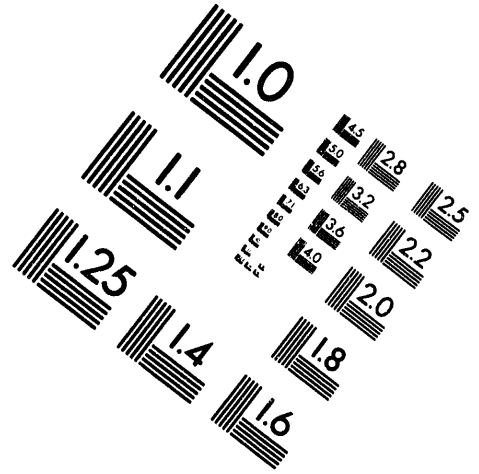
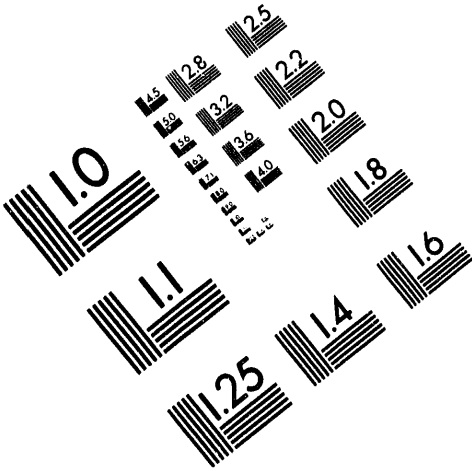




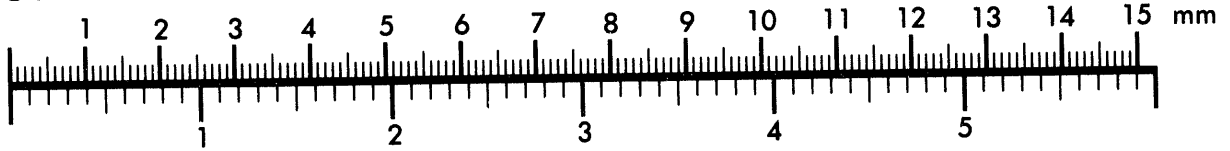
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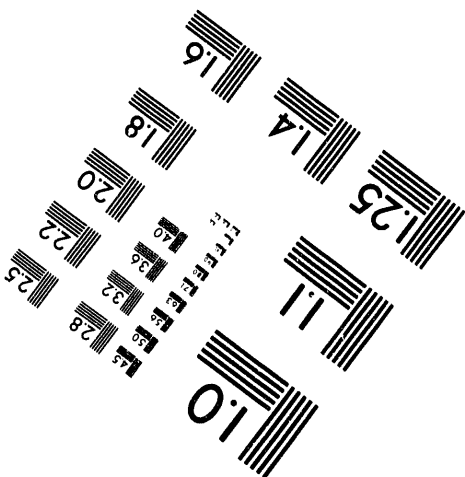
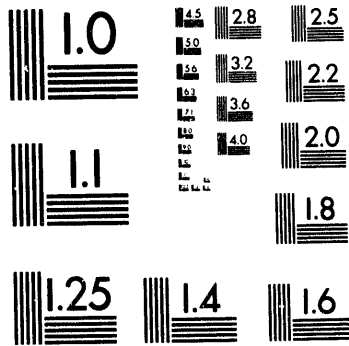
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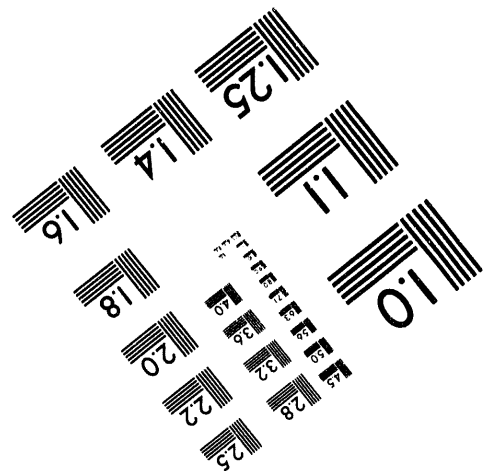
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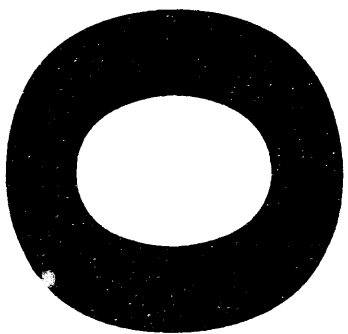
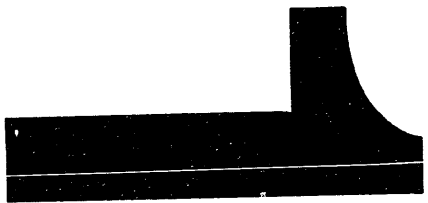


