for glycolate and oxalate were observed. The dilute base method was expected to give similar values to the CQ method. This method may require a longer waiting time and/or higher base addition such as 0.2 M NaOH to more closely match the CQ method. The CQ method has the potential of rapidly disrupting organic acid metal complexes that are then solubilized for analysis. Since the difference in glycolate values is within the error of the method, addition work was performed to confirm the observation.

Table 3-8. Caustic Quench versus Dilute Base

Units: mg/kg (NaOH quenched)- 10g of sample + 2g NaOH → 1g quenched sample to 100g H2O			
Sample ID	Lab ID	C2H3O3	C2O4
14-GN78-S2180 (A)	S2180	43400	2840
14-GN78-S2180 (B)	S2180	43900	2940
14-GN78-S2180 (C)	S2180	43200	2840
Units: mg/kg (NaOH diluted)- 1g sample in 100 g 0.1 M NaOH solution			
Sample ID	Lab ID	C2H3O3	C2O4
14-GN78-S2180 (A)	S2180	39600	2640
14-GN78-S2180 (B)	S2180	39900	2680
14-GN78-S2180 (C)	S2180	38800	2640

A blind study was performed at AD that limited the independent variables by preparing 5.0 grams of GN77 S-1975 SRAT using water, 0.1 M NaOH, or CQ. All samples were diluted to 500 mL followed by a 1 to 10 fold dilution by weight. These results were the only samples in this report analyzed at AD instead of PSAL using the AS-11HC method. Table 3-9 summarizes the results including comparing to values reported at PSAL. The trend of the data was the same as above where CQ gave the highest glycolate values. The water dilutions gave about 12% lower glycolate values while the 0.1 M NaOH dilution was lower by about 2%.

Table 3-9. AD Blind Study of Glycolate Analysis in SRAT Product using PSAL IC Method

Laboratory	Sample ID	Matrix	Glycolate, mg/kg
AD	1	Water	42700
AD	2	Water	42900
AD	3	0.1 M NaOH	47300
AD	4	CQ	48200
AD	5	Water	43000
AD	6	CQ	48400
AD	7	0.1 M NaOH	47600
AD	8	0.1 M NaOH	47500
AD	9	CQ	48900
PSAL	SRAT Product 14-GN77-S1975	CQ	49100
PSAL	SRAT Product 14-GN77-S1975	Water	43300

For SME product, again the same trend was observed were CQ gave the highest glycolate value and water dilution gave the lowest glycolate value. Table 3-10 summarizes the data where the water dilution is 16% lower and the dilute caustic is 3% lower than the CQ.

Table 3-10. AD Blind Study of Glycolate Analysis in SME Product using PSAL IC Method

Laboratory	Sample ID	Matrix	Glycolate, mg/kg
AD	1	CQ	41300
AD	2	Water	35500
AD	3	0.1 M NaOH	40400
AD	4	Water	35600
AD	5	CQ	41200
AD	6	CQ	42300
AD	7	0.1 M NaOH	40000
AD	8	0.1 M NaOH	40600
AD	9	Water	35700
PSAL	SME Product 14-GN75-S1778	CQ	42300
PSAL	SME Product 14-GN75-S1778	Water	33400

3.9 Addition of More NaOH

Adding more than 2 g for caustic quench was tested with GN 71 SME, GN 73 SRAT and GN 76 SRAT products. An initial study indicated adding more base may increase the glycolate values further as shown in Figure 3-12 where 3 g of 50% NaOH was added. Further investigation where 2, 3, 4, and 5 grams were added to samples found no trend as shown in the remaining figures.

