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NOTE: Final Patent Questionnaire sent to PDPI.

# ATW Slurry Program: Zirconium and Aluminum Colloidal Behavior

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## Abstract

Synthetic sludges, consisting of aluminum and neodymium precipitates, were prepared and washed with distilled water and distilled water adjusted to pH 8 with NaOH. Repeated washing increases sludge settling times and eventually results in nearly-stable colloids and secondary precipitates which settle at much slower rates than the original sludge. Four successive washes with an accumulative dilution factor of 9.5 transfers over 97% of the Na and 15-20% of the Nd initially in the sludge to the supernate. Sludge washing, even with pH 8 washwater, quickly yields acidic mixtures as Na values are depleted. Thus in-tank washing using carbon steel vessels may result in unacceptably high tank corrosion rates.

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## Experimental Methods

Distilled water was boiled to remove dissolved carbon dioxide, and stored in stoppered containers. Stock solutions were prepared using reagent or certified grade sodium hydroxide, nitric acid, sodium nitrate, aluminum nitrate nonahydrate, and neodymium nitrate hexahydrate obtained from Fisher Scientific and Aldrich Chemicals. One molar aluminum nitrate and sodium nitrate stock solutions were prepared gravimetrically. One molar caustic and acid solutions were prepared gravimetrically and calibrated using certified potassium hydrogen phthalate and sodium carbonate as the primary standards. Tenth molar caustic and acid stock solutions were prepared volumetrically and standardized using either potassium hydrogen phthalate or sodium carbonate. After preparation, stock solutions were stored in sealed glassware until use.

Test solutions were prepared either by titrating stock solutions from burets or by transfers using volumetric pipettes. Sample preparation protocol varied with the experiment. In most cases solution volumes are also weighed to yield density estimates.

Solution pH was measured using a Fisher Model 805 dual electrode pH meter with digital readout and calibrated using buffer solutions with pH 4.00 and 8.00 to accuracy of  $\pm 0.02$ .

Conductivities were measured using a YSI Model 35 Conductance Meter, calibrated with NIST Traceable Conductivity Calibration Standards from Fisher.

Sodium, Nd, and Al concentrations were measured by flame emission using a Varian Atomic Absorption Spectra 5. Aluminum and Nd were measured at 396.1 and 660.8 nm, respectively, in an acetylene and nitrous oxide flame. Sodium was measured at 589.0 nm in an acetylene and air flame. Flame emission standard solutions were prepared using 99.99% pure NaCl, Al metal wire, and  $\text{Nd}_2\text{O}_3$ .

Interference was measured for each element by measuring flame emission using standard solutions for a single element. This analysis shows that neither Nd nor Al interferes significantly with Na flame emission in an acetylene and air flame. However, Na interferes slightly with Nd emission in an acetylene and nitrous oxide flame and Nd measurements were corrected for this effect.

Both Na and Nd interfere strongly with Al flame emission so that Al concentrations cannot be accurately reported using measurements completed

at this time. Additional testing is needed to develop an accurate method for Al in the presence of Na and Nd.

## **Synthetic Purex Sludge Preparation**

Batches of synthetic sludge are prepared by neutralizing a reference Purex solution that is initially 1 M  $\text{Al}(\text{NO}_3)_3$ , 2 M  $\text{HNO}_3$ , and 0.2 M  $\text{Nd}(\text{NO}_3)_3$ . Half liter batches of Purex waste solution for neutralization are prepared by adding 187.56 g of aluminum nitrate nonahydrate and 43.84 g of neodymium nitrate hexahydrate to a 500 mL volumetric flask. Solids are washed into a volumetric flask using 2.45 M  $\text{HNO}_3$ . Solids are allowed to dissolve by gentle mixing. After cooling to room temperature, the flask is made to the mark with 2.45 M  $\text{HNO}_3$  and sealed. This mixture gives approximately 2 M  $\text{HNO}_3$  with the desired metal concentrations.

Typically 20 or 40 mL aliquots of the Purex waste solution are neutralized to pH of 8 using 4 M NaOH. Titrating 28 mL of 4 M NaOH into a 20 mL aliquot of synthetic Purex waste solution yields an equilibrium pH of about 11.3 with precipitates. After gentle mixing for 5 to 10 minutes, the precipitate solution is allowed to cool and settle to yield a reference Purex sludge, typically about 45–45 vol% of the final mixture volume.

## **Sludge Washing Protocol**

A 20 mL aliquot of reference Purex solution is neutralized in a tared beaker by adding 25.4 mL of 4 M NaOH. An additional aliquot of distilled water (e.g., 90 mL) is added as the first wash with gentle mixing, and the solution is allowed to settle by gravity. During this time the sludge height is repeatedly measured. After at least 24 h settling time, the supernate is withdrawn by pipette and the residual sludge weighed. A second wash aliquot (e.g., 100 mL) is then added by volumetric pipette, gently mixed with the sludge, and then allowed to settle by gravity. This procedure is repeated as desired to completely wash the sludge.

Supernate samples are analyzed for conductivity, pH, and metal concentrations.

The same procedure is used in sludge washing experiments with pH 8 water. In some cases the wash volumes added are slightly different. In all cases, solutions are mixed volumetrically and weighed. Direct measurements

are performed on the supernates. Sludge compositions are estimated by difference.

## Results and Discussion

Two series of wash experiments are reported here. One series used distilled water as wash reagent; a second series used distilled water with a small amount of NaOH added to give pH of about 8 (actually, pH 8.11). In both cases, the results presented are for freshly formed sludges that were not aged more than 48 h prior to initial washing. The experimental conditions and results are further summarized in Tables 1 and 2.

In both tests reported here, solution pH decreases as washing proceeds. Initially, the solutions were adjusted to pH 8, but both were acidic after the first wash. Solution conductivities and pH both decrease with the number of washes. Turbidity increases dramatically with the third and fourth washes. After the first and second washes, the clear supernate/solids interface is quickly defined, but not thereafter.

We conclude that sludge washing must be carefully monitored for pH if it is carried out in carbon steel tanks. Otherwise, sludge washing may result in unacceptably high tank corrosion rates.

Results are presented as a function of the accumulative dilution factor  $\Psi$ :

$$\Psi = \frac{S_1 + \sum_{i=1}^4 W_i}{S_1} \quad (1)$$

where  $S_1$  is the initial sludge volume and  $W_i$  is the volume of the  $i$ th wash.

Figure 1, for example, shows the sodium concentrations for the initial sludge and after four washes in both tests. Except for the points at  $\Psi = 1$ , the sodium concentrations are as measured by flame emission. The concentrations at  $\Psi = 1$  were calculated<sup>1</sup> from the supernate concentrations and dilution factors, assuming that the Na concentration is uniform throughout the supernate and sludge phases. As can be seen in Fig 1, the experimental Na concentrations agree well with theoretical values, assuming a single homogeneous phase and perfect mixing. This observation suggests that, at least in

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<sup>1</sup>This approach was used to provide meaningful separation factor calculations, and to minimize accumulative errors from differencing.

Table 1: Results of sludge washing tests using pH 7 and pH 8 water.

Wash No	Volumes (mL)		Density g/cm <sup>3</sup>	Dilution Factor	Concentrations		Observations
	Sludge	Wash			Na (M)	Nd (mM)	
pH 7 Water Washes							
Initial	45.4		1.159	1.00	2.386 <sup>a</sup>		
A1	45.4	90	1.052	2.98	0.841	1.91	
A2	54.5	100	1.035	5.19	0.233	1.74	
A3	59.1	100	1.013	7.39	0.093	2.26	Cloudy
A4	63.6	100	1.005	9.59	0.056	2.91	No visible interface
	49.8						
pH 8 Water Washes							
Initial	45.3		1.201	1.00	2.481 <sup>a</sup>		
B1	45.3	95	1.079	3.10	0.863	1.77	
B2	56.7	100	1.035	5.31	0.230	1.27	
B3	52.5	90	1.019	7.29	0.093	1.47	Cloudy
B4	65.0	100	1.014	9.50	0.055	2.36	No visible interface
	49.4						

<sup>a</sup>Back calculated from supernate concentrations and volumes.

*dam*

Table 2: Observed pH and conductivity changes with supernate aging. Also see Table 1.