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WSRC-MS-94-0121

**A COMPARISON OF THREE METHODS FOR DETERMINING
THE AMOUNT OF NITRIC ACID NEEDED TO TREAT HLW
SLUDGE AT SRS**

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A document prepared for SPECTRUM '94 at Atlanta, GA from 8/14/94 thru 8/18/94.

DOE Contract No. DE-AC09-89SR18035

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A COMPARISON OF THREE METHODS FOR DETERMINING THE AMOUNT OF NITRIC ACID NEEDED TO TREAT HLW SLUDGE AT SRS

by

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A paper proposed for presentation at the
Spectrum '94 meeting
Atlanta, Georgia
August 16, 1994

and for publication in the proceedings

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ABSTRACT

A comparison was made of three methods for determining the amount of nitric acid which will be needed to treat a sample of high-level waste (HLW) sludge from the Savannah River Site (SRS) Tank Farm. The treatment must ensure the resulting melter feed will have the necessary rheological and oxidation-reduction properties, reduce mercury and manganese in the sludge, and be performed in a fashion which does not produce a flammable gas mixture. The three methods examined were an empirical method based on pH measurements, a computational method based on known reactions of the species in the sludge, and a titration based on neutralization of carbonate in the solution.

Results from the computational method had to be adjusted to ensure the oxidation-reduction potential of the product would be compatible with the vitrification process. The predicted nitric acid requirement from the empirical method was three times greater than the requirement from the computational method. Although the nitric acid volumes varied greatly, both products were compatible with the DWPF vitrification process. Because appropriate samples will not be available at the Defense Waste Processing Facility (DWPF), the titration method that was initially examined, was not used in the final comparison of the methods.

Because more nitric acid was used, more of the sludge solids were solubilized using the result from the empirical method, including manganese which can be involved in foaming during the vitrification process.

The two methods were equally as effective at reducing the mercury and keeping hydrogen generation rates low enough to avoid flammability concerns during sludge slurry treatment.

I. INTRODUCTION

HLW sludge and supernate will be immobilized by vitrification at SRS. The sludge and supernate must first be treated to make them compatible with the vitrification process. The supernate will be treated by precipitating the radionuclides from the solution and concentrating the

resulting slurry. Organic material in the resulting concentrated slurry will then be destroyed by hydrolysis with formic acid to form a material called the precipitate hydrolysis aqueous (PHA).

The sludge will be treated with nitric acid and then PHA which contains formic acid. The treatment process must

- remove mercury from the sludge
- reduce manganese from MnO_2 to Mn^{2+}
- be performed without producing a flammable mixture of hydrogen from the noble metal catalyzed decomposition of formic acid
- produce material with the proper oxidation-reduction potential
- produce material with the proper rheological properties

To treat the sludge, formic acid in the PHA and 8 N nitric acid are to be used. To determine the amount of nitric acid which is needed, three methods have been used, an empirical method based on the effect of nitric acid on the pH of the sludge slurry,¹ a computational method based on the known reactions of species in the sludge,² and a high temperature titration of the sludge.

The goal of this study was to compare these three methods.

II. EXPERIMENTAL

This study was performed in two phases. First, each method was used to determine the nitric acid volume needed. Then, the results from two methods were compared by treating and then analyzing the sludge.

The radiation fields produced by the sludge required most of this work to be done remotely. The tests were performed by highly-skilled manipulator operators.

parallel to the DWPF process.¹ Ten milliliters of the sludge mixture were added to each of ten centrifuge tubes. The tubes were then kept at 92°C for an hour.

Then, different aliquots of 8 N nitric acid were added to each tube, and they were again held at 92°C for an hour. Afterwards, twelve milliliters of PHA were added to each tube. The PHA volume was based on the sludge-to-PHA ratio from a DWPF material balance.³ The tubes were then held at 92°C for six hours.

After the final heating, slurries were allowed to cool, and pH values were measured. The nitric acid requirement was determined by the acid necessary to bring the slurry pH to below 5.