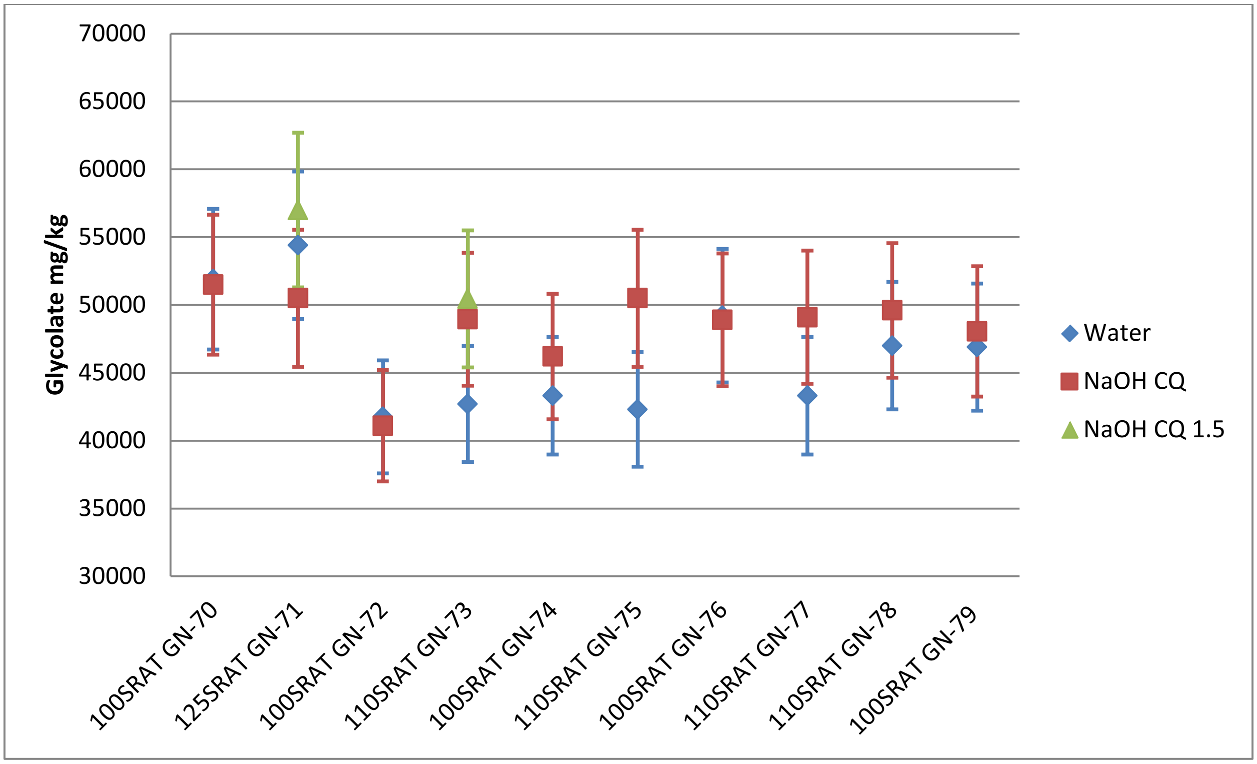

Figure 3-12. SRAT Product CQ at 2 levels of 50% NaOH addition

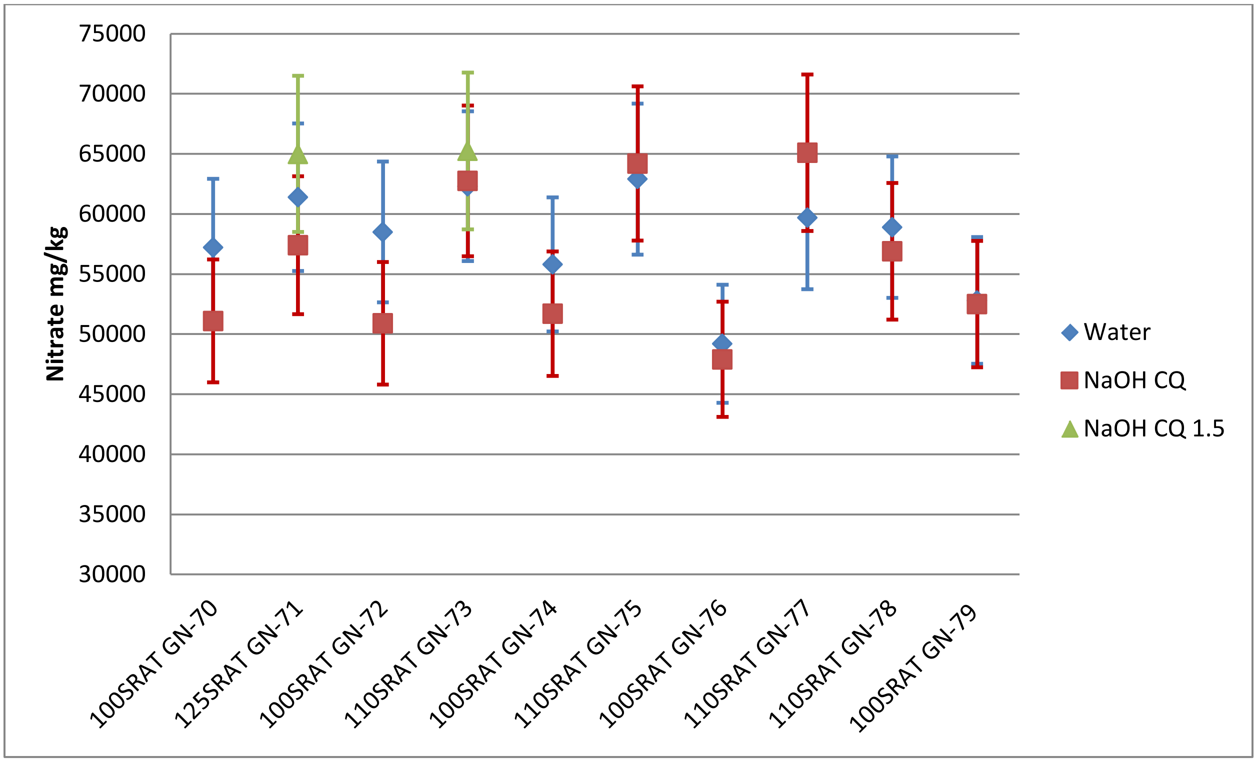

Figure 3-13. SRAT Product CQ at 2 levels

3.10 Impact of Acid Stoichiometry on Caustic Quench Mass Requirement

SRAT and SME product from higher acid stoichiometry runs will have a lower pH and might require a larger caustic addition that lower acid stoichiometry runs. To determine whether the 2 g caustic quench was adequate for all acid stoichiometries, a set of five caustic dilutions was completed for runs GN71 (125% acid stoichiometry), GN73 (110% acid stoichiometry) and GN76 (100% acid stoichiometry were completed. For GN71, the water dilution glycolate value was lower than any of the GN 71 SME product glycolate analyses with base added. The samples plotted along the x-axis are the water dilution, first CQ, and the base addition samples where the grams added are at the end of the name. The addition of additional base does not cause the glycolate or nitrate values to trend upward as shown in the figures below.

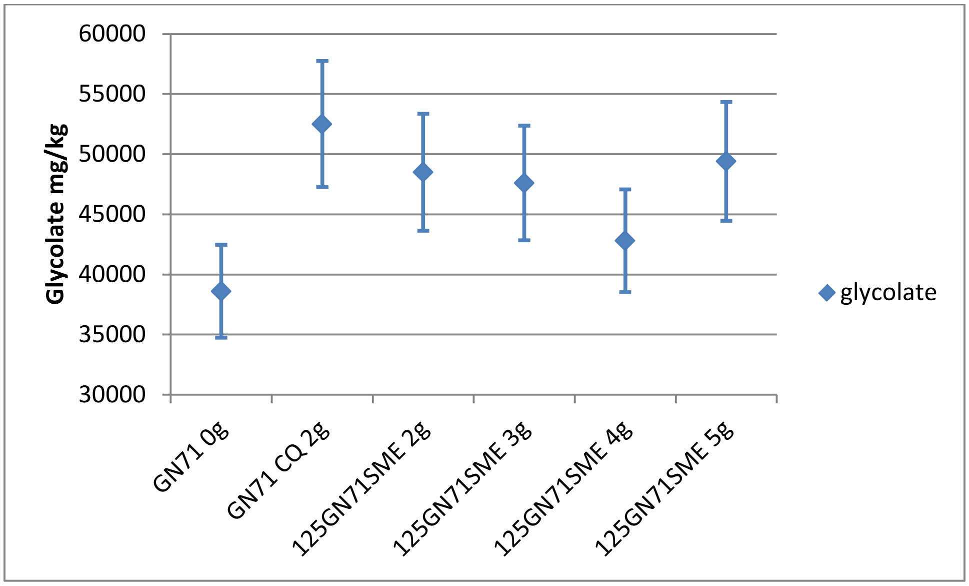

Figure 3-14. SME Product

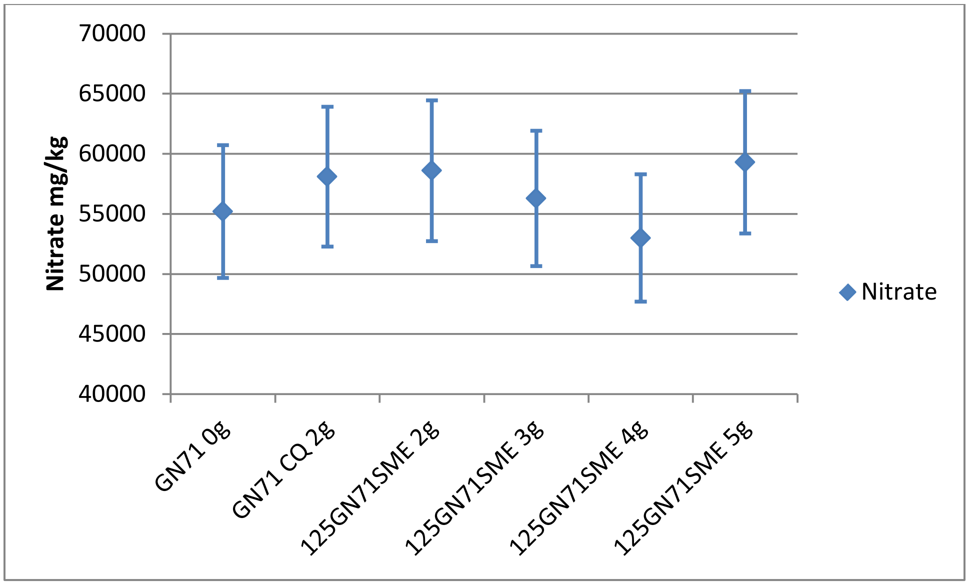

Figure 3-15. SME Product

For GN73 (110% acid stoichiometry), the water dilution glycolate value was lower than any of the GN 73 SRAT product glycolate analyses with base added. The samples plotted along the x-axis are the water dilution, the first CQ, and the base addition samples. The 4g-2 and 5g samples were analyzed on a different day than the 2g, 3g, and 4g-1 samples. The addition of additional base does not cause the glycolate or nitrate values to trend upward as shown in the figures below.