Wash No	Measurement Date	Conductivity $(\Omega\text{-cm})^{-1}$	pH	% Transmittance
pH 7 Water Washes				
Initial	8/23/94		8.19	
A1	8/24/94	56.1	7.01	98
	8/27/94	53.0	6.26	98
A2	8/25/94	24.5	6.96	98
	8/29/94	22.0	6.01	99
A3	8/26/94	9.6	5.54	87
	8/29/94	9.2	5.78	98
A4	8/31/94	4.2	6.64	74
pH 8 Water Washes				
Initial	8/23/94		8.00	
B1	8/24/94	54.3	7.64	99
	8/29/94	51.8	6.65	100
B2	8/25/94	24.3	6.80	98
	8/29/94	21.5	6.30	100
B3	8/26/94	9.5	5.31	97
	8/29/94	9.0	5.42	99
B4	8/31/94	3.8	5.65	92





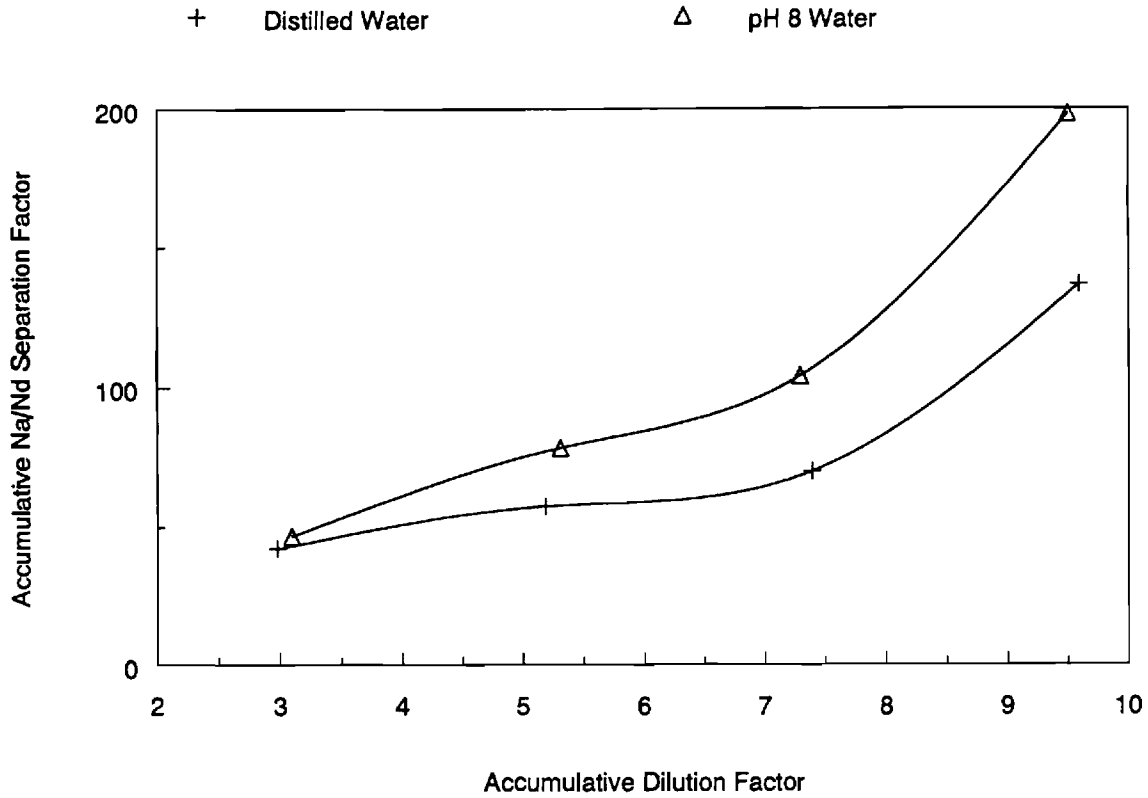


Figure 2: Accumulative Na/Nd separation factor as a function of the dilution factor,  $\Psi$ . Higher separation was achieved with pH 8 water washes.

Similarly, define an accumulative separation factor  $SF_{ijk}$  as:

$$SF_{ij} = \frac{\sum_{\ell=1}^k W_{i\ell}/S_{ik}}{\sum_{\ell=1}^k W_{j\ell}/S_{jk}} \quad (3)$$

where  $W_{i\ell}$  is the moles of the  $i$ th species in the  $\ell$ th wash.

Figure 2 illustrates the accumulative Na/Nd separation factors that resulted from these tests. After diluting the original waste volume by a factor of 9.5, the pH 8 water washes yield a separation factor of about 200. As can be seen in Figure 3, over 97% of the Na originally in the sludge has been removed at that point. Also, about 15-20% of the Nd originally in the sludge has transferred into the supernate. More Nd transfers into the supernates with pH 7 wash, and this is apparently the primary reason why a higher Na/Nd separation factor was achieved with the pH 8 water wash.

The accumulative sodium decontamination factors are summarized in Fig 4. Approximately the same results were achieved at both pH 7 and

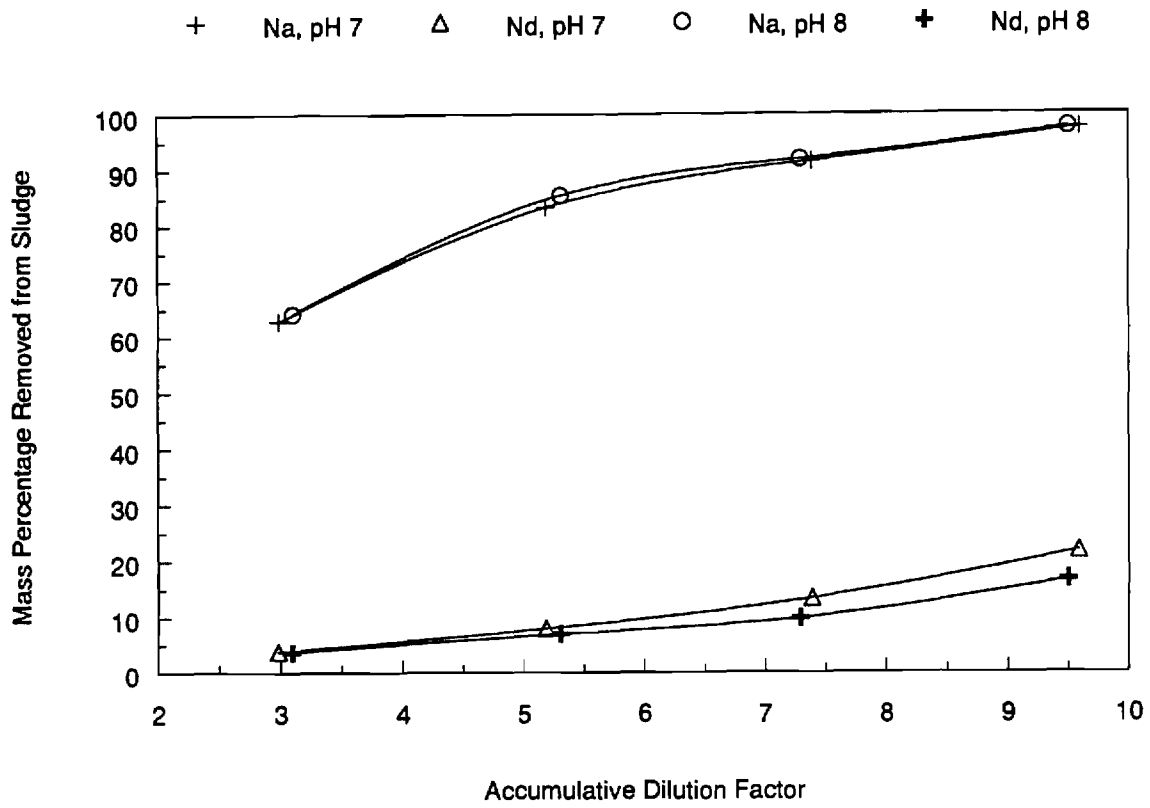
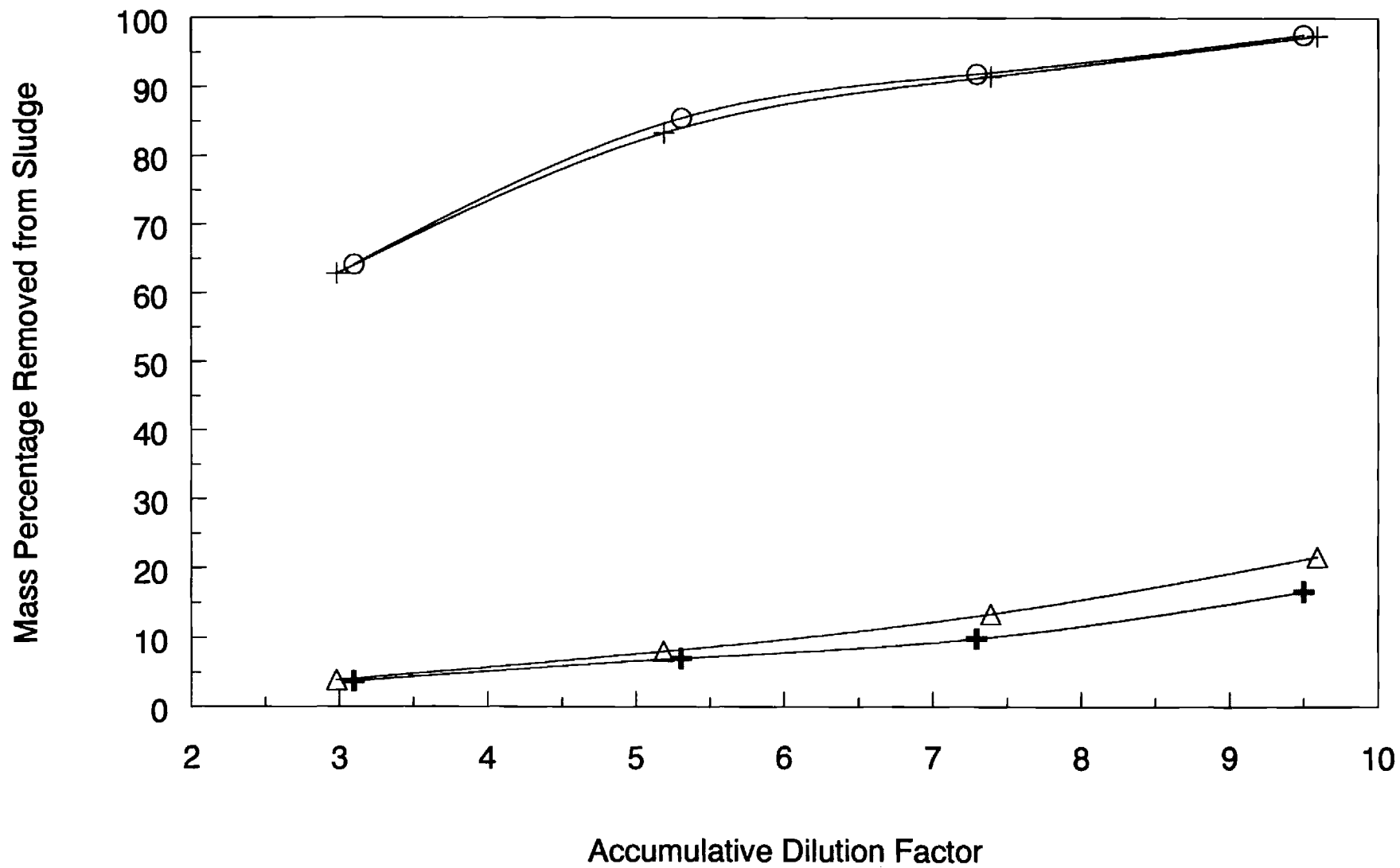