Although the empirical method was performed with twelve milliliters of PHA and ten milliliters of sludge, a model developed to optimize the glass wastefrom composition indicated 146 milliliters of PHA would be more appropriate for 90 milliliters of sludge. Therefore, slight adjustments were made in the nitric acid needed.

While the empirical method was developed to determine the acid needed to bring the sludge to a pH of 5, the computational method was created to determine the acid needed to react with the primary acid-consuming species in the sludge. The computational method was performed by determining the concentrations of several species known to react with formic and nitric acids.² To determine these concentrations, the slurry was filtered. The filtrate was analyzed for nitrite, manganese, and hydroxide. In addition, the carbonate/bicarbonate concentration in the slurry was determined by measuring the carbon dioxide released as the slurry was titrated with 8 N nitric acid.

To determine the mercury and manganese concentrations, a sample of the slurry was dried in a microwave oven and digested by peroxide fusion.

The formic acid concentration in the PHA was determined by titrating the slurry to a pH of 7, and the nitric acid concentration was measured by ion chromatography. Other analyses used are listed in Table 1.

Once the concentrations were measured, the nitric acid needed was determined by an algorithm based on reaction stoichiometries and the amount of sludge to be dissolved.²

Finally, the third method used to determine the nitric acid needed was by titrating the slurry with 8 N nitric acid at 92°C. The endpoint was the point at which the slurry was depleted of carbonate. The endpoint was identified by measuring carbon dioxide using gas chromatography.

<u>Analysis Method</u>	<u>Species</u>	<u>Matrix</u>
Ion Chromatography	NO ₂ ⁻	Sludge Filtrate
ICP-AES	Soluble Mn	Sludge Filtrate
Titration	OH ⁻	Sludge Filtrate
Atomic Absorption	Hg	Sludge Solids
ICP-AES	Total Mn	Sludge Solids
Titration	HCO ₃ ⁻ , CO ₃ ²⁻	Sludge Slurry
Titration	HCO ₂ ⁻	PHA
Ion Chromatography	NO ₃ ⁻	Nitric Acid

B. Comparison of the Sludge Products from the Three Determination Methods

The method and apparatus used to treat the sludge slurry has been described⁴ and will be summarized here.

The treatment was modeled after the DWPF process. It was performed by holding 90 milliliters of the slurry at 92°C as the appropriate volume of 8 N nitric acid was added. The slurry was then held at 92°C for an hour.

Next, the slurry was boiled as 146 milliliters of nonradioactive PHA were added over twenty hours.

After all the PHA was added, the mixture was refluxed for nine hours to continue mercury removal. Once the slurry cooled, samples were taken, diluted, and analyzed.

During this process, the offgas was monitored for hydrogen, nitrous oxide, and carbon dioxide. Only hydrogen results are discussed here.

To characterize the treated sludge, samples were analyzed by techniques listed in Table 1.

III. RESULTS

This study was performed in two parts. First, the three methods were used to determine the nitric acid needed to treat the radioactive sludge. Then, two portions of the slurry were treated with PHA and the nitric acid using results from two methods. The treated sludge slurries were characterized and compared.

A. Nitric Acid Determinations

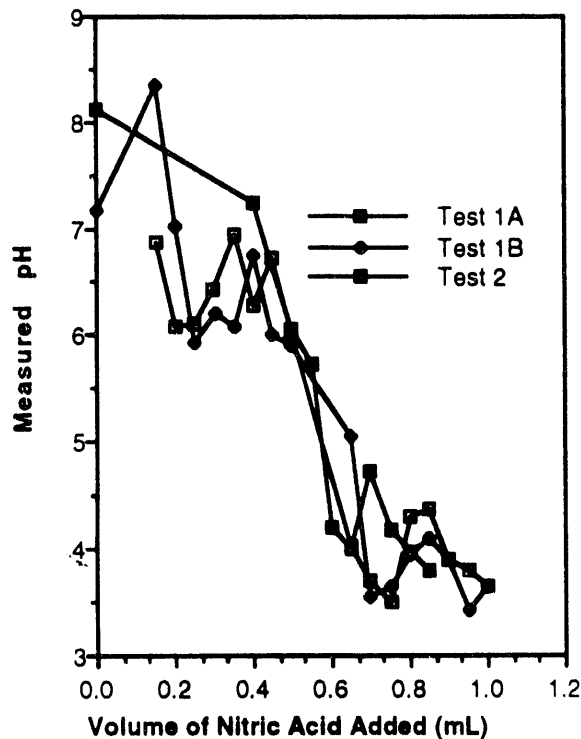
The results of the three methods differed significantly. The results are summarized in Table 2. This difference was not expected since studies with a simulated,

Table 2. 8 N HNO₃ Needed to Treat 90 mL of Sludge

Acid Prediction Method	Volume to Be Added (mL)
Empirical Method	5.0
Computational Method	1.5
Titration Method	2.4

1. The Empirical Method. This method was performed three times. First, duplicate tests, Test 1A and Test 1B, were performed. Then, a second test, Test 2, was completed. The results are shown in Figure 1.

Fig. 1. Measured pH of 10 mL Sludge and 12 mL PHA Heated with Nitric Acid



In the samples with no nitric acid, enough formic acid was present in the PHA to bring the pH from 9.9 to about 8. The acid present in the PHA was enough to neutralize essentially all of the soluble hydroxide, reduce the mercury species to metallic mercury, and bring the pH to well below 8. This suggests that some other species was reacting with the acid. In fact, evidence has been reported for insoluble sodium compounds^{6,7} which are easily dissolved.

As a consequence of the reduction of mercury, the pH of the slurry dropped to about 4. The pH of the slurry once again plateaued. Previous work has shown that once the pH drops to below approximately 5, more sludge solids dissolve⁷ preventing further pH drops.

With further nitric acid addition, the pH suddenly dropped from about 6 to about 4. At this point, the pH once again plateaued. Previous work has shown that once the pH drops to below approximately 5, more sludge solids dissolve⁷ preventing further pH drops.

To ensure sufficient mercury has been removed from the sludge slurry, sufficient manganese has been reduced, and appropriate rheological properties have been established, the slurry had been thought to require a pH of less than 5. This corresponds to the point in Figure 1 at which 0.6 mL of 8 N nitric acid was added. For the simulated DWPF process, the nitric acid requirement was scaled up from 10 milliliters of sludge slurry to 90 milliliters, and adjusted to take into account that 146 milliliters of PHA would be used. The result was that to treat 90 milliliters of sludge, 5.0 milliliters of 8 N nitric acid were needed.

Not considered in any of the acid determination methods was the oxidation-reduction potential of the resulting melter feed. To control the oxidation-reduction potential, a limit has been set for the difference between the concentration of formate and nitrate in the feed.⁸ This limit is 0.5 M.

To ensure this limit was met, the formate-nitrate concentration difference was calculated for the melter feed from treatment as determined by the empirical method. To do this, the moles of formate and nitrate in the treated sludge were calculated from the formate and nitrate to be added during the treatment. To determine the concentrations in the melter feed, the moles of formate and nitrate were divided by the expected melter feed volume. The predicted concentration difference was 0.17 M. Therefore, the oxidation-reduction properties of this material met the DWPF specifications.

As shown in Table 2, the volume from this method was significantly higher than from the others. The other methods were designed to reach the end of the first plateau. This may have accounted for some of the difference in the predicted nitric acid requirement. The large difference may also have been caused by the presence of an unidentified species which would consume acid during sludge treatment.

2. The Computational Method. Concentrations of the known, significant nitric and formic acid-consuming species are summarized in Table 3. In addition, the acid equivalents needed to react with each have been included.

Species	Concentration	Acid Equivalents
Hydroxide	0.058 N	0.0052
TIC	520 ppm	0.0090
Nitrite	6007 ppm	0.010
Mercury	1048 ppm	0.00055
Manganese	6562 ppm	0.015

All the species listed in Table 3 were measured directly except the carbonate (expressed as total inorganic carbon, TIC). The dose rates associated with the slurry made a 1000X dilution necessary to reduce personnel exposure to radiation. This brought the concentration of the carbonate to below the detection limit (1 ppm) of the analyzer. Therefore, the carbonate concentration was determined from the carbon dioxide that was generated when the sludge was titrated with 8 N nitric acid. Based on the data in Table 3, 0.040 equivalents of acid would have been needed to treat the sludge slurry. Formic acid from the PHA would supply all except 0.0019 acid equivalents. The remaining equivalents would have been supplied by the 0.24 milliliter of 8 N nitric acid.

The formate-nitrate concentration difference was calculated for the melter feed which would have been produced if 0.24 milliliter of nitric acid was used with 90 milliliters of sludge and 146 milliliters of PHA. The difference between the formate and nitrate concentrations would have been 0.55 M.

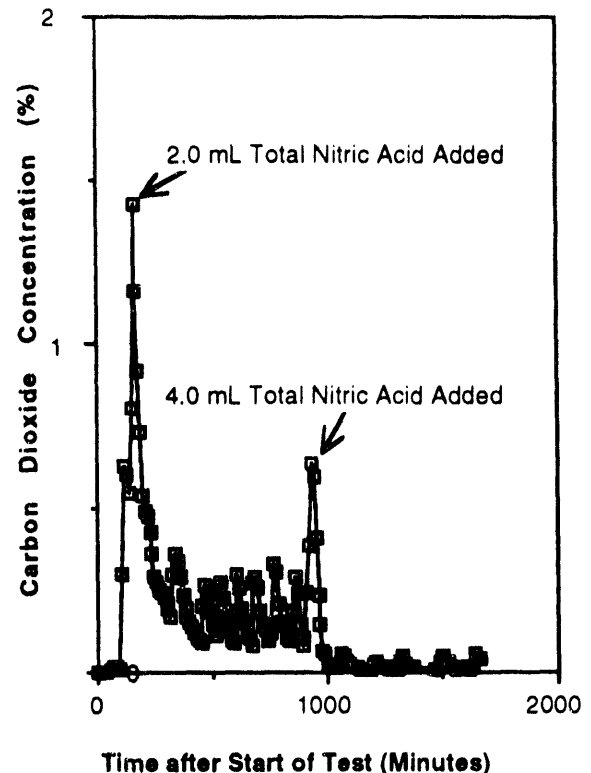
Using a similar calculation, 0.8 milliliter of 8 N nitric acid was determined to be necessary to adjust the formate-nitrate concentration difference to 0.5 M. To ensure the product would meet the limit, 1.5 milliliters of 8 N nitric acid were used. This acid was calculated to produce a melter feed slurry with a formate-nitrate difference of 0.45 M.

Even using the acid needed to meet the oxidation-reduction requirement, the acid volume predicted from the computational method was much lower than that from the empirical method. As discussed previously, this may have been due to an unknown acid-consuming species and, to some extent, the fact that the computational method was not designed to bring the pH to below 5.

3. The Titration Method. Data from the 92°C titration of the sludge with 8 N nitric acid are shown in Figure 2.

With the initial addition of a large aliquot of the nitric acid (2 milliliters), the carbon dioxide concentration immediately went to above 1.4 %. This carbon dioxide peak was caused by the interaction of the 8 N nitric acid

Fig. 2. Carbon Dioxide Concentrations during the Tank 42/51 Sludge Titration



When the ninth acid aliquot was added (4.0 milliliters of 8 N nitric acid), the carbon dioxide concentration went to over 0.6 %, and subsequent acid additions produced essentially no carbon dioxide. The ninth aliquot seems to have been enough to deplete the slurry of carbonate.

The endpoint of this titration was after 4.0 milliliters of 8 N nitric acid were added to the 100 milliliters of sludge slurry. This would have been 3.6 milliliters of 8 N nitric acid for 90 milliliters of the slurry. To account for formic acid in the PHA and for the reactions of mercury, manganese, and nitrite with formate, this volume was further adjusted. This adjustment was made by adding acid equivalents needed to reach the endpoint to equivalents needed to react with the mercury, manganese, and nitrate, and subtracting equivalents provided by formic acid in the PHA. The result was 2.4 milliliters of 8 N nitric acid.

The nitric acid requirement from this method was significantly lower than from the empirical method. The difference was probably caused by the difference in the

endpoint that is difficult to identify using Litmus II and phenolphthalein as indicators.

Although well-suited for laboratory studies, the titration method is not compatible with the DWPF system. Slurry to be processed at the DWPF will have a significant amount of material from previously processed sludge. Formic acid in this material can decompose to form carbon dioxide which would hinder the endpoint identification.

B. Comparison of Treated Radioactive Sludges

Sludge was treated using results from both the empirical and the computational methods. Some of the more important characteristics of the treated sludge slurry are summarized in Table 4.

Table 4. Characteristics of Treated Radioactive Sludge

Method	Target ^{a,b}	Product Concentration	
		Empirical	Computational
Final pH	(<5)	4.1	4.2
TIC	(~0)	<100 ppm	410 ppm
Nitrite	(~0)	<100 ppm	<500 ppm
Mercury	≤0.45wt%	0.050wt%	0.048wt%
Mn Ratio ^c	≥0.4	0.54	0.25
Peak H ₂	≤3e-3 g/hr	<3e-5 g/hr	<3e-5 g/hr

a DWPF target specifications

b () indicate expected values rather target values.

c Ratio of soluble Mn to total Mn

The pH values in the products were similar to those expected.

As expected, the nitrite concentrations were below the detection limits of the ion chromatography method used showing essentially all of the nitrite reacted with the acids. The total inorganic carbon concentrations were also expected to be below the detection limits. The measured concentration was above the detection limit for the product from the computational method. This was probably caused by the dilution needed to handle the sample. The dilution water would have only needed 4 ppm carbonate to cause the effect observed. This may not have occurred in the product from the empirical method since significantly more acid was added here.

Only 25 % of the manganese was reduced in the product from the computational method. In the product from the empirical method, 54 % was reduced. Studies have shown the manganese solubility to be dependent on acid addition.⁷ No foaming problems have been seen using melter feed with even less soluble manganese.

Mercury was successfully reduced from the slurry using the computational method. The concentration in the slurry was 0.048 wt% and 0.050 wt% for the empirical and computational methods respectively.

Although low levels of hydrogen were seen during both treatment processes, concentrations were never high enough to quantify. The 3×10^{-3} g/hr target (Table 4) is equivalent to the limit set for operation of the DWPF during radioactive operations (0.2 lbm hydrogen/hr for 5500 gallons of sludge slurry).⁹

Finally, the elemental composition of the supernate was determined. These results are summarized in Table 5.

Table 5. Soluble Fraction of Elements in the Treated Slurry

Element	Soluble Fraction (%)	
	Empirical	Computational
Ca	78	38
Cd	33	10
Cu	56	8.8
Mg	93	53
Mn	54	25
Zn	9.2	8.1
Al	0.66	0.049
Ba	25	1.8
Fe	0.016	<0.003
La	20	<10
Na	100	100
Ni	23	2.3
Sr	62	31
B	88	80
Si	2.8	3.0

Most species were more soluble in the product from the empirical method than they were in that of the computational method. Previous work has shown that partially soluble species dissolve as acid is added.⁷

IV. CONCLUSIONS

To determine the nitric acid requirement, the three methods were applied to the radioactive sludge from the SRS Tank Farm; however, only the empirical and the computational methods are applicable to the DWPF system. The titration method cannot be used in the DWPF system since the titration method relies on monitoring carbon dioxide to indicate when all the carbonate has been neutralized. Treated material from the previous batch of sludge will be left in the DWPF reaction tank. This

the amount of acid needed to bring the pH of the slurry to a target value. The empirical method is the closest to the procedure which is used to treat the sludge. In addition, this method can be performed in such a fashion that the results can be applied directly to the treatment process without the need for additional calculations. Although the pH measurements used in this method are simple, the results may be hindered by pH drifts caused by decomposition of formic acid. The time and space requirements for this method may be limiting in a process application.

Except for the solubility of the sludge solids, the two products seem to be very similar. As long as enough acid is present to bring the pH of the slurry to below 5, the amount of acid added does not seem to have a great effect on the compatibility of the product with vitrification.

Of the three methods used, the empirical method is the closest to the procedure which is used to treat the sludge. In addition, this method can be performed in such a fashion that the results can be applied directly to the treatment process without the need for additional calculations. Although the pH measurements used in this method are simple, the results may be hindered by pH drifts caused by decomposition of formic acid. The time and space requirements for this method may be limiting in a process application.

The computational method is easy to apply to sludge treatment because most of the terms in the algorithm are data which vitrification processes need for other aspects of a process control. Unaccounted for reactions would, however, be a problem using this method. In addition, in shielded cells facilities where space is limited, analysis of the sludge slurry for carbonate may not be as routine as the other measurements.

Finally, regardless of the method used, consideration must be taken for requirements not considered by these methods. In this study, for example, results from the computational method had to be adjusted to take into account the oxidation-reduction potential.

ACKNOWLEDGMENTS

The authors are extremely thankful for the advice and guidance given by C. J. Coleman, C. W. Hsu, and N. E. Bibler. Without their expertise and experience, this study would not have been possible.

We are also thankful for the work of the Savannah River Technology Center Shielded Cells Operations group. Their outstanding skills at performing the necessary tasks remotely was essential to the completion of this study.

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