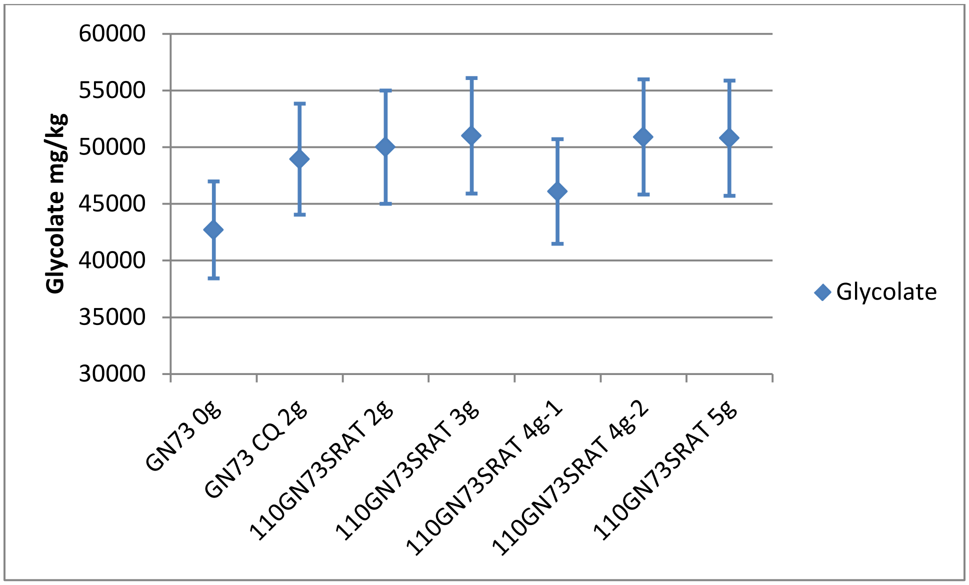

Figure 3-16. SRAT Product

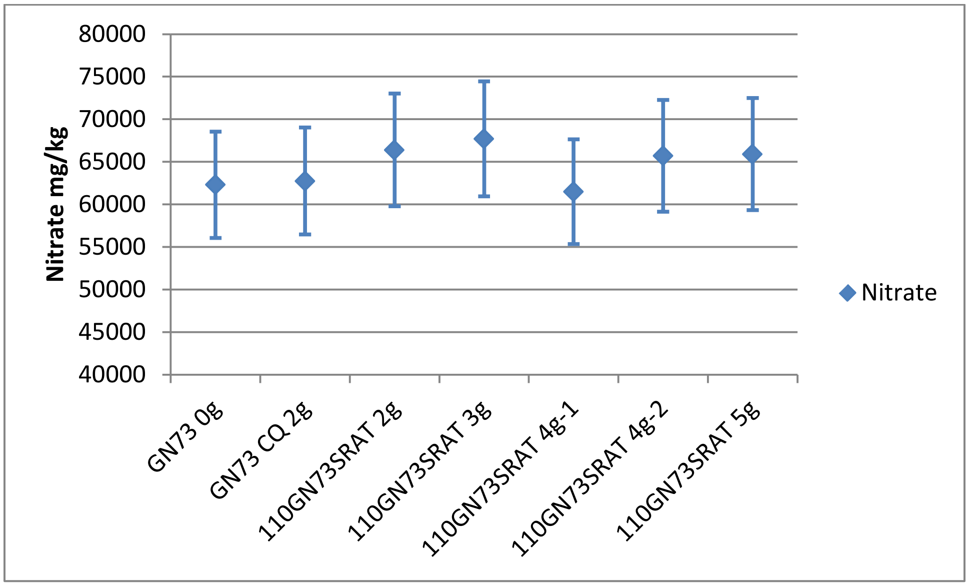

Figure 3-17. SRAT Product

For GN76 (100% acid stoichiometry), the water dilution glycolate value was similar to the GN 73 SRAT product glycolate analyses with base added. This sample had an acid stoichiometry of 100% where the water dilution and CQ tend to give similar values for glycolate and nitrate. The 4g and 5g samples were analyzed on a different day than the 2g, 3g, and 4g samples. The addition of additional base does not cause the glycolate or nitrate values to trend upward as shown in the figures below.