Figure 3: Mass percentage of Na and Nd removed from the sludge as a function of the dilution factor,  $\Psi$ . More Nd transfers to the supernate due to pH 7 water washes.

+ Na, pH 7     $\Delta$  Nd, pH 7     $\circ$  Na, pH 8    + Nd, pH 8



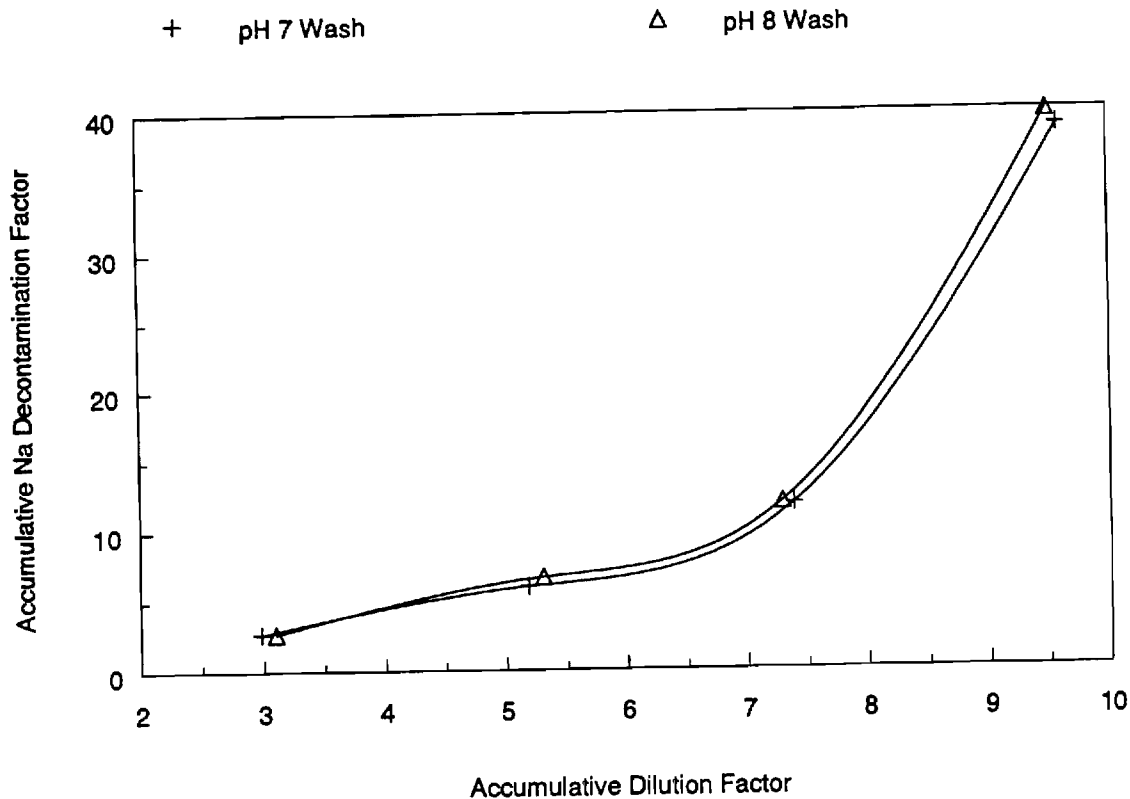


Figure 4: Sodium decontamination factors. A measure of Na removal from the sludge as a function of the dilution factor,  $\Psi$ .

pH 8.

Sodium concentrations in the supernates are, of course, much lower than originally in the sludge. Thus extensive washwater concentration (e.g., evaporation) would be needed in downstream processing since the original waste volume has been increased by nearly a factor of ten.

On the other hand, Nd concentrations in the supernate (see Fig 5) appear to increase slightly with successive washes. This result may be partly due to colloid formation and less complete settling with latter washes, but it may also be partly attributable to decreasing pH values and, as a consequence, higher Nd solubilities in the supernates. After each wash, the supernate concentration is in equilibrium with Nd precipitate and, therefore, at its saturation value.

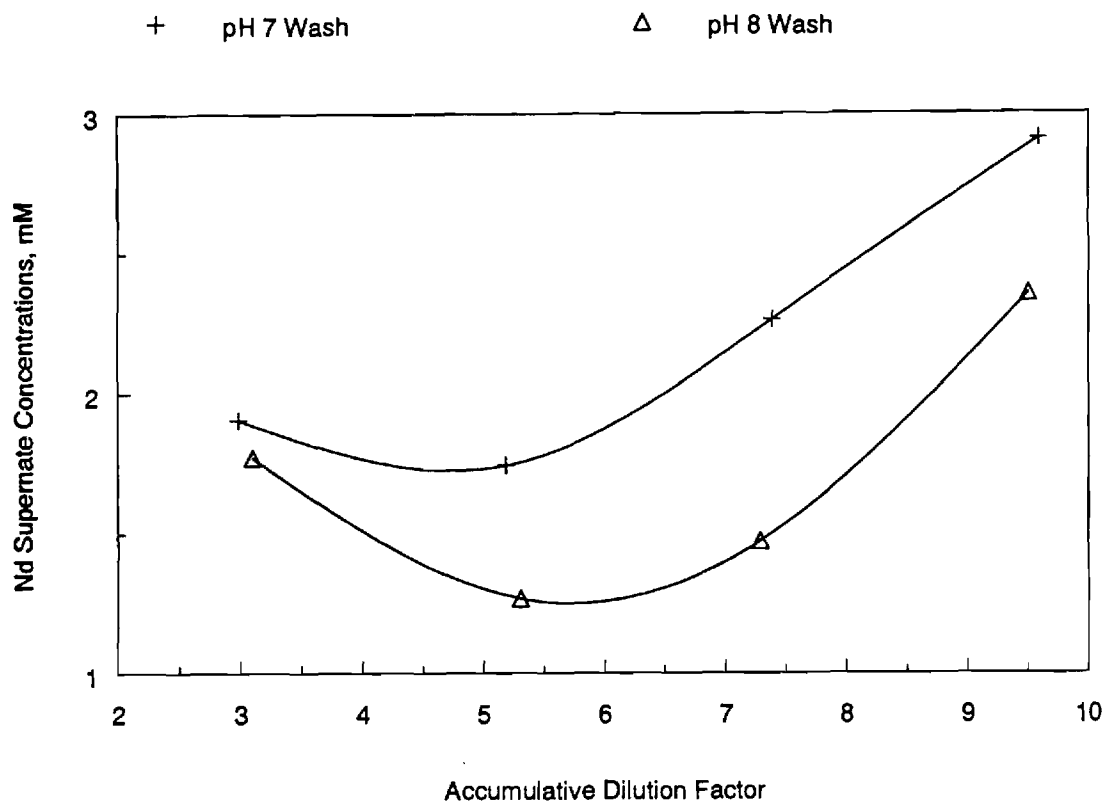


Figure 5: Neodymium concentrations in the supernate as a function of the dilution factor,  $\Psi$ .

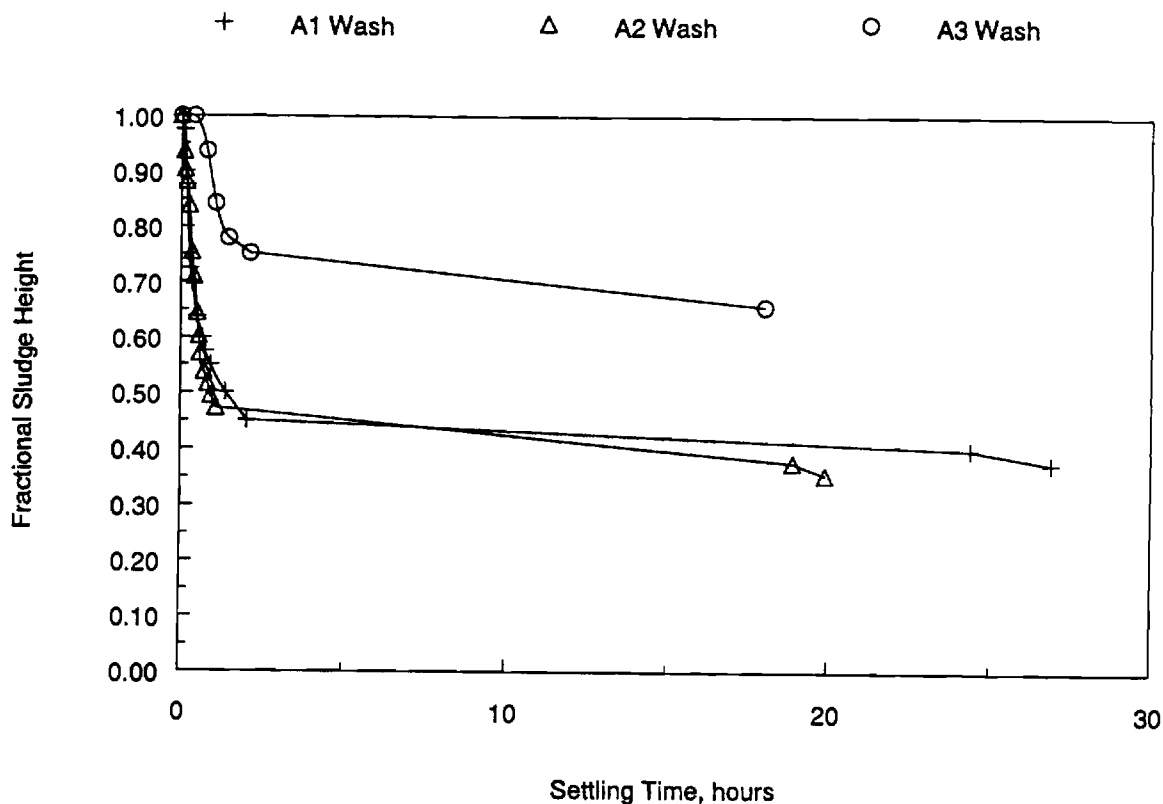


Figure 6: Sludge settling for first three pH 7 washes.

## Settling and Colloid Behavior

Both series of wash experiments formed colloids by the third wash, and the interface from solids settling became difficult to discern by the fourth. The settling rates decrease with repeat washing and in some instances a secondary precipitate forms, apparently from colloid agglomeration. Figure 6 depicts the settling results obtained from the first three washes at pH 7. The settling rate for the third wash is notably slower, and the final settled volume is about 70% of the initial volume, rather than 45% as for the first two washes.

The appearance of a secondary haze after the second or third washes complicates settling rate measurements and their interpretation. Figure 7, for example, shows results from the pH 8 wash in which the primary solids and secondary haze levels were recorded separately. The change in settling rate for the secondary haze at the end of the measurement period is attributable to colloid agglomeration.

Settling behavior in these systems is complex. The gradual changes in pH (see Table 2) and the settling behavior with time and the degree of

### B3: Time vs. Settling

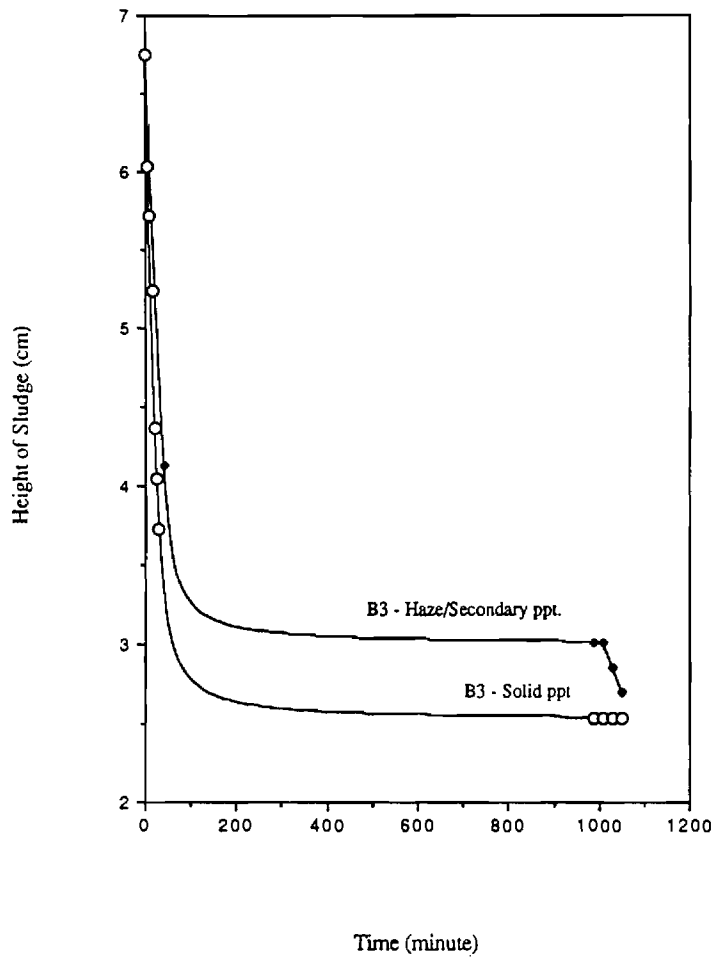


Figure 7: Primary sludge and secondary haze settling rates after third wash with pH 8 water.



washing suggest that multiple reactions and significant shifts in chemical equilibria occur, at least in freshly formed sludge that has not been aged for extended times. Solution turbidity, and colloid stability, both increase with the number of washes. As fresh wash is added, solids partly redissolve as sludge equilibrates with the aqueous phase. As time passes, secondary particulates form from the supernate.

This behavior may be partly attributable to kinetic and localized mixing effects. We observe in parametric composition studies, for example, that precipitates initially form for virtually all NaOH and  $\text{Al}(\text{NO}_3)_3$  concentration ratios, and for a wide range of pH values. However, in many cases solids that are initially formed redissolve as solutions are equilibrate. Moreover, the equilibrium concentration range over which solids coexist with supernate is much smaller than the concentration and pH range over which they first form.

For this reason, equilibrium measurements alone may not be a reliable indicator of potential process fouling problems. Kinetic and localized mixing effects exacerbate this problem and are probably contributing factors to the gradual drift in pH and conductivity values summarized in Table 2, and to the formation of secondary precipitates during sludge washing. Further evidence for continued chemical reaction during colloid formation is given by the fact that pH and conductivity values appear to change over small increments for several days after initial equilibration.

## Notation

$S_i$	$i$ th sludge volume
$W_i$	$i$ th wash volume
$\Psi$	Accumulative dilution factor
$\Omega$	ohm resistance

## **ATW Slurry Program: Zirconium and Aluminum Colloidal Behavior**

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### **Executive Summary**

A variety of precipitates, gels, sols, and stable colloids result from mixing aluminum salts with acids and bases. Freshly formed aluminum precipitates redissolve if sufficient NaOH is added to maintain the solution pH above 13, but aluminum precipitates neutralized to a pH no greater than 8 or 9 become acidic and peptize after repeated water washes. Aluminum sludges that are first neutralized to a higher pH (e.g., 12 or 13), and then partly reacidified, are less likely to peptize and become acidic from water washing.

Synthetic sludges formed from precipitating mixtures of aluminum, iron, zirconium and neodymium nitrate salts with NaOH can be washed to remove much of their sodium content if they are first neutralized to at least a pH of 12 or 13, and if they are not subjected to excessive mixing. Sludge settling rates and final settled sludge densities both tend to decrease with repeat washings.

Repeat water washing of inadequately neutralized sludge results in nearly stable colloids under acidic conditions and the suspension of neodymium precipitates. By inference, transuranic materials would also peptize under these conditions.

Gentle mixing over short time periods has a measurable effect on increasing sludge settling times and decreasing final settled sludge densities, even if the sludge was properly neutralized before mixing. However, aggressive sludge mixing quickly forms nearly stable, viscous colloidal suspensions. Their appearance is similar to that of warm yogurt.

Our preliminary mixing studies suggest that even gentle sludge mixing over extended time periods may have serious adverse effects on sludge washing and the ability to handle radioactive sludges in general. Although the results presented here are qualitative, they suggest that additional work is needed to understand this phenomena and how it can be managed. The effects of mixing on centrifugation or filtration properties

may also be important. Studies thus far have been limited to mixtures of Al, Fe, Zr and Nd precipitates.

Sludge settling times generally increase with repeated washings. Also, the percentage solids in the settled sludges after extended settling times is low. So sludge washing with gravity settling to produce a supernate will be inefficient, and will generate large quantities of dilute supernates that must be managed (e.g., by evaporation).

Concentrated sodium hydroxide washes with heating can be used to redissolve freshly formed aluminum precipitates and may be useful as a means to separate nonradioactive aluminum precipitates from fission products and transuranics.

## **Introduction**

Historically, DOE sludges have resulted mainly from the neutralization of Purex raffinates. This occurred because Purex operates under acidic conditions, but high-level storage tanks are constructed of carbon steel which corrodes at high rates in acidic

High-level sludges at many DOE sites may require washing to reduce the concentrations of aluminum, sodium and other non-radioactive chemical species. The goal is to provide washed sludges suitable for incorporation into borosilicate glass, and to reduce the rates at which high-level glass is produced by producing low level solid wastes from the sludge washing operations that contain most of the non-radioactive waste constituents.

Under certain conditions, washing can peptize the sludge and suspend radioactive species. Transuranic (TRU) elements are of particular concern. Since the production of radioactive suspensions during washing may preclude on-site disposal of supernate solutions as low-level waste or cause additional waste processing problems (e.g., unfilterable slurries), factors causing such behavior must be clearly understood before DOE initiates sludge washing operations on actual wastes.

This research examines conditions that may result in stable colloids or slurries with poor filtration characteristics in the presence of aluminum, iron, zirconium, sodium salts, and other contaminants as may be present in existing DOE wastes. Aluminum colloids are potential problems in sludge washing. Zirconium, iron, and silicate species may also result in the suspension of transuranics. Additional factors such as the presence of surfactants and tramp organics, solvent degradation products, sludge mixing, shear rates during mixing, pH adjustment, and heat treatment may also be important.

Solution chemistry is initially characterized by producing synthetic sludge mixtures and measuring sludge settling heights over time. Wash solutions are added to wet precipitates, mixed, and allowed to gravity settle. Solution conductivities and pH are also measured; turbidity is measured when supernates are visibly hazy. Metal concentrations in the supernates are measured using atomic absorption and flame emission spectroscopy. By comparing metal ion concentrations in supernates with equilibrium metal concentrations, we obtain a measure of the potential to suspend TRU activity using neodymium as an actinide surrogate.

Additional factors may be important in the formation of colloids and will be examined. These potential effects include silicate (typically added to 5% to 10% of total solids as oxides), mixing and shear rates, temperature (maximum of 50-60 °C), partial

neutralization to pH 10-11 (starting with sludges at pH 13-14), and the effects of tramp organics (e.g., TBP, DBP, HDEHP, detergents, and butyl nitrite).

Lab conditions will be set to simulate liquid waste treatment at ORNL, Hanford, and SRP. Initial sludges are formed starting with neutralization of acidic solutions to pH 13-14, at which conditions silicates may be solubilized at high pH from sand or other sources (e.g., zeolites) in the HLW tanks during storage and waste transport operations. Although Purex raffinates are normally steam stripped prior to neutralization, organophosphates are known contaminants as well as small concentrations of detergents which also tend to form colloidal suspensions.

The potential impact of these effects will be assessed by measuring turbidity, pH, conductivity, sludge settling times, and Nd and other metal concentrations in supernates. Situations that result in Nd concentrations measurably greater than equilibrium concentrations anticipated from Nd solubility alone will indicate suspension by colloid formation. By implication, similar conditions would result in actinide suspension into HLLW supernates and the potential undesirable formation of TRU waste after sodium salts are isolated from the sludges.

### Sludge "A" Preparation

This sludge is about 3 wt % solids and contains one part by weight each of  $\text{Al}(\text{OH})_3$ ,  $\text{Fe}(\text{OH})_3$ , and  $\text{ZrO}(\text{OH})_2$ . The required additions to make 10 L of sludge are tabulated below. It contains 100 g of each hydroxide. Supernate should contain 0.1 M NaOH and about 0.5 M  $\text{NaNO}_3$ .

	Al(OH) <sub>3</sub>	Fe(OH) <sub>3</sub>	Zr(OH) <sub>3</sub>	Moles Metal	Moles NaOH reqd to ppt
Mol Wt.	78	106.8	141.2		
Moles metal hydroxide	1.28	0.94	0.71	2.93	8.07
Mole %	43.8	32.0	24.2		

Dissolve 1.3 mole of an aluminum nitrate salt, 0.94 moles of a ferric nitrate salt, and 0.7 moles of a zirconyl nitrate in 1 to 2 L of water. Some solids may initially dissolve and then reprecipitate. Slowly add the solution of salts to 4 L of a stirred solution of 2 M NaOH. Check pH of supernate and, if necessary, add 2 M NaOH to pH of about 7. Allow to settle and decant mother liquor. Dilute the settled colloids to 10 L with 0.1 M NaOH -- 0.5 M  $\text{NaNO}_3$ . Final solution pH should be about 13. About half of liquid is removed as clear supernate before diluting to 10 L. Slurry should be about 0.5 M in sodium ion after diluting to 10 L.

### Sludge Washing Experiments

Synthetic sludges were prepared using combinations of aluminum, zirconium, iron, neodymium and sodium nitrate solutions by precipitating with NaOH. Sludge settling

times, conductivities, pH values, and supernate metal concentrations were measured as a function of sludge wash numbers and dilution factors.

solutions. As a consequence, Purex raffinates were neutralized to pH 13-14 with sodium hydroxide and concentrated as needed to produce sludge mixtures that could be stored safely in carbon steel tanks.

### **Effects of Cold Mixing & Chemicals (Exp 100)**

#### **I. Experiment Description:**

The combined effects of mixing (at room temperature) and chemicals on settling times and metal contents in supernates were examined in these experiments. Two control experiments (mixing and nonmixing) were run in order to look at the mixing effect one more time and two chemical effects [dibutyl phosphate (DBP) and silicate] were investigated. Except the nonmixing control sample, all the sludges (type Sludge "A") were mixed while bases were being added and the mixing continued for another 30 min after base addition was finished.

a) DBP effect: Twenty mL of 0.064 M DBP solution (5 % to sludge solid) was added to 20 mL of sludge A. The pH value was adjusted to 13.04 by 32.0 mL of 3.92 M NaOH. Electrodes were washed with 10 mL distilled water. Mixing continued for 30 min.

b) Silicate effect: Two mL of 20 % wt/wt silicate solution (8 % to sludge solid) and 18 mL of distilled water were added to 20 mL of Sludge A. The pH value was adjusted to 13.03 by 30.0 mL of 3.92 M NaOH. Electrodes were washed with 10 mL distilled water. Mixing continued for 30 min.

c) Controls: Twenty mL of distilled water were added to the two controls. The pH values were adjusted to 13.03 and 13.01 for mixing and nonmixing control by 30.3 and 33.0 mL of 3.92 M NaOH, respectively. Electrodes were washed with 10 mL of distilled water. Mixing continued for 30 min for the mixing control.

#### **II. Results:**

##### **1. Initial Supernate:**

	Mixed Control	DBP Test	Unmixed Control	Silicate Test
Vol (mL)	29.5	31.5	34.0	24.5
Weight (g)	31.1	33.3	36.5	25.8
pH	12.73	12.75	12.77	12.75
Cond. (mΩ)	106.4	111.1	118.8	112.8

The initial supernate settling curves are shown in Figure 100.1

2. First Wash

Supernate: 100 mL distilled water was added.

	Mixed Control	DBP Test	Unmixed Control	Silicate Test
Vol (mL)	97.0	97.0	96.0	98.0
Weight (g)	99.5	98.8	97.6	100.5
pH	12.49	12.52	12.56	12.56
Cond. (mΩ)	46.8	47.5	51.3	52.8

The First Wash settling curves appear in Figure 100.2

3. Second Wash

Supernate: 100 mL distilled water were added.

	Mixed Control	DBP Test	Unmixed Control	Silicate Test
Vol (mL)	97.0	91.0	99.0	100.0
Weight (g)	98.0	91.7	99.7	100.4
pH	12.23	12.24	12.31	12.28
Cond. (mΩ)	18.8	17.8	19.5	21.4

The Second Wash settling curves appear in Figure 100.3

4. Third Wash

Supernate: 100 mL distilled water were added.

	Mixed Control	DBP Test	Unmixed Control	Silicate Test
Vol (mL)	102.0	99.0	100.0	101.0
Weight (g)	102.1	98.7	99.8	101.5
pH	11.83	11.81	11.91	11.84
Cond. (mΩ)	7.20	6.70	7.10	7.70

The Third Washing settling curves appear in Figure 100.4

## 5. Fourth Wash

Supernate: 100 mL distilled water were added.

	Mixed Control	DBP Test	Unmixed Control	Silicate Test
Vol (mL)	98.0	100.0	102.0	97.2
Weight (g)	97.9	100.0	102.5	96.4
pH	11.46	11.48	11.65	11.57
Cond. (mΩ)	2.70	2.60	2.80	2.90

The Fourth Wash settling curves appear in Figure 100.5

Supernate metal concentrations are plotted in Figures 100.6-100.10.

## Effects of Neutralization (Exp 101)

### I. Experiment Description:

The effect of neutralization was examined in this experiments. The pH value of Sludge A was adjusted to about 13 followed by partial neutralization with acid. The settling time curves were measured and metal concentrations in supernates were measured to see if the neutralization has any effect on these values.

a) Control: The pH value of 20 mL of Sludge A was adjusted to 13.01 by 31.3 mL of 3.92 M NaOH. Electrodes were washed with 40 mL distilled water.

b) Neutralization effect: The pH value of 20 mL of sludge A was adjusted to 13.13 by 32.0 mL of 3.92 M NaOH. Thirty mL of 1 M HCl solution to neutralize the sludge to pH 10.52. Electrodes were washed with 10 mL distilled water.

### II. Results:

#### 1. Initial Supernate:

	Control	Neutralization
Vol (mL)	51.0	40.0
Weight (g)	53.6	42.6
pH	12.68	11.83
Cond. (mΩ)	100.6	89.8

Initial supernate settling curves appear in Figure 101.1

2. First Wash

Supernate: 100 mL distilled water was added.

	Control	Neutralization
Vol (mL)	96.0	97.0
Weight (g)	97.9	98.6
pH	12.57	11.58
Cond. (mΩ)	35.4	37.6

First Wash supernate settling curves appear in Figure 101.2

3. Second Wash

Supernate: 100 mL distilled water was added.

	Control	Neutralization
Vol (mL)	98	100.0
Weight (g)	97.9	100.9
pH	12.21	11.37
Cond. (mΩ)	14.0	15.4

Second Wash supernate settling curves appear in Figure 101.3

4. Third Wash

Supernate: 100 mL distilled water were added.

	Control	Neutralization
Vol (mL)	104.5	98.0
Weight (g)	103.3	95.8
pH	11.86	11.22
Cond. (mΩ)	4.84	6.03

Third Wash supernate settling curves appear in Figure 101.4.

5. Fourth Wash



Supernate: 100 mL distilled water was added.

	Control	Neutralization
Vol (mL)	102.0	101.0
Weight (g)	102.4	101.2
pH	11.82	11.41
Cond. (mΩ)	1.74	2.15

Fourth Wash supernate settling curves appear in Figure 101.5

Supernate metal concentrations are plotted in Figures 101.6 - 10.

### Effects of Surfactants (Exp 102)

#### I. Experiment Description:

The effects of surfactants on settling times and metal contents in supernates were examined in these experiments. Two non-ionic surfactants (TERGITOL TMN-6 and 15-S-9) and butanol were used. In all cases, sludge was mixed while base was added and continued being mixed for another 30 minutes after base addition was finished.

a) Control: To 20 mL of sludge A, 32.1 mL of 3.92 NaOH was added to adjust the pH to 13.01 with stirring. Electrodes were washed with 20 mL distilled water. Mixing continued for another 30 min.

b) TMN-6: To 9.5 mL of distilled water, 0.5 mL of TMN-6 was added and the solution was well mixed. This solution was added to 20 mL of sludge A to which 30.7 mL of 3.92 NaOH was then added to adjust the pH to 13.04 with stirring. Electrodes were washed with 10 mL distilled water. Mixing continued for another 30 min.

c) 15-S-9: To 9.5 mL of distilled water, 0.5 mL of 15-S-9 was added and the solution was well mixed. This solution was added to 20 mL of sludge A to which 30.0 mL of 3.92 NaOH was then added to adjust the pH to 13.03 with stirring. Electrodes were washed with 10 mL distilled water. Mixing continued for another 30 min.

d) BuOH To 9.0 mL of distilled water, 1.0 mL of BuOH was added and the solution was well mixed. This solution was added to 20 mL of sludge A to which 29.9 mL of 3.92 NaOH was then added to adjust the pH to 13.01 with stirring. Electrodes were washed with 10 mL distilled water. Mixing continued for another 30 min.

## II. Results:

### 1. Initial Supernate:

	Control	TMN-6	15-S-9	BuOH
Vol (mL)	25.0	15.5	21.0	22.5
Weight (g)	26.1	15.8	21.7	23.4
pH	12.71	12.82	12.75	12.77
Cond. (mΩ)	119.6	112.9	107.6	108.8

Initial supernate settling curves appear in Figure 102.1

### 2. First Wash Supernate: 100 mL distilled water was added.

	Control	TMN-6	15-S-9	BuOH
Vol (mL)	98.0	100.0	100.0	99.0
Weight (g)	100.7	103.2	102.2	101.3
pH	12.87	13.00	12.78	12.88
Cond. (mΩ)	50.4	54.6	48.8	49.5

First Wash settling curves appear in Figure 102.2

### 3. Second Wash Supernate: 100 mL distilled water was added.

	Control	TMN-6	15-S-9	BuOH
Vol (mL)	94.0	97.0	102.5	104.0
Weight (g)	94.5	97.1	103.8	103.7
pH	12.50	12.44	12.33	12.29
Cond. (mΩ)	17.7	19.4	16.5	16.8

Second Wash settling curves appear in Figure 102.3

Supernate metal concentrations are plotted in Figures 102.6 - 102.10

## **Partial Neutralization Effects (Exp 103)**

### I. Experiment Description

Experiment 103 investigates the effect that a partial neutralization may have on the formation of colloids. In past experiments, colloidal formation after washing was seen when the sludge was initially neutralized to a pH of 8-10. In this experiment, the sludge is neutralized to an initial pH of approximately 13.4, then, the sludge's pH is reduced using hydrochloric acid. This experiment will compare the effects of partial neutralization to complete neutralization followed by a reduction of pH.

The sludge used in this experiment was prepared by combining the following nitrate salts in a one liter flask:

96.03 g	$\text{AlNO}_3 \cdot 9\text{H}_2\text{O}$
75.95 g	$\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$
32.83 g	$\text{ZrO}(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$
43.90 g	$\text{Nd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$

Twelve molar HCl was added until the salts dissolved. The one liter flask was then filled to the mark with distilled water. There was some reprecipitation overnight but the bulk of the salts stayed in solution. Since the number of water molecules in the hydrated zirconyl nitrate was unknown, molarity was calculated considering the anhydrous salt.

Five identical 20 ml aliquots of a sludge containing the estimated metal ion concentrations were used for the preparation of Experiment 103 sludges.

Aluminum	0.256 M
Iron	0.188 M
Zirconium	0.112 M
Neodymium	0.100 M

Each of the sludge samples were first neutralized to a pH of approximately 13.4 with 4.0 M NaOH. Then one sample was kept at a pH of 13.4. Then the remaining four samples were lowered in pH with the addition of hydrochloric acid to each sample. Each sample was prepared so that the experiment would be run on samples with an approximate initial pH of 13, 12, 10, 9, and 8. These samples were labelled 103-13, 103-12, 103-10, 103-9, and 103-8, respectively.

The initial settling times for each of the samples was recorded and the samples were allowed to sit overnight. The initial supernates were removed, its physical properties recorded, and its metal concentration analyzed by flame emission spectroscopy.

Then each sample was washed with 100 ml of distilled water which had its pH raised to the approximate pH of the initial sludge. For example, 103-13 was washed with 100 mL of water with an approximate pH of 13. Likewise, the pH of 103-8's wash water was approximately 8. The height of the interface was measured as a function of time and the sample was allowed to sit overnight. The supernate was then removed and analyzed and another wash was done in the same manner as before with equivalent pH wash water.

This washing procedure was repeated several times.

## II. Results

The supernate's physical properties for the different washings of each sample are given in Table 103.1. The metal concentration in each sample's supernate is shown in Table 103.2. The settling times for each wash is given in Figs. 103.1-103.4.

### III. Conclusions

Although a longer settling time was seen in the lower pH samples, there was no colloidal formation through three washings. The metal ion concentrations are relatively uniform across the varying pH samples except for aluminum. Samples 103-13 and 103-12 show at least an order of magnitude increase in supernate Al concentrations compared to supernates at lower pH. This result is due to higher Al solubilities in the 12-13 pH range.

## Aluminum Leaching (Exp 104)

The purpose of this experiment is to determine if it is possible to leach Aluminum from a sludge which has been washed exhaustively to the point where there is very little metals diluted in the supernates from washing.

### II. Procedure

In Experiment 104, two sludges (henceforth called 104-1 and 104-2) were used. These sludges were the results of an earlier washing experiment. In this earlier washing experiment, a 20 ml aliquot of sludge was diluted to a pH of approximately 13 with sodium hydroxide. This sludge initially had a metal ion concentration approximately equal to:

Aluminum	0.256 M
Iron	0.188 M
Zirconium	0.112 M
Neodymium	0.100 M

The same methods were used to prepare this sludge as for Exp 103.

This neutralized sludge was then repeatedly washed with 100 ml distilled water washings. This washing procedure was repeated nine times until the supernates showed very little metal ion concentration. At this point, the remaining sludges were then used as the starting point for Experiment 104.

The first step in Experiment 104, was to wash sludges 104-1 and 104-2 with 100 ml of approximately 4.0 M sodium hydroxide. The washed sludges were then placed on a magnetic stirrer hot plate. The sludges were stirred and heated until the temperature reached approximately 80 degrees Celsius. At this point, the solution was allowed to cool while stirring was continued. Once the mixture cooled to approximately room temperature, the stirring was discontinued and the height of the sludge/supernate interface was recorded as a function of time. The total mixing time was approximately one hour.

After the sample was allowed to settle overnight, the clear supernate was removed and its physical properties were recorded. The supernates were then analyzed by flame emission to determine the metal ion concentrations in the supernate.

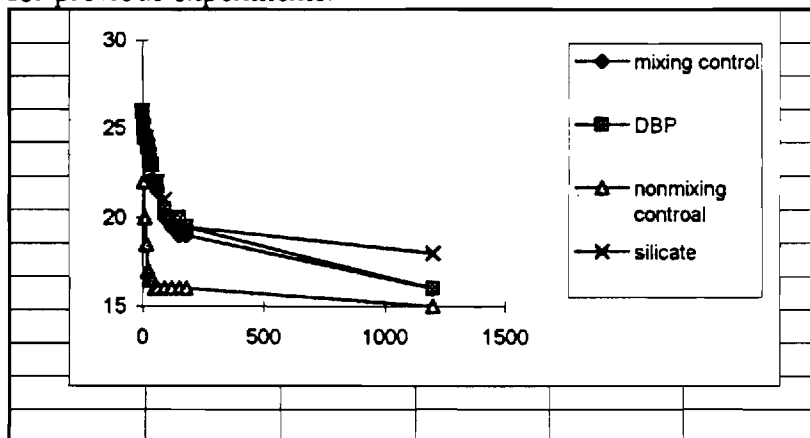
After the supernates were removed, the 100 ml sodium hydroxide washing, heating/stirring, and settling procedure was repeated. The supernates were once again removed.

## II. Results

The physical properties of the first wash supernate is shown in Table A and the ion concentrations are given in Table B. The settling times for the first two washes is given in Figs 104.1 and 104.2.

## III. Conclusions

The settling times of each sample are uniform over the two washings and there is no colloidal formation. The metal concentrations were much higher in this experiment than in the final distilled water washings which lead to the sludges used in this experiment. The aluminum concentration increased by at least two orders of magnitude from the last distilled water washing. This shows that there is indeed still aluminum precipitated in the sludge. The measured Nd and Fe concentrations were also higher in these supernates than for previous experiments.



## Sludge and Precipitate Formation

Precipitates are formed in these experiments by mixing measured volumes of standard solutions. Solution concentrations and aliquot additions are adjusted to span the range of conditions likely to result in the formation of precipitates, sludges, colloids, and gels. Solution conductivity, turbidity, volume percentages solids, and pH are measured. The results indicate stoichiometric mixtures leading to precipitate and colloid formation, and the pH and conductivities under such conditions.

Precipitates were formed in the following aqueous systems: (1) neodymium nitrate alone, (2) aluminum nitrate alone, (3) aluminum nitrate and sodium hydroxide, (4) neodymium nitrate and sodium hydroxide, (5) neodymium nitrate, aluminum nitrate, and sodium hydroxide.

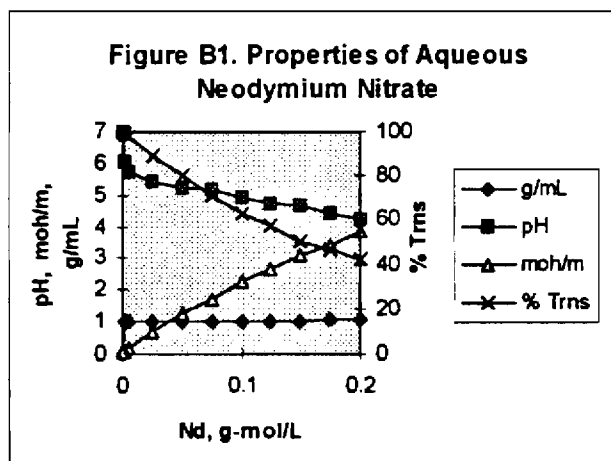
Solution pH was measured using a Fisher Model 805 dual electrode pH meter and calibrated with pH 4 and 8 buffer solutions. Conductivities were measured using a YSI Model 35 Conductance Metrer, calibrated with NIST Traceable Conductivity Calibration Standards from Fisher Turbidities were measured with a Beckman 21 spectrophotometer at 580 nm, and are reported as percentage transmittance (% Trns) in the tables.

### Neodymium Nitrate

Neodymium nitrate was dissolved in distilled water. Solution conductivities, pH and densities were measured. Results are summarized in Table B1 and Figure B1.

Table B1.

Properties of Neodymium Nitrate in water at 23 C.				
Nd, M	g/mL	pH	moh/m	% Trns
0.200	1.053	4.23	3.850	42.4
0.175	1.044	4.43	3.420	46.8
0.150	1.040	4.66	3.110	50.9
0.125	1.031	4.75	2.650	57.5
0.100	1.022	4.90	2.250	63.1
0.075	1.021	5.15	1.710	71.2
0.050	1.010	5.23	1.270	79.8
0.025	1.005	5.43	0.680	89.3
0.005	0.997	5.76	0.162	98.0
0.001	0.995	6.05	0.032	99.2
0.000	0.997	7.00	0.032	100.0



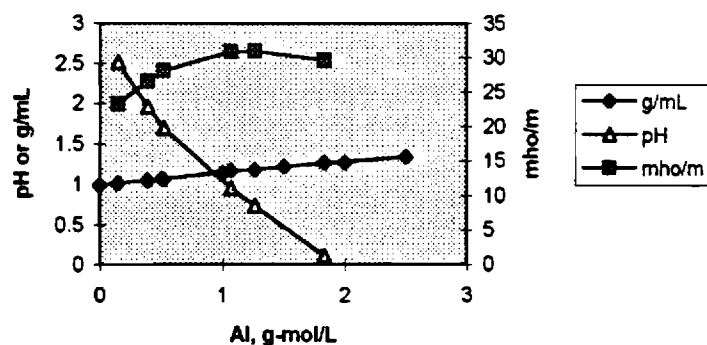
## Aluminum Nitrate

Aluminum nitrate solutions were prepared gravimetrically using reagent grade aluminum nitrate nonahydrate from Fisher Scientific, and boiled, filtered distilled water. The pH and conductivity measurements for these solutions are summarized in Table C1 and Figure C1

Table C1.

Properties of Aluminum Nitrate in water at 23 C.			
Al, M	g/mL	mho/m	pH
0.148	1.011	23.240	2.510
0.386	1.040	26.610	1.960
0.520	1.055	28.080	1.700
1.070	1.166	30.790	0.950
1.260	1.179	30.930	0.740
1.830	1.268	29.570	0.110
2.504	1.339		
2.000	1.268		
1.500	1.220		
1.000	1.133		
0.500	1.062		
0.000	0.983		

Figure C1. Aqueous Aluminum Nitrate Properties



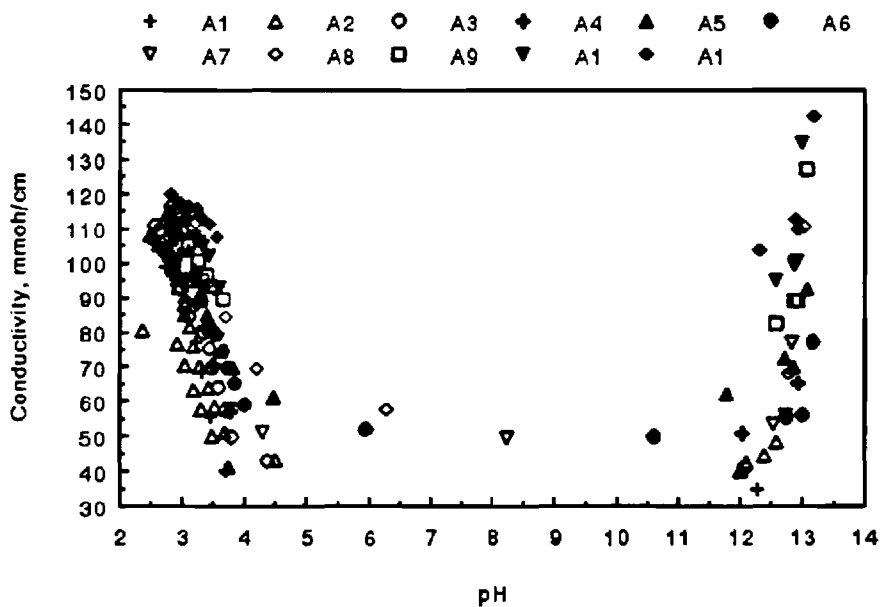
After preparation, the Al solutions and a blank were checked for turbidity using a Beckman 21 spectrophotometer at 540 nm, a ruby laser, and a Malvern Autosizer II,

scanning from the range 200 to 2000 nm. Colloidal Al was not detectable using these methods.

These same solutions were analyzed by NMR for aluminum chemical shift using a Varian XL400 NMR Spectrometer with an external Al standard. All sample peaks appear at the same frequencies, regardless of concentration. Based upon this analysis, we were unable to detect the presence of more than one Al species in solution which appeared to be  $Al^{3+}(H_2O)_6$ .

### Aluminum Nitrate and Sodium Hydroxide

Experimental results are summarized in Tables A1-A11 in the Appendix. Figure 1 shows the changes in conductivity with pH. A minimum is observed between a pH of 4 and 11 due to the formation of aluminum precipitates as shown in Figure 2. The change in pH with the Na/Al ratio is shown in Figure 3. A very rapid change occurs between stoichiometric ratios of 2 to 3 in Na/Al.



**Figure 1 Change in conductivity with pH.**



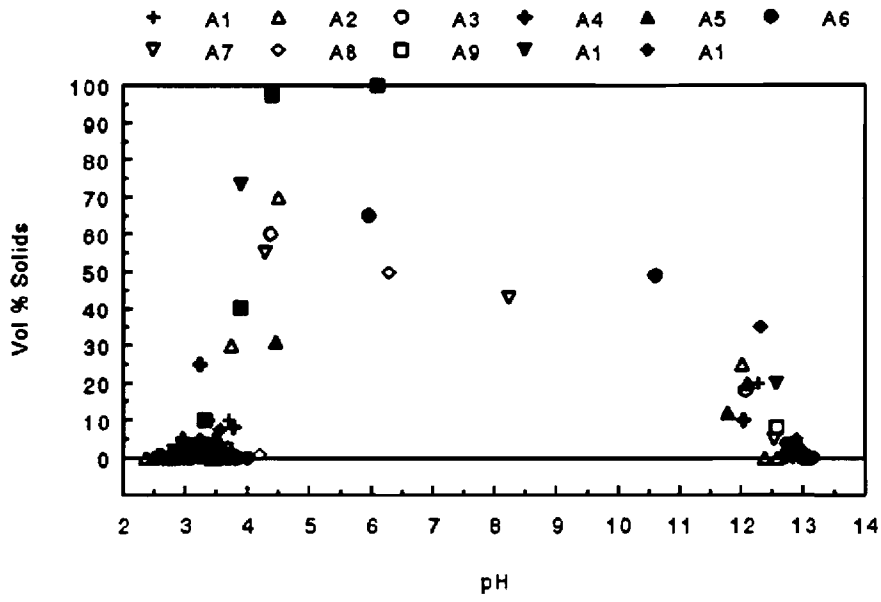


Figure 2 Change in vol% solids with pH.

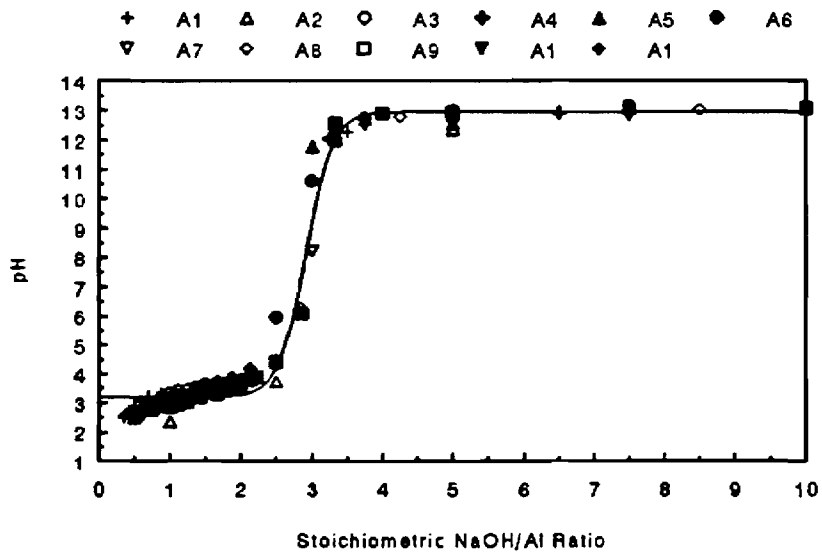


Figure 3 Change in pH with Na/Al ratio.

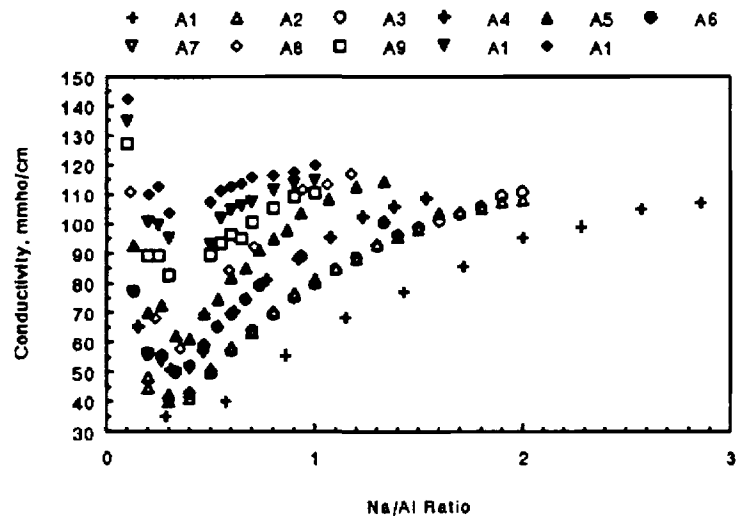


Figure 4 Change in conductivity with Na/Al ratio.

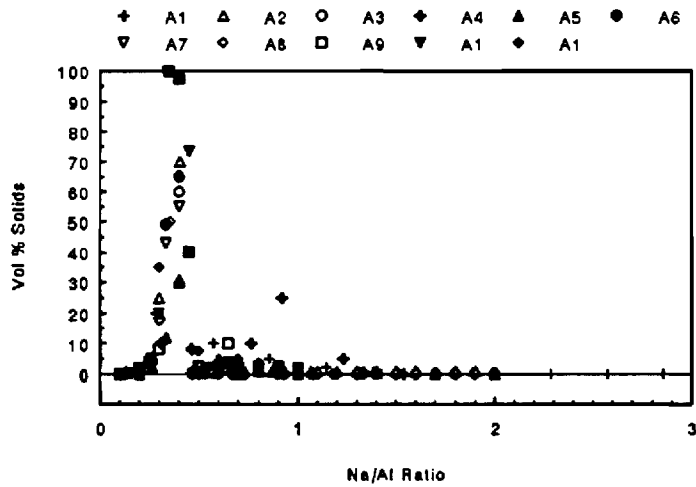


Figure 5 Vol % solids as function of Na/Al ratio.

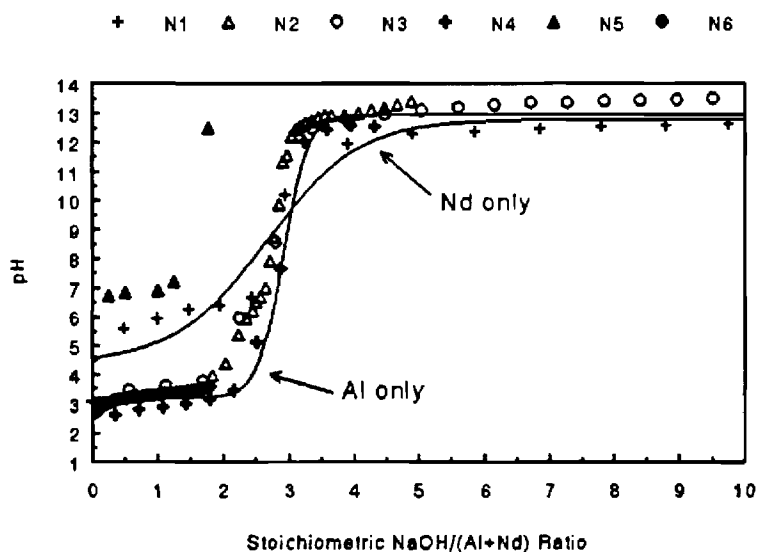
The changes in conductivity and vol % solids with the Na/Al ratio are illustrated in Figure 4 and in Figure 5. The greatest rate of change in both cases occurs between a Na/Al ratio of 3 to 6.

## Neodymium Nitrate and Sodium Hydroxide

The measured behavior in these mixtures is summarized in Tables N1 and N5 of the Appendix. Colloid forms around a pH of 5 to 6. The percentage transmittance is 76% (% Trns) for clear Nd solutions due to their purple color. As NaOH is added, turbidity increases until virtually all Nd precipitates from solution. The supernate is then colorless and clear with 100% transmittance.

## Neodymium Nitrate, Aluminum Nitrate, and Sodium Hydroxide

The behavior for these mixtures is summarized in Tables N2-N4, N6 in the Appendix. Figure 6 illustrates the pH dependence in this system. Limiting behaviors for the Nd + NaOH and Al + NaOH are indicated as solid lines.



**Figure 6** pH dependence on the Na/(Al+Nd) ratio.

## Appendices

### Effects of Al/NