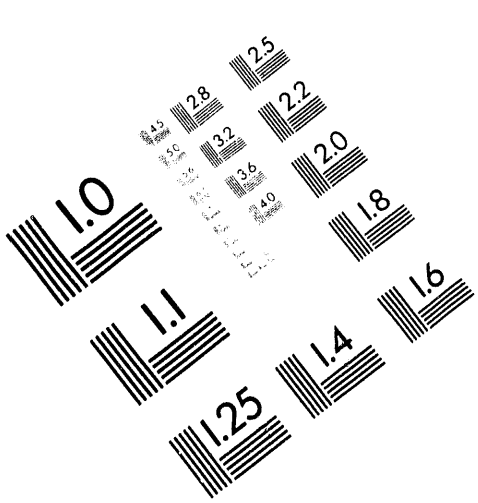

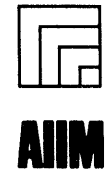

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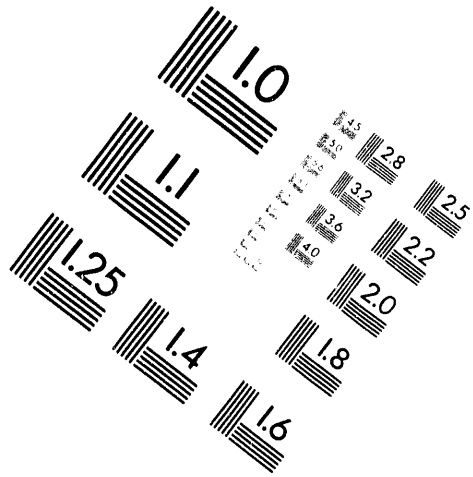

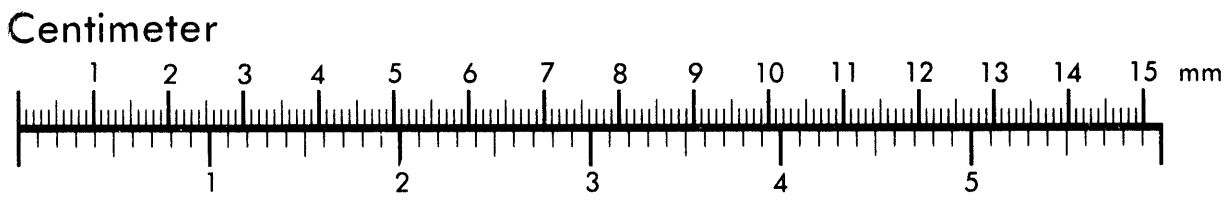

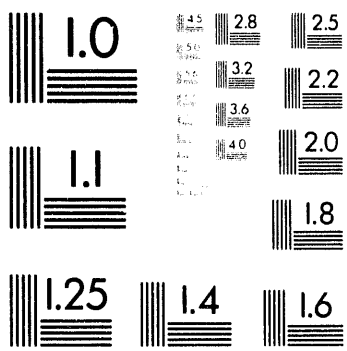

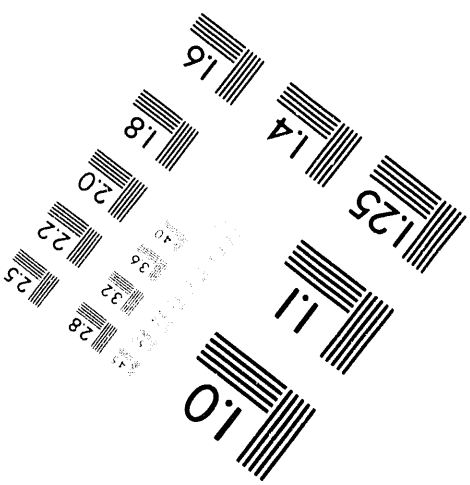

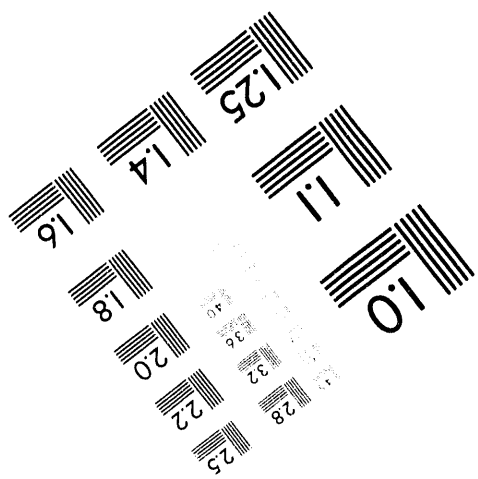

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by

C. J. Coleman

Westinghouse Savannah River Company
Savannah River Site
Aiken, South Carolina 29808

N. E. Bibler
D. M. Ferrara
S. F. Siegwald

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C.J. Coleman, N.E. Bibler, and D.M. Ferrara

Westinghouse Savannah River Company
Savannah River Technology Center
Aiken, South Carolina

S.F. Siegwald
Vanderbilt University
Nashville, Tennessee

Abstract

The Defense Waste Processing Facility (DWPF) at the Savannah River Site (SRS) will combine borosilicate frit with highly radioactive waste sludge to produce glass waste forms for disposal. A key step in the DWPF will be acidification of the sludge with formic and nitric acids prior to vitrification. The reducing properties of formic acid will be used to reduce mercury (II) oxide and salts to elemental mercury. The mercury will then be steam-stripped, recovered, and purified. Another benefit of acidifying the sludge will be to reduce its viscosity so that a sludge-frit mixture can be pumped to the melter. The sludge viscosity decreases with pH as various sludge components dissolve with increasing acidity.

To predict the effect of acids on sludge characteristics, two radioactive SRS sludges that will comprise the initial sludge feed to the DWPF were treated with formic and nitric acids. Experiments were performed to measure how the sludge pH changed with added acids under simulated process conditions. The solubility of important metal oxides and radionuclides were measured as a function of pH. Increasing amounts of acid were added to sludge samples, heated to 95°C, and kept at this temperature for 6 hours. The smallest incremental addition of formic acid used in the experiments reduced the pH from 10.2 to 7. At this pH, the sodium concentration in the supernate doubled and the ^{90}Sr

concentration increased by three orders of magnitude. These solubility characteristics indicate the presence of insoluble sodium and strontium species in the caustic sludge that dissolve at pH above 7. Additional formic acid did not change the concentration of sodium in the supernate, indicating complete dissolution of the sodium species at pH 7. Additional acid increased the fraction of soluble ^{90}Sr, but only about half of the total ^{90}Sr had dissolved at the final experimental pH of 3.2. Other sludge components showed a wide range of solubility characteristics as the acid concentration increased. At pH 4.5-5.5, the approximate pH range at which the processing step of acid addition to sludge will be operated, 50% of the magnesium and calcium, 40% of the manganese, 10% of nickel, and less than 5% of iron, aluminum, silicon and chromium were dissolved. Additional experiments were performed with sludge blends and mixtures of formic and nitric acids. In the pH range 4.5-5.5, essentially no soluble mercury was measured. Acid mixtures containing an excess of the oxidizing nitric acid were then used to drop the pH below 4. Under these acid conditions, only a small fraction of the mercury was dissolved, indicating that only a large excess of nitric acid would be sufficient to dissolve enough mercury to adversely affect the steam stripping process.

INTRODUCTION

Highly radioactive defense wastes at SRS are currently stored in underground steel tanks with capacities up to 1.3 million gallons. The caustic waste consists of two fractions: (1) sludges that contain most of the fission and activation products; and (2) solutions of water-soluble alkali metal salts that contain most of the ^{137}Cs. The salt solution fraction will be decontaminated by adding sodium tetraphenylborate to precipitate ^{137}Cs, along with nonradioactive cesium and potassium that are present. The tetraphenylborate salts will then be hydrolyzed with formic acid to yield benzene and an aqueous fraction that

contains the ^{137}Cs. After distilling the mixture to remove benzene, the aqueous phase will be combined with sludge that has been washed to remove excess aluminum and alkali metals. Borosilicate frit will then be added to the sludge and this mixture will be melted at 1150 °C in a joule-heated glass melter. The molten glass will be poured into stainless steel canisters and stored at SRS until a geological repository is selected for final disposal.

The caustic sludge stream will be combined with the aqueous phase product of the tetraphenylborate hydrolysis in the DWPF Sludge Receipt and Adjustment Tank (SRAT). The function of the SRAT processing will be to modify the sludge characteristics to make them compatible with the vitrification process. The sludge entering the SRAT is too viscous to be easily pumped to the melter after the frit is added. Previous work performed at SRS with nonradioactive simulated sludge slurries indicated that sludge is much easier to pump when the pH is reduced from about 11 to 6 [1]. Moreover, the sludge contains mercury (II) oxide and salts in concentrations in the range 0.2-2.0 weight percent (on a dried solids basis). The mercury salts would decompose to elemental mercury vapors in the melter and foul the melter off-gas system.

To make the sludge properties more suitable for the vitrification processes, the sludge will be acidified and heated in the SRAT for 6 hours at 95 °C. The aqueous product will contain sufficient formate ion from the tetraphenylborate hydrolysis process to chemically reduce the mercury (II) oxide and salts in the sludge to elemental mercury. For most sludge batches, additional acid in the form of nitric acid will be required to reduce the sludge viscosity such that a mixture of sludge and frit can be more easily pumped to the melter. Nitric acid will be used rather than additional formic acid to avoid the reducing conditions in the DWPF melter, which could adversely affect melter durability. The amount of nitric acid to the sludge will be determined on a batch-to-batch basis, but will be added to yield a sludge pH approximately in the range 4.5-5.5. After heating the acidified sludge

for 6 hours, elemental mercury will then be steam-stripped from the sludge and collected. The mercury content of the sludge will then be reduced to a level compatible with the melter off-gas system. The action of both acids will reduce sludge viscosity by partially dissolving the sludge. The acidified sludge will then be pumped from the SRAT into another processing tank, mixed with frit, and fed to the melter for vitrification.

This paper discusses results of shielded cell experiments that measured the effects of adding formic and nitric acids to radioactive SRS sludge under conditions that simulated acid and temperature conditions of the SRAT. The changes in pH and the solubility of both radioactive and nonradioactive sludge components were measured as function of increasing acidity.

EXPERIMENTAL

All reactions with SRS radioactive sludge were performed in the Savannah River Technology Center (SRTC) Shielded Cell Facility. Determination of how pH and solubility of sludge components changed as a function of increasing acidity under SRAT conditions was accomplished with a series of simultaneous but independent reactions. The sludge quantity was kept constant while the acid concentration was incrementally increased for each set of duplicate reactions. Either formic acid (95%) was used alone or a mixture of formic acid and concentrated nitric acid was used to acidify the sludge. The acids were added with calibrated pipets to approximately 15 g of sludge and the mixture heated in a capped 16 ml polysulfone centrifuge tube for 6 hours. The amount of acid added ranged from none (the blank) to 1.2 ml. After the heating step, the slurry was filtered and the filtrate analyzed for pH, elemental, and radionuclide composition. The pH was measured in the Shielded Cell Facility. Elemental and radionuclide analyses were performed in radiohoods after the samples were diluted to reduce the dose to workers. Elemental determinations were made with inductively coupled plasma-atomic emission

spectroscopy (ICP-AES) and Atomic Absorption Spectroscopy (AAS) methods . Radionuclide measurements of gamma emitters were made by gamma ray pulse height analysis (PHA). Alpha emitters were measured by using alpha PHA. Beta emitters were measured by liquid scintillation spectroscopy after using the appropriate separation techniques to produce single-radionuclide spectra.

Sludge was dissolved by two independent methods to optimize the analysis of all sludge elements of interest for DWPF process control purposes. A mixture of 0.2 g of sludge and 1.5 g of sodium peroxide and 1.0 g of sodium hydroxide was fused at 600 °C for 10 minutes in a covered zirconium or nickel crucible. Deionized water and concentrated hydrochloric acid were then added to dissolve the mixture. The solution was diluted to 250 ml with deionized water for elemental analysis.

Sludge was also dissolved with hot aqua regia. A mixture of 0.2 g of dried sludge and 12 ml of aqua regia was heated for 2 hours at 110 °C in sealed Teflon reaction vessels designed for elevated pressure reactions. After cooling, the mixture was diluted to 250 ml for analysis.

In general, the two dissolution methods yield comparable analytical results for most elements. The peroxide fusion method cannot be used for sodium or the crucible material (either nickel or zirconium) since these elements are introduced in the dissolution. Aqua regia is effective for sodium and most other elements but may not completely dissolve silicon or zirconium in the sludge. Sludge is dissolved for zirconium analysis with either a fusion in a nickel crucible or by using a mixture of hydrofluoric and hydrochloric acids. A standard glass or well-characterized sludge is dissolved and analyzed concurrently with every batch of sludge samples to check the analytical accuracy and to help select the better dissolution method for each element.

RESULTS AND DISCUSSION

CHANGE OF pH AS A FUNCTION OF ADDED ACID

An important process control analysis in the DWPF will be acid addition to achieve a pH in the range 4.5-5.5 for the sludge in the SRAT. To study the pH changes of SRS sludge with added acid under SRAT conditions, Tank 51 sludge was treated with formic acid in a set of simultaneous 6-hour reactions. The plot of the pH versus formic acid added is shown in Figure 1. The initial volume (0.2 ml) of formic acid combined with 15 ml of Tank 51 sludge reduced the pH from 10.2 to about 7. The pH curve becomes much flatter as the acid is consumed in the dissolution of sludge components. An acid volume of 0.6 ml added to 15 ml of sludge is sufficient to drop the range into the control range of 4.5 to 5.5.

A closer representation of the way the pH will change in the actual SRAT operation is shown in Figure 2. A blend of Tank 51 and Tank 42 sludge was treated with the aqueous hydrolysis product that contains unreacted formic acid and sodium formate that forms as the formic acid is consumed in the tetraphenylborate hydrolysis . The pH immediately dropped from 11 to about 8 with the addition of the hydrolysis product. Nitric acid was then added to reduce the sludge viscosity. After the initial drop in pH from the addition of the unreacted formic acid from the hydrolysis product, the pH plot as a function of acid added is similar to that observed for formic acid added to Tank 51.

EFFECT OF pH ON TANK 51 SLUDGE SOLUBILITY

The solubility of various sludge components as a function of pH under SRAT conditions was measured to ensure that enough sludge will be dissolved in the pH range 4.5-5.5 to permit pumping. This information also indicated which sludge components could be expected to consume the formic acid added to the SRAT. To measure the soluble fraction, the soluble concentration is divided by the total concentration in the sludge. The

compositions (on a dried solids basis) of Tank 51 sludge and the Tank 42/Tank 51 sludge blend are shown Table 1.

Figure 3 is a plot of iron,aluminum, and sodium concentration in solution after additions of increasing aliquots of formic acid. Iron and aluminum, the two elements with the highest concentrations in the Tank 51 sludge, are insoluble at neutral or higher pH. As acid is added to the sludge, neither iron and aluminum have dissolved until pH 4.5. At this pH , a small fraction of aluminum begins to dissolve, but the soluble fraction is still very low at the final pH of 3.2. Iron is even less soluble than aluminum, and shows no measurable solubility until the pH reaches 3.8. Therefore, less than 5% of iron and aluminum will dissolve when the SRAT is operated in the pH range 4.5-5.5.

Sodium, the element with the third highest concentration in Tank 51 sludge, exhibits (Figure 3) high solubility as expected. However, the sludge contains an unidentified form of sodium that is insoluble at high pH.. About 50% of the sodium is insoluble at the initial high pH of the sludge. This sodium species is completely dissolved by the addition of acid and heating so that by pH 7 all of the sodium is in solution.

Manganese, calcium, magnesium, and nickel exhibit solubility characteristics that are intermediate between sparingly soluble iron and aluminum and soluble sodium. As shown in Figure 4, about 50 % of the magnesium and calcium and 40% manganese in the sludge are dissolved in the pH range 4.5-5.5. Nickel is the least soluble of these elements, with only 10% of the nickel in solution after being heated in the acidic solution..

Mercury Solubility of Acidified Tank 42/51 Blend

One of the primary functions of the SRAT is to reduce mercury (II) oxide and salts to elemental mercury for removal by steam stripping. The reducing conditions of the SRAT will be adjusted to add enough formate ion to reduce the mercury. However, a large excess of formate could result in reducing conditions in the DWPF melter. Other workers

have demonstrated that under reducing conditions metals can precipitate in the melt and short-circuit the melter electrodes [2-4]. Moreover, noble metals in the sludge can catalyze the decomposition of formic acid to hydrogen and carbon dioxide [6]. Therefore, a balance must be struck to add enough formic acid to the SRAT to reduce mercury (II) compounds without compromising either the durability of the melter or the safety of the DWPF. For this reason, additional acid needed to reduce the sludge viscosity will be from nitric acid, rather than formic acid.

The concentration of mercury as a function of acid added to a blend of Tank 42/ Tank 51 sludge is shown in Figure 5. The unreacted formic acid from the tetraphenylborate hydrolysis step reduces the pH to 7. At this stage, no soluble mercury was measured. Nitric acid was then added to reduce the pH to simulate the SRAT operations. Again,no soluble mercury was measured above pH 4.5. As the pH dropped below 4, low concentrations (less than 20 mg/L) of soluble mercury were measured. The mercury solubility behavior is consistent with formate reduction of mercury (II) to elemental mercury, which is insoluble in the neutral pH range. As the concentration of the oxidizing nitric acid increases, nitric acid consumes the excess formate in solution. Mercury then becomes available to react with nitric acid to form soluble mercury (II) nitrate.

These results indicate that the addition of nitric acid will not have to be tightly controlled to avoid re-oxidizing enough mercury to affect the steam stripping of mercury from the sludge. The minor quantities of mercury that dissolve should not have a measurable effect on the efficiency of mercury stripping. A large excess of nitric acid would be required to dissolve a significant fraction of the mercury. Since the nitrate/formate ratio will be monitored as a process control analysis in the DWPF, the nitrate concentration will not be allowed to affect the mercury removal process.

Radionuclide Dissolutions and Dose Rates for Samples

The solubility of the radionuclides in the sludge as a function of pH is of interest to estimate the dose rate of samples removed from the shielded cells for analysis. The total radionuclide concentrations in the Tank 51 sludge are listed in Table 2. The predominant radionuclide exposure will be from ^{90}Sr, since this radionuclide is about 10 times greater than any other in the sludge. Figure 6 shows that, as expected, ^{90}Sr is insoluble at high pH values. As the pH decreases, the concentration of ^{90}Sr in the solution increases until about 20% of the total has dissolved at pH 5.

The dose rates from the solutions following acid addition to sludge are summarized in Table 3. The highest dose rates were from the Tank 42/ Tank 51 sludge Blend and the blend of Tank 42 sludge and the precipitate hydrolysis aqueous (PHA) product. The PHA contains the ^{137}Cs from the hydrolysis of radioactive cesium tetraphenylborate. The largest dilution factors will be required to deal with this material because of the relatively high gamma dose from the ^{137}Cs. The factor of 100 dilution required to reduce the dose rate to a level acceptable for radiohood work had no significant effect on analytical precision and accuracy.

Conclusions

Results of this paper support the following conclusions:

1. Acid addition to sludge in the SRAT results in pH dependent dissolution of sludge which helps reduce the sludge viscosity. In the pH range 4.5 -5.5, no iron, aluminum, or mercury are dissolved, but 100% of sodium, 50% of magnesium and calcium, 40% of the manganese, and 10 % of the nickel are dissolved.

2. A unreasonably large excess of nitric acid would be required to dissolve elemental mercury to the extent that mercury removal by steam stripping would be affected.

3. The largest dose rate from working with solutions of acidified sludge results from a sample of Tank 42/Tank 51 sludge following a dilution factor of 20. The dose rate is 100 mrad/hr and 2 mrem/hr.

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Table 1

Major Nonradioactive Components
Tank 51 Sludge and Tank 42/Tank 51 Sludge Blend

Element	Tank 51 Concentration (wt%)	Tank 42/51 Blend Concentration (wt%)
Fe	30.5	27.0
Al	8.9	8.4
Na	4.0	3.3
Mn	3.3	3.5
Ca	2.9	2.9
Mg	1.5	1.5
Ni	0.4	0.4
Hg	0.2	0.6

Table 2

Major Radioactive Components
Tank 51 Sludge

Radionuclide	mCi/100 g sludge
^{90}Sr	96.9
^{137}Cs	7.5
^{241}Am	1.4
^{144}Ce	1.2
^{154}Eu	0.3
^{60}Co	0.3
^{155}Eu	0.2
Total Alpha	10.7
Total U (wt.%)	3.5

Table 3

Dilutions and Dose Rates for Sludge Samples

	Tk 51 Sludge	Tk42/51 Sludge	Tk 42 Sludge + PHA
Dose Rate (mrem/hr)	< 1	2	20
Dose Rate (mrad/hr)	270	100	200
Dilution Factor Used	1	20	100

Figure 1. pH of Tank 51 Sludge Slurry Treated with Formic Acid

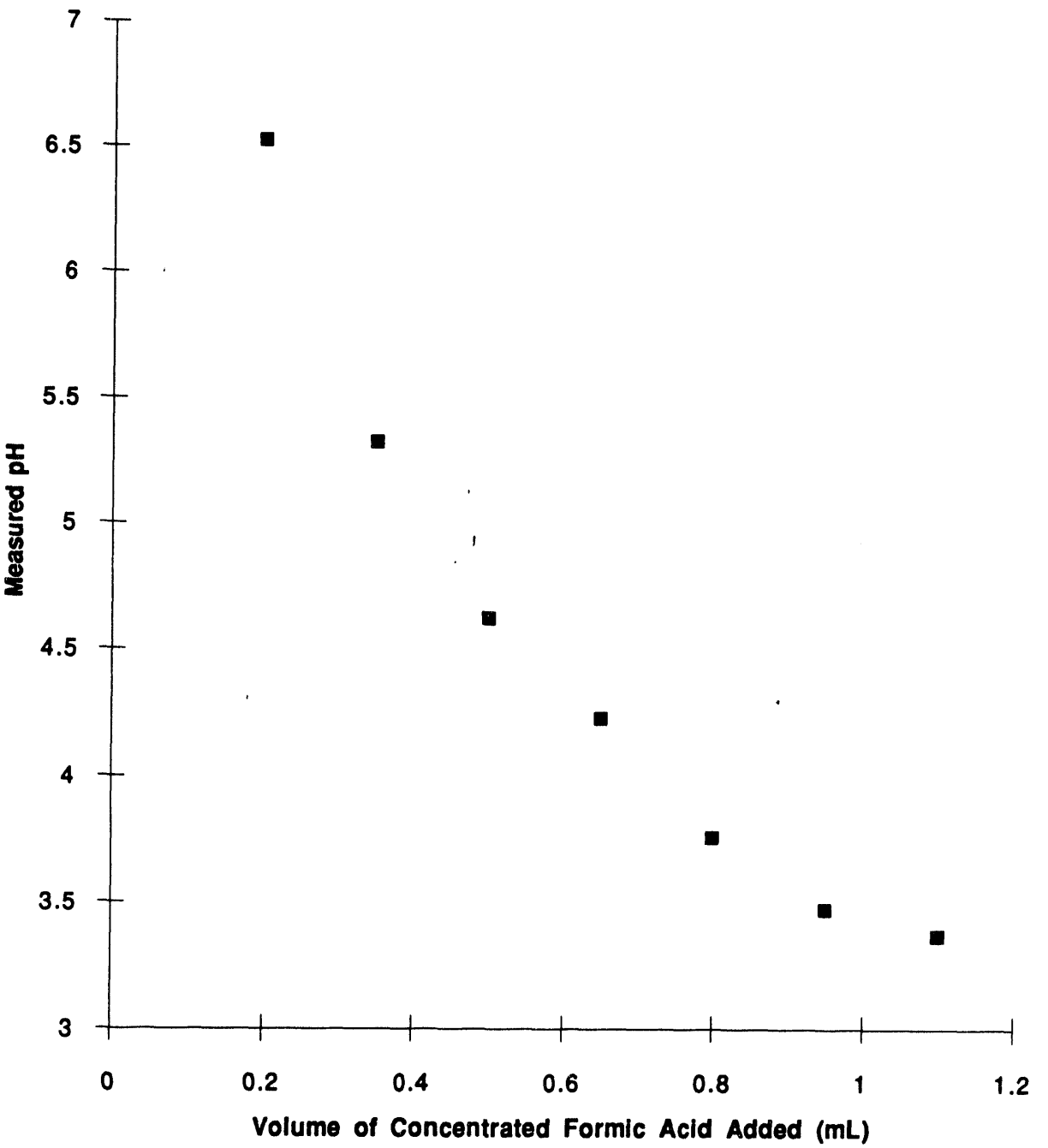


Figure 2. pH of Tank 42/51 Sludge Slurry Treated with Nitric Acid

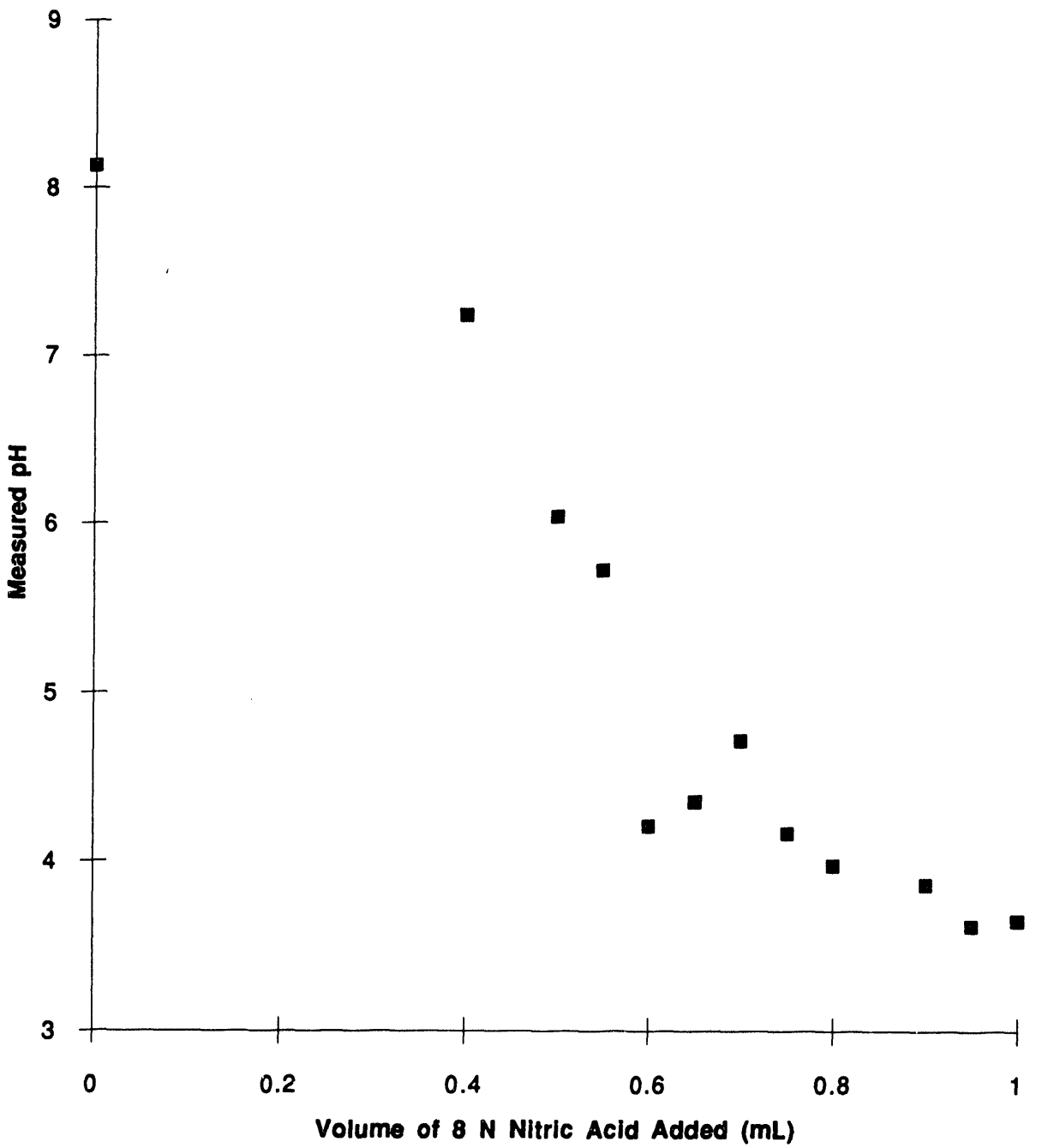


Figure 3. Fraction of Fe, Al, and Na in Tank 51 Sludge Supernate

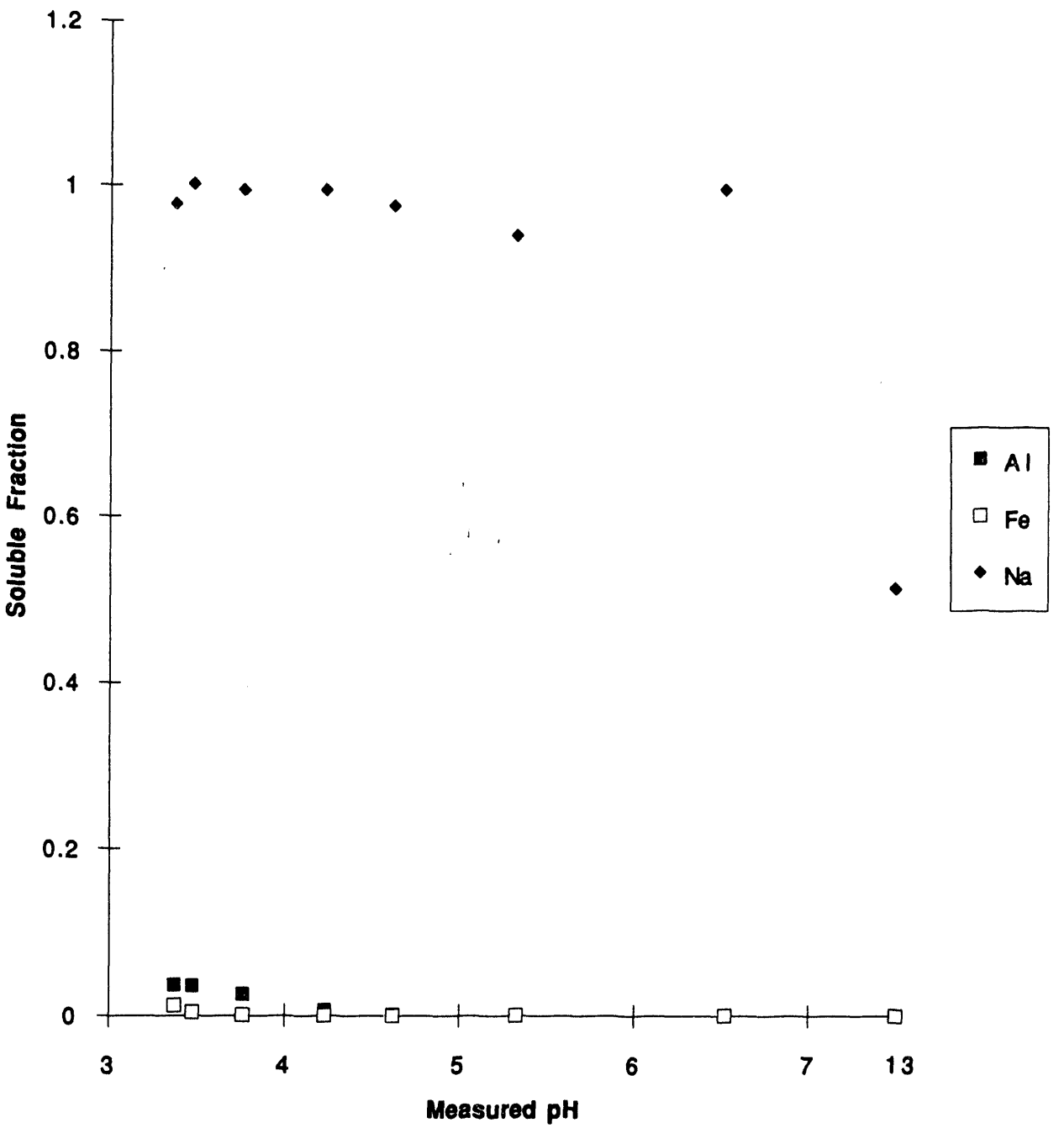


Figure 4. Fraction of Mn, Ca, Mg, and Ni in Tank 51 Sludge Supernate

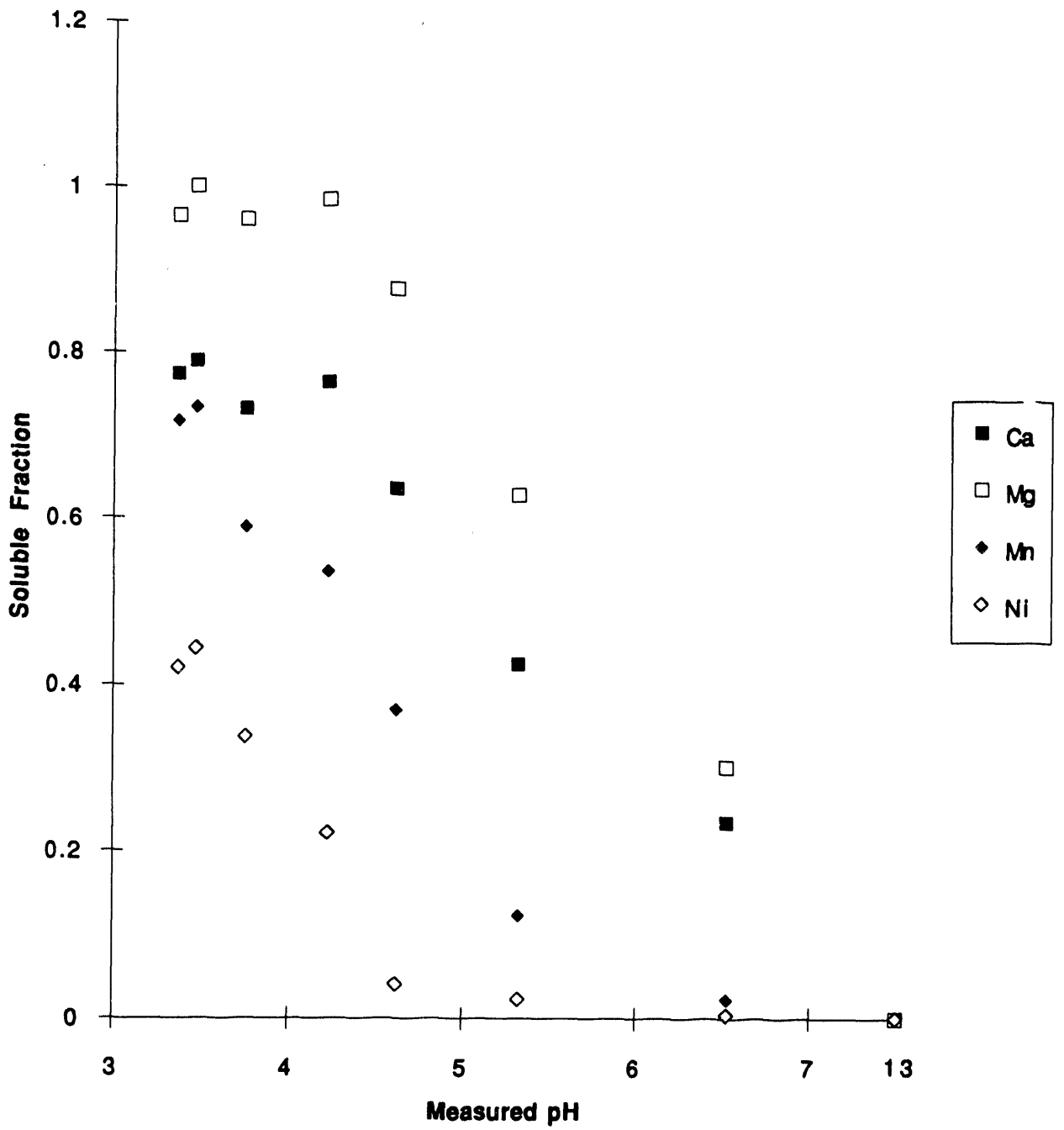


Figure 5. Fraction of Hg in Tank 42/51 Sludge Supernate

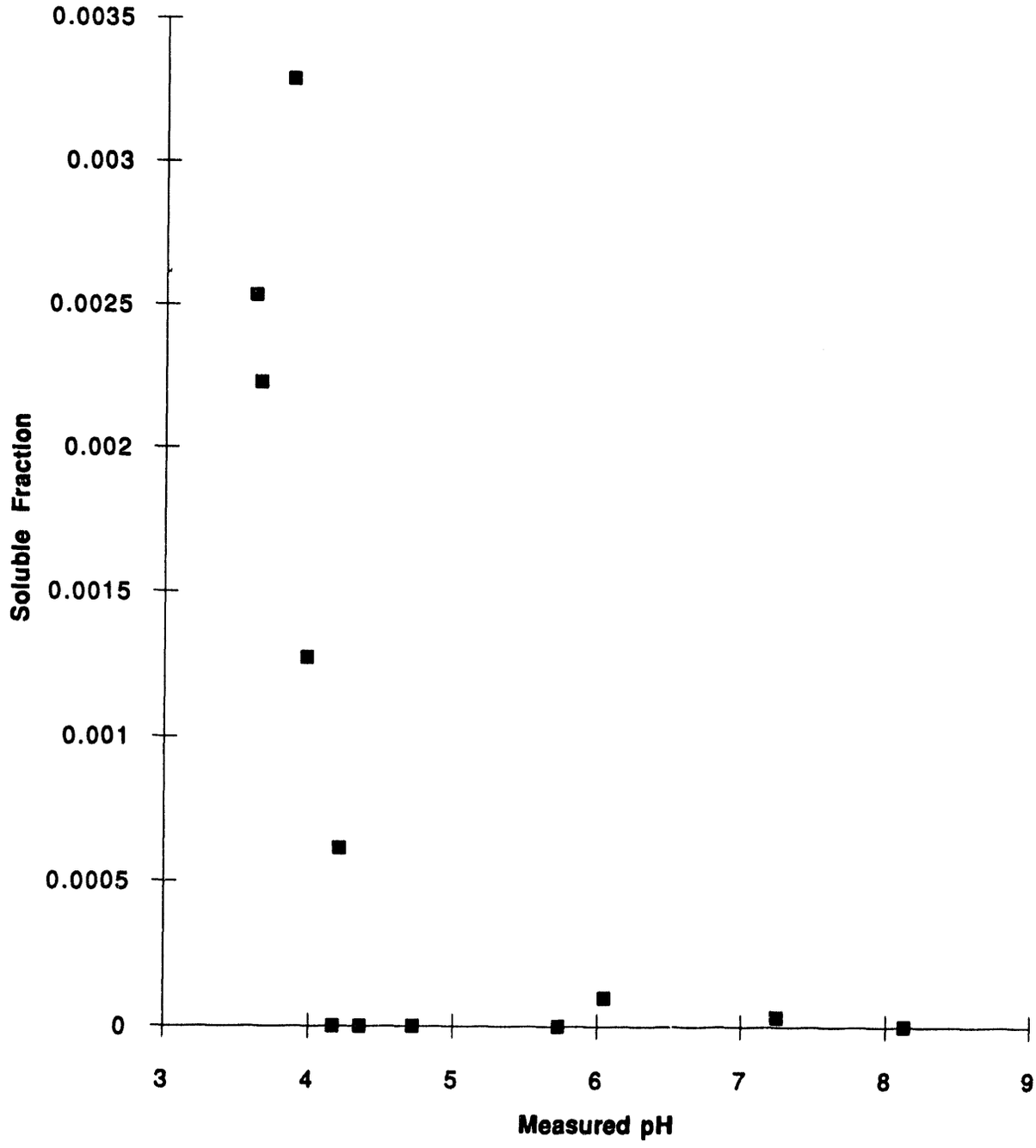
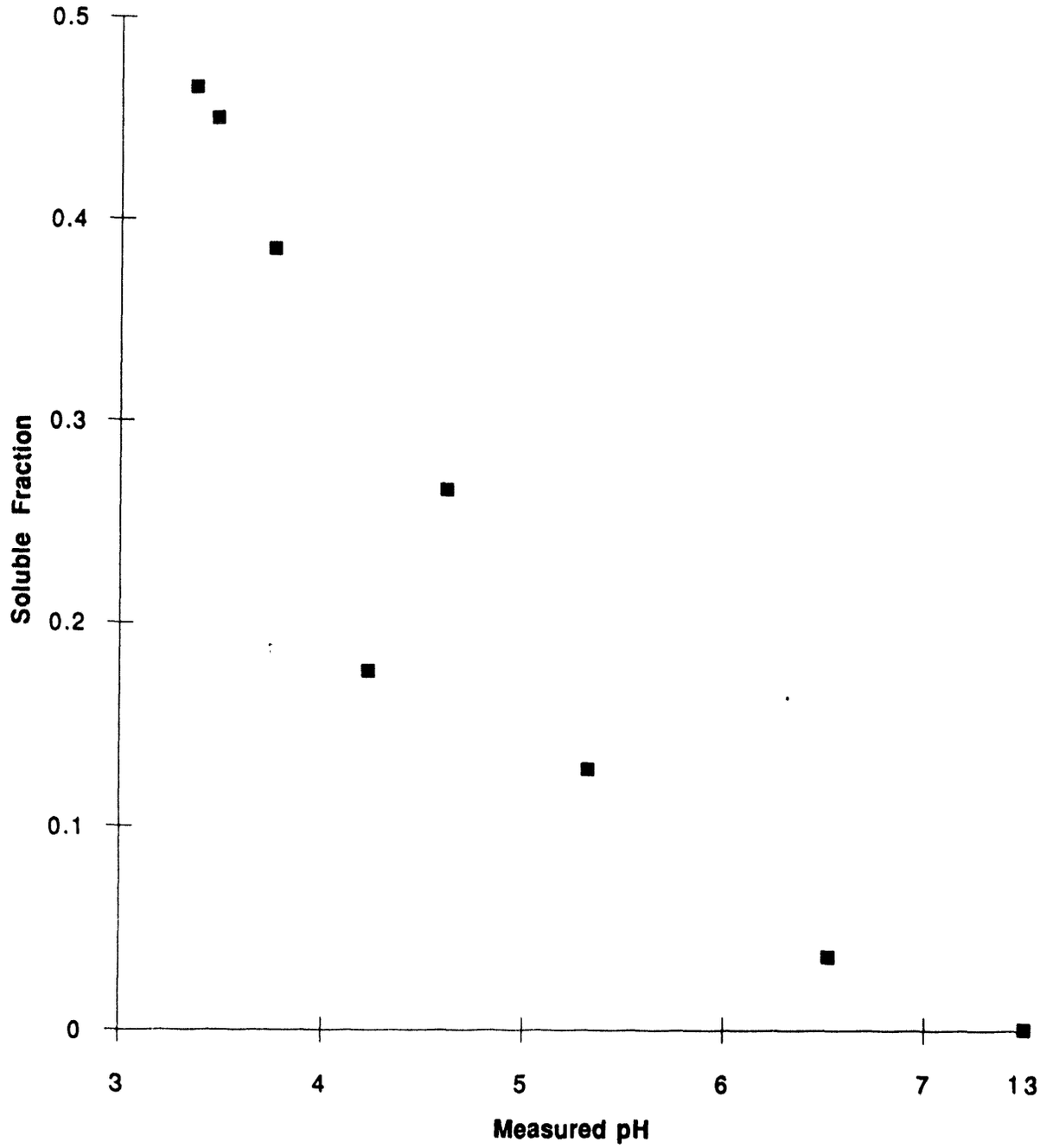


Figure 6. Fraction of Sr-90 in Tank 51 Sludge Supernate



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