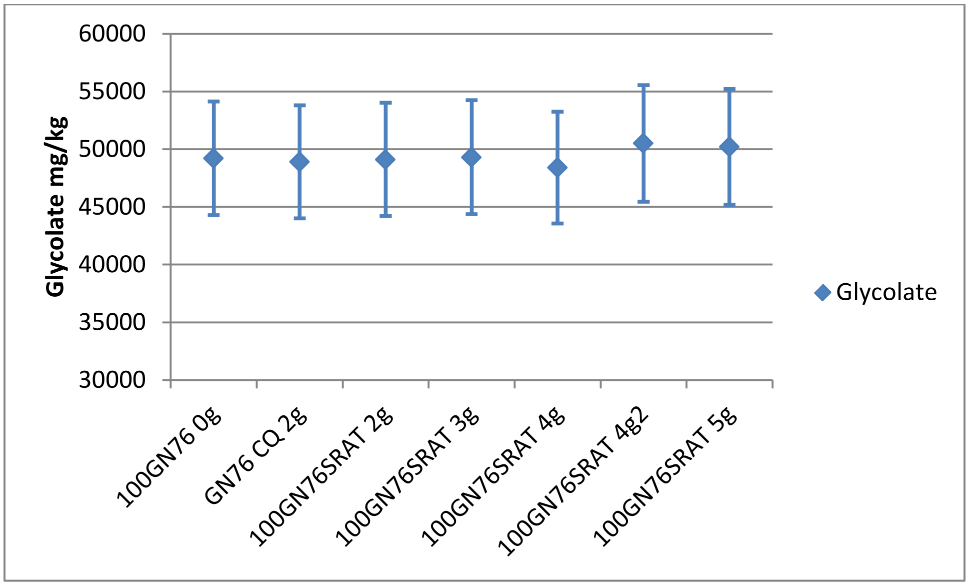

Figure 3-18. SRAT Product

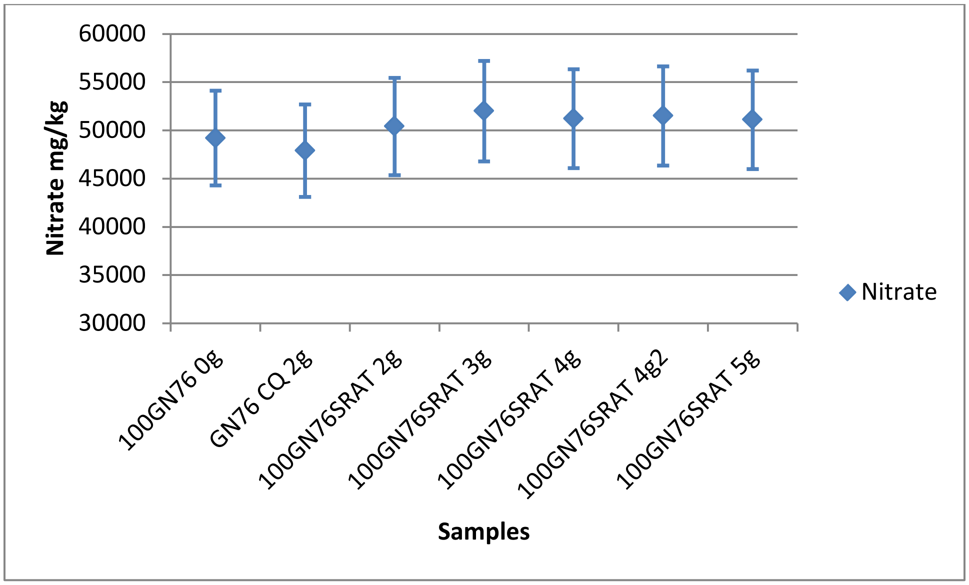

Figure 3-19. SRAT Product

Oxalate increased in value over the water dilution for all three runs as shown below.

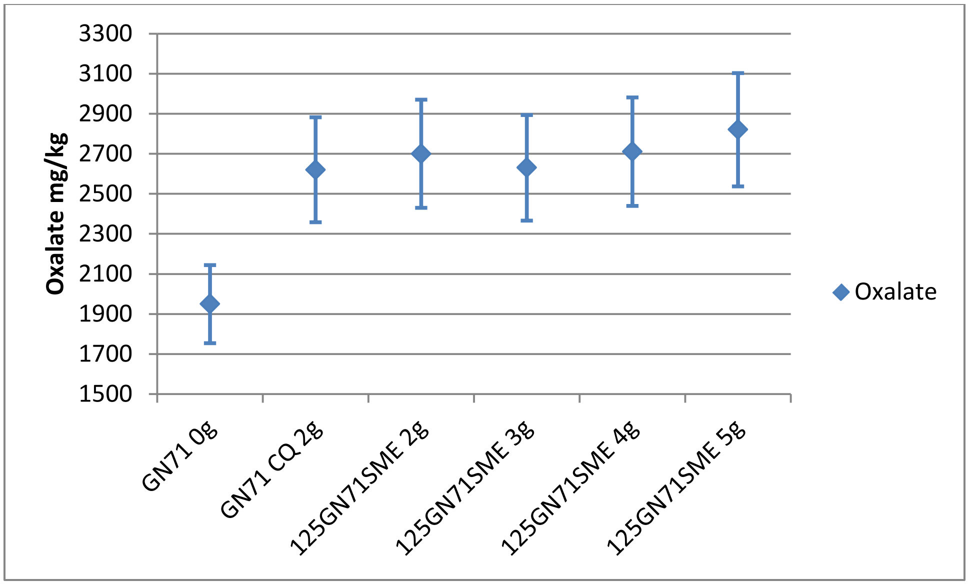

Figure 3-20. SME Product

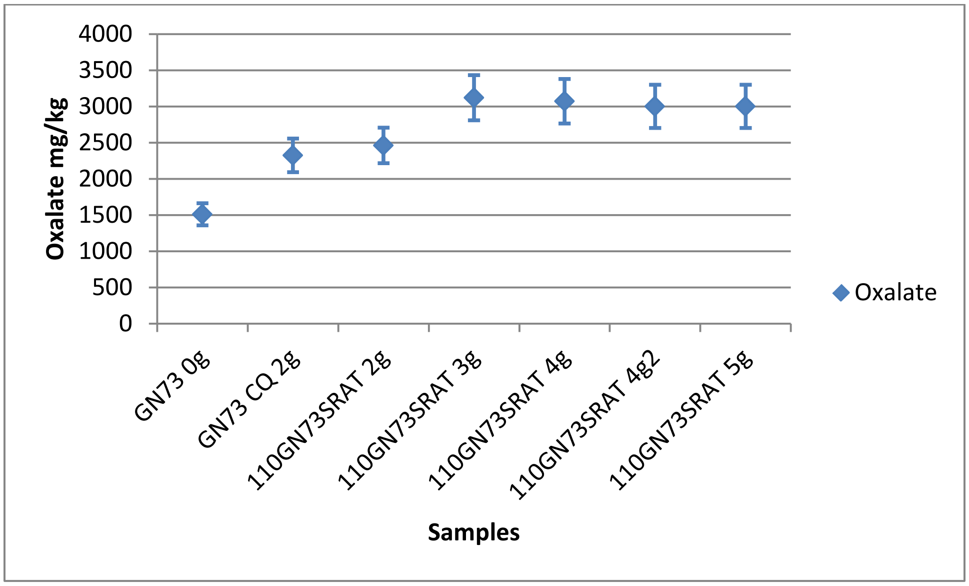

Figure 3-21. SRAT Product

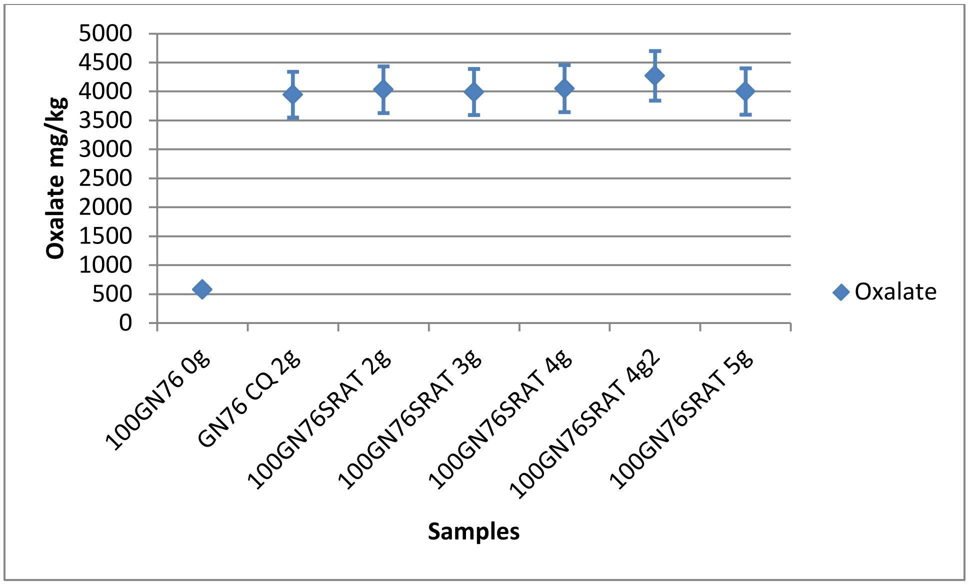

Figure 3-22. SRAT Product

Formate also increased from water dilutions. This result is different from the analysis from the archived samples that did not change in value.

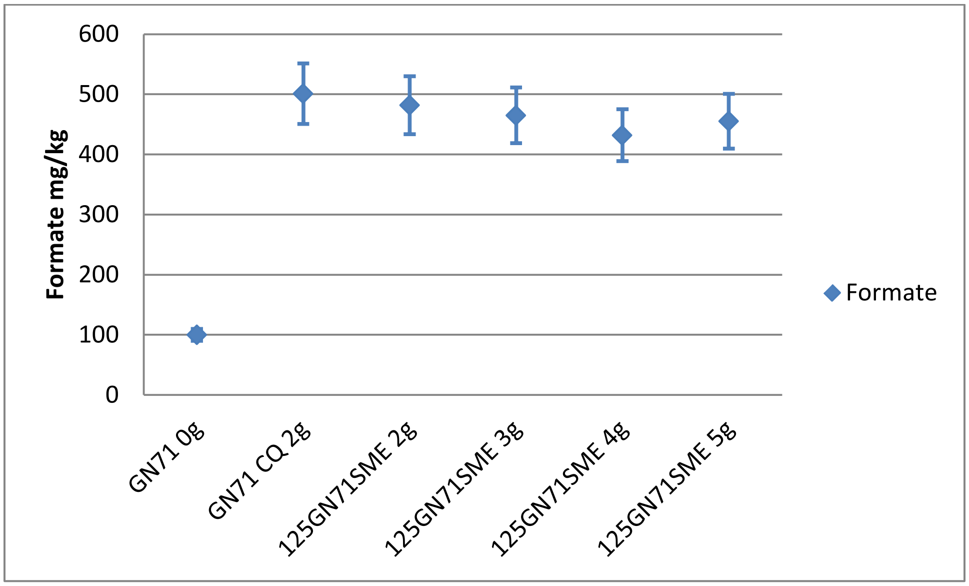

Figure 3-23. SME Product

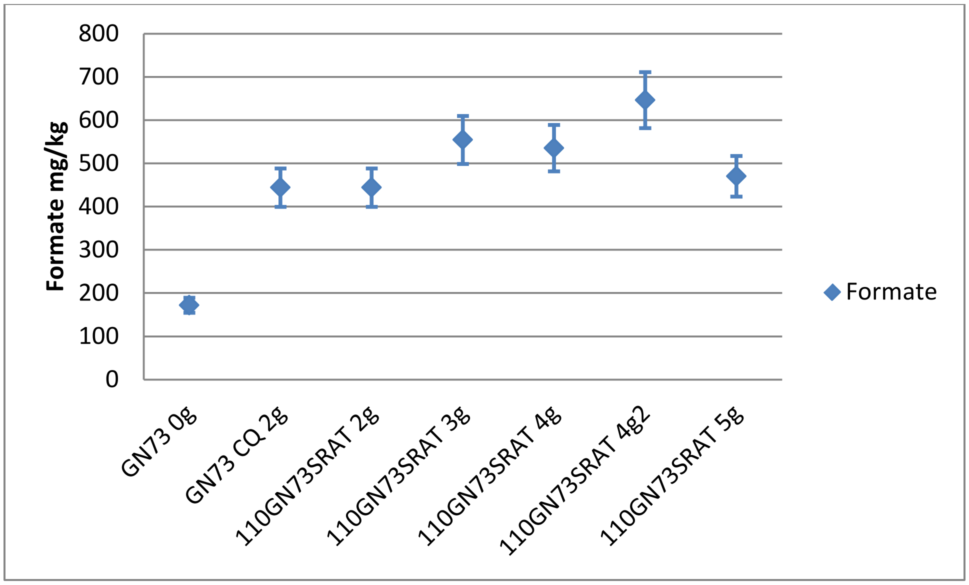

Figure 3-24. SRAT Product

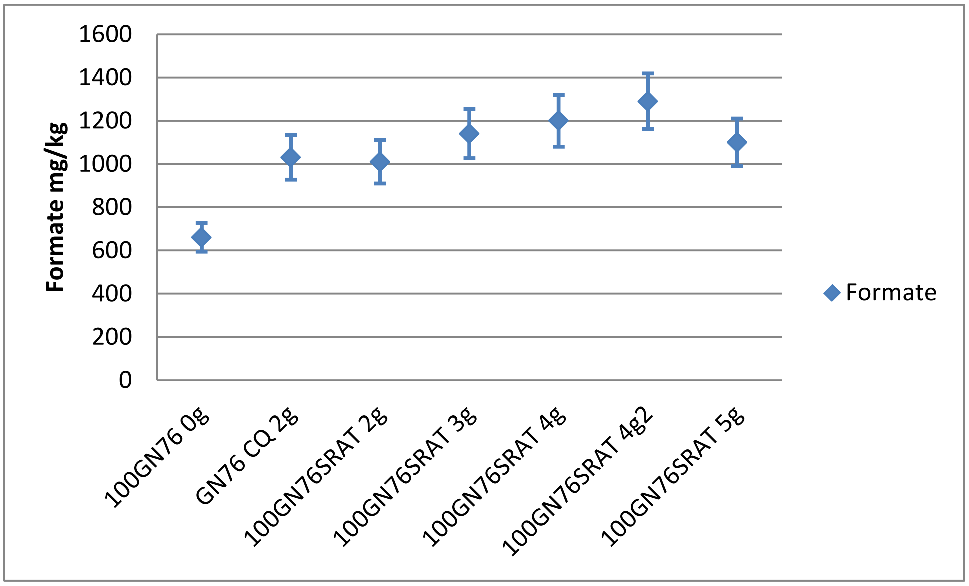

Figure 3-25. SRAT Product

3.11 Oxalate results for CQ versus water dilution

During the development of the CQ method, it was found that the oxalate values were much higher than for the water dilution. Currently, DWPF does an additional set of analyses using an HCl/HNO_3 digestion to more accurately measure oxalate. However, this is a very aggressive dissolution method (similar to aqua regia) that often leads to lower than actual oxalate results if not analyzed quickly or when exposed to light. Figure 3-26 and Figure 3-27 summarize the oxalate values from the bench scale runs. All oxalate values for the CQ method were higher than the values from water dilution. The nominal value for oxalate for the runs was around 2500 mg/kg which is near the values found by the CQ method. Note that oxalate can be formed during the SRAT reactions, so the exact value in SRAT and SME products is not known. Implementation of the CQ method might eliminate the need for a special method for oxalate. However, further testing would be required to determine if the CQ method was effective in dissolving relatively insoluble oxalates such as calcium oxalate.

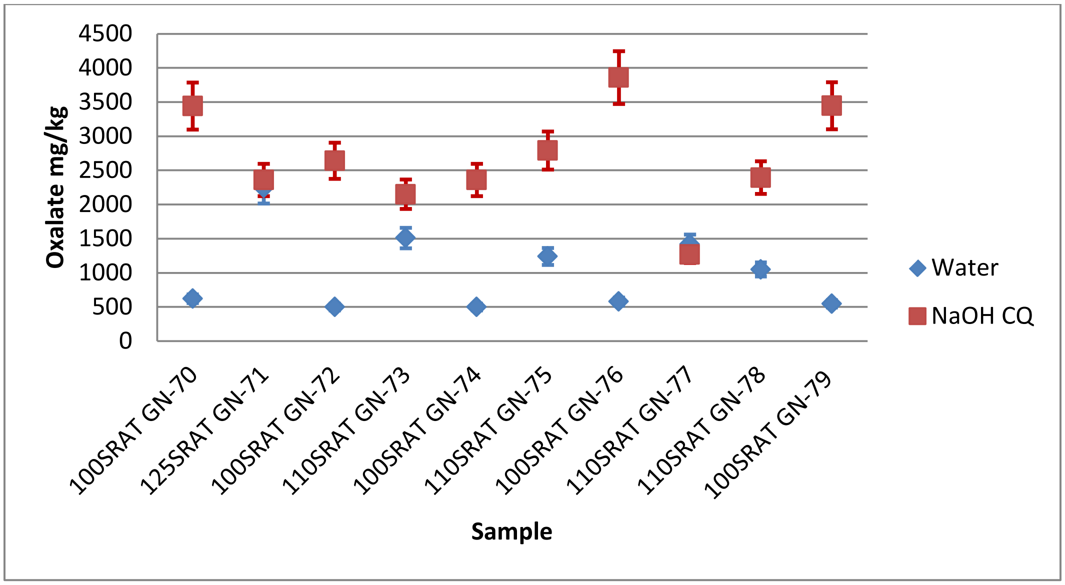

Figure 3-26. SRAT Product

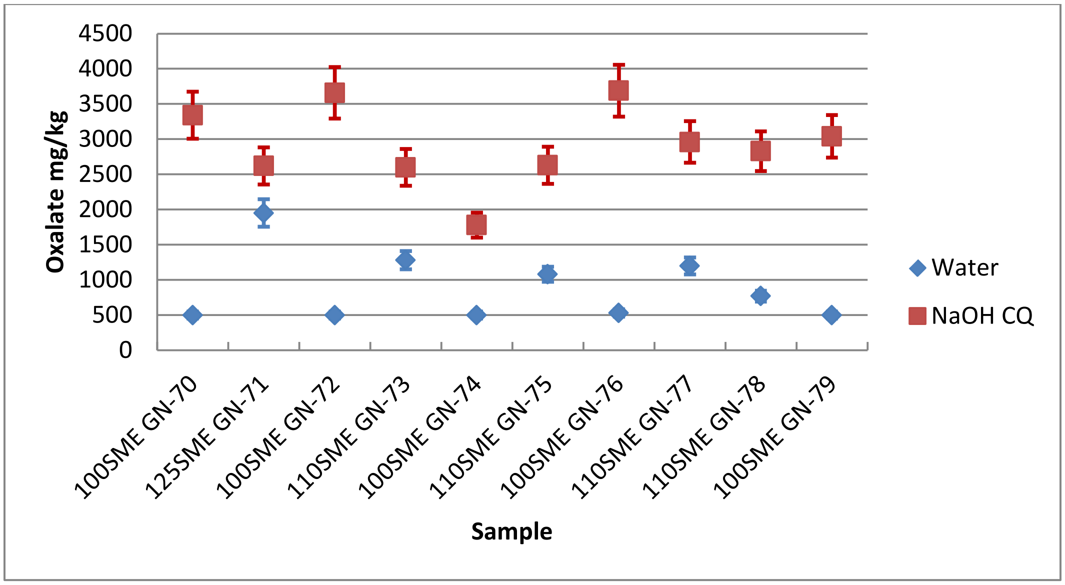

Figure 3-27. SME Product

3.12 Water versus IC CQ on archived samples

In order to demonstrate that the IC CQ method works for sludge batches other than SB9 and both sludge preparation methods (simple precipitation of Fe and Ni versus co-precipitation of all metals) other samples from CPC runs were examined. As a result, samples from previous bench-scale glycolate flowsheet runs were examined by CQ and compared to the water diluted results. The expectation from prior results was higher glycolate values, higher oxalate values, and little change in the nitrate values. Figure 3-29 shows the glycolate values were higher for CQ in all cases while the values for nitrate in Figure 3-30 were slightly elevated and all error bars over lapped. Oxalate showed elevated values while formate values were similar regardless of sample preparation. The CQ values matched the off-gas data better than the water dilution values, although several off-gas points do not overlap the CQ data. These archived samples were several years old, so it does not seem unlikely that some of the glycolate could have decomposed. Also, the Total Inorganic Carbon (TIC) values for the feeds for some of these runs were higher than expected, so the amount of CO_2 subtracted would be higher, and result in lower glycolate destruction and higher equivalent product glycolate.

Table 3-11. Archived Samples

Sample	Sludge Batch	Acid Stoichiometry (%)
106_GN36-S2864	SB6i	106
100_GN34b-S2865	HiFeHiMn	100
100_GN38-S2866	LoFeLoMn	100
130_GN40-S2867	2.0M Na SB8-B	130
85_GN44-S2868	SB6J blend	85
90_GN46-S2869	SB6J	90
100_GN49-S2870	SB6J	100
100_GN52-S2871	SB6i	100
110_GN64-S2872	-	110
100_CEF Phase 2-S2873	-	100

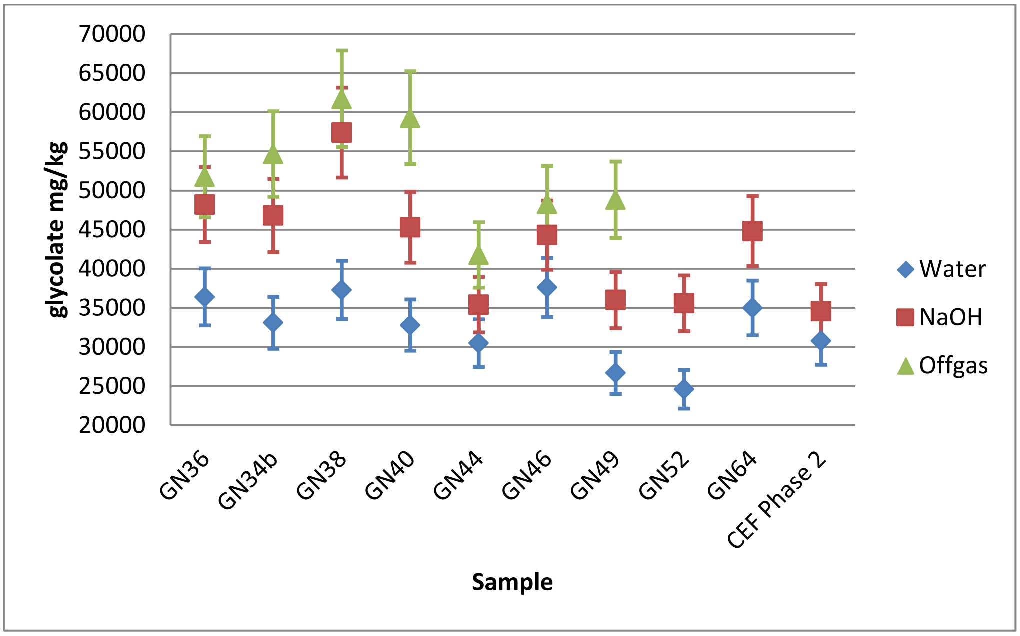

Figure 3-28. Glycolate in Archived Alternate Reductant Samples.

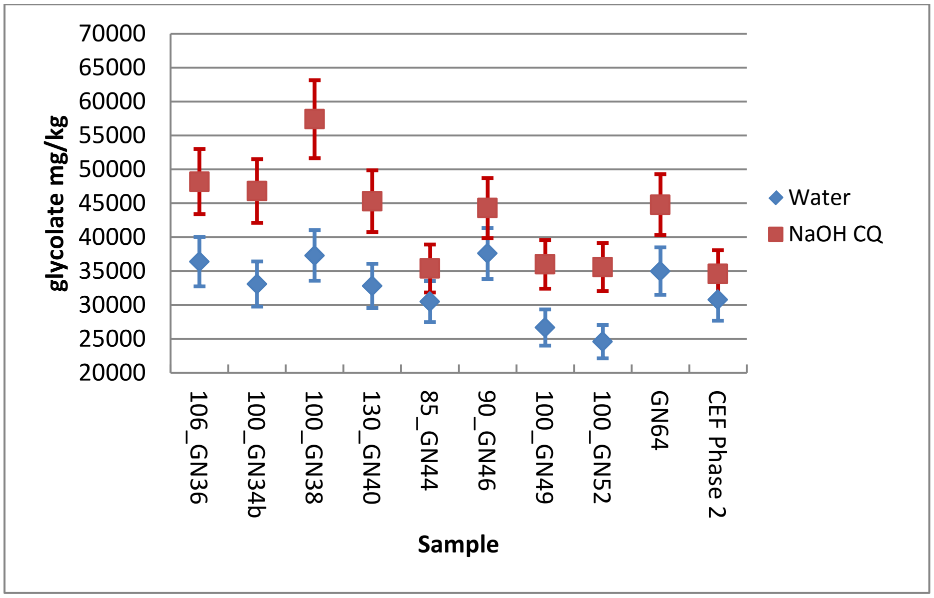

Figure 3-29. Glycolate in Archived Alternate Reductant Samples.

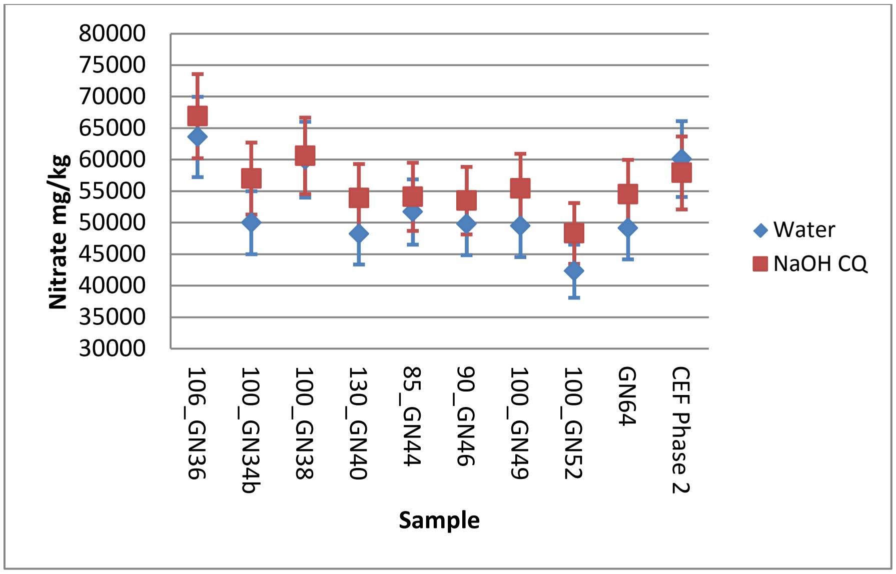

Figure 3-30. Nitrate in Archived Alternate Reductant Samples.

Oxalate showed increase values as seen with the GN70 to GN79 runs.

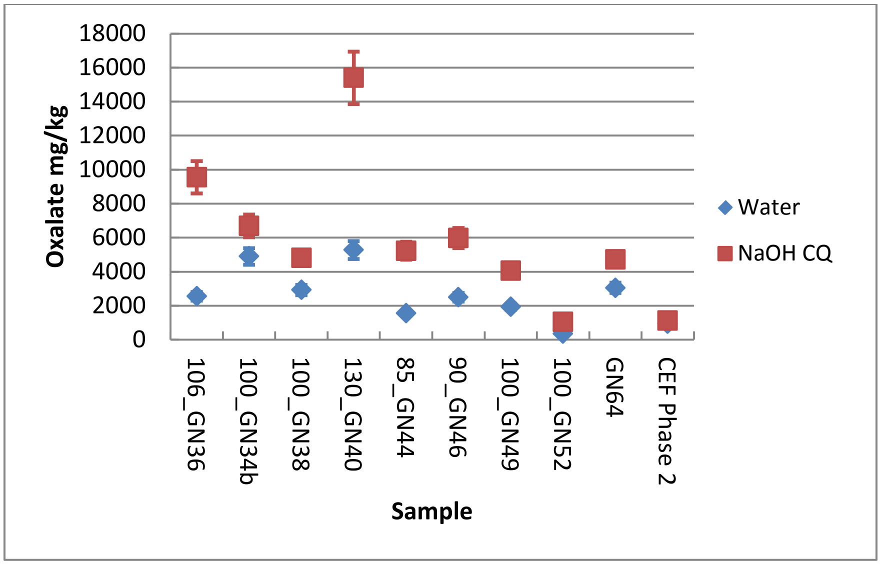

Figure 3-31. Oxalate in Archived Alternate Reductant Samples.

Formate values were similar for CQ and water dilution. For the

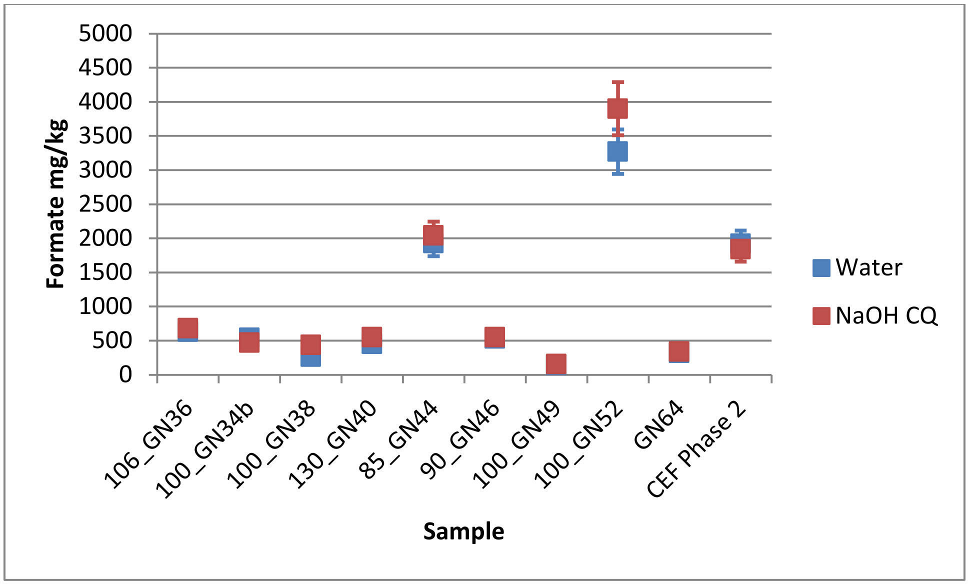

Figure 3-32. Formate in Archived Alternate Reductant Samples.

3.13 Formic acid flowsheet QC vs water initial testing

Formic acid and nitrate values were similar by IC while oxalic acid values were increased. The oxalate increase follows what was observed with the glycolate flowsheet analyses.

Table 3-12. Formic acid Flowsheet Samples

Units: mg/kg				
Sample ID	Method	NO3	HCO2	C2O4
14-SB8-D9-S2807 (A)	Water	36800	46400	886
14-SB8-D9-S2807 (B)	Water	33000	42000	929
14-SB8-D9 SRAT- S2807 NaOH	CQ	36000	47100	6670
14-SB8-D8-S2781 (A)	Water	35300	45400	595
14-SB8-D8-S2781 (B)	Water	34700	46200	527
14-SB8-D8 SRAT S-2781	CQ	34900	47900	6500

4.0 Conclusions

The CQ method is recommended as the preferred anion method for the nitric-glycolic flowsheet for acid slurries. Initial testing for the formic ac recommended as an improved method for the current nitric-formic flowsheet as an improved method for all anions, including oxalate and might eliminate the need for DWPF to use an additional IC method for oxalate. The CQ method for IC gave similar or higher glycolate and higher oxalate values than the water dilution sample preparation method without changing the values for the other anions (especially nitrate and formate, which are important for REDOX prediction).

To demonstrate that the CQ values are accurate, they were compared to two independent methods. First, the measured anion values were used to calculate the TOC value and this was compared to values measured by the DWPF laboratory. The CQ glycolate values plus other carbon species matched well with DWPF TOC analyses for the SME. The same comparison for the SRAT showed about a 10% difference between the two methods where IC values were lower. Lastly, offgas data collected during SRAT and SME cycles (CO and CO_2 generation) were used to calculate the glycolate destruction. This glycolate destruction was compared to the glycolate destruction calculated from the SRAT and SME product anion results. The CQ method anion data values compare well with off-gas data from bench-scale CPC studies. This agreement demonstrates that the CQ method for acid slurries can be accurate at predicting the anion concentrations.

It was demonstrated that adding additional hydroxide above the nominal 2 grams per 10 g of sample used in the CQ method did not give improved results. Addition of dilute base to acid slurries gave slightly lower values than the CQ method.

After development of the CQ protocol, a SRAT product and SME product was analyzed by AD using the PSAL IC method. Three sample preparation methods were used on 5 grams of sample, mainly, water dilution, 0.1 M NaOH dilution, and CQ. The results for glycolate matched PSAL results within 5% for water dilution and CQ. Glycolate values by water dilution were the lowest and the CQ protocol gave the highest values.

Recommendations

The CQ method should be used for acidic slurry IC anion measurements for SRAT product and SME product with the glycolic acid flowsheet.

When using the CQ method, it is recommended to analyze multiple samples and average to limit error.

Future Work

No testing of the CQ method has been completed with actual waste. The CQ method should be tested with actual waste when appropriate.

The CQ method should be tested on Formic acid flow sheet SME samples.

Test against AD higher pH mobile phase method should occur.

Test method on caustic solutions such as SRAT heel and incoming caustic sludge should occur.

Additional testing is needed to determine if the CQ method could be simplified for use at DWPF.

Spike addition of 5000 mg/kg oxalate into sample GN70-S1141 containing 3440 mg/kg of oxalate gave 4180 mg/kg or 84% recovery. Follow on work is suggested to add oxalate at 3 levels into a post nitric sample and a time study to determine how long the sample should be in contact with the base prior to analysis. In addition, a comparison between the current DWPF acid strike method for oxalate and CQ should be made.

5.0 References

Edwards, T. B. *Uncertainties of Anion and TOC Measurements at the DWPF Laboratory*, SRNL-STI-2011-2014 Revision 1, Technical Report for Savannah River National Laboratory: Aiken, SC, April 2011.

Jantzen, C. M.; Johnson, F. C. *Impacts of Antifoam Additions and Argon Bubbling on Defense Waste Processing Facility (DWPF) REDuction/Oxidation (REDOX)*, SRNL-STI-2011-00652, Technical Report for Savannah River National Laboratory: Aiken, SC, June 2012.

Karraker, R. H. Stability Constants of Some Rare-earth-metal Chelates, PhD. Thesis, Iowa State University of Science and Technology, 1961.

Lambert, D. P.; Zamecnik, J. R.; Best, D. R. FY13 Glycolic-nitric Acid Flowsheet Demonstrations of the DWPF Chemical Process Cell with Simulants, SRNL-STI-2013-00343, Technical Report for Savannah River National Laboratory: Aiken, SC, March 2014.

J.D. Newall, D.P. Lambert, J.R Zamecnik Impact of Scaling on the Glycolic-Nitric Acid Flowsheet, SRNL-STI-2014-00306, Technical Report for Savannah River National Laboratory: Aiken, SC, Draft.

Pickenheim, B. R.; Stone, M. E.; Peeler, D. K. *Selection and Preliminary Evaluation of Alternative Reductants for SRAT Processing*, SRNL-STI-2009-00120, Technical Report for Savannah River National Laboratory: Aiken, SC, June 2009.

Portanova, R.; Lajunen, L. H. J.; Tolazzi, M.; Piispanen, J. Critical Evaluation of Stability of Constants for Alpha-hydroxycarboxylic Acid Complexes with Protons and Metal Ions and the Accompanying Enthalpy Changes Part II. Aliphatic 2-Hydroxycarboxylic Acids, *Pure Appl. Chem*, **2003**, *75*, 495-540.

Wiedenman, B. J.; White, T. L.; Mahannah, R. N.; Best, D. R.; Stone, M. E.; Click, D. R.; Lambert, D. P.; Coleman, C. J. *Development of Ion Chromatography Methods to Support Testing of the Glycolic Acid Reductant Flowsheet in the Defense Waste Processing Facility*, SRNL-STI-2013-00294, Technical Report for Savannah River National Laboratory: Aiken, SC, October 2013.

Zamecnik, J. R. Alternative Reductant REDOX Prediction and CPC Chemistry – Path Forward, SRNL-L3100-2014-00254, Rev. 0, Memorandum for Savannah River National Laboratory: Aiken, SC, February 2015.

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A. Samadi-Dexfouli, 704-27S
H. B. Shah, 766-H
D. C. Sherburne, 704-S
M. E. Stone, 999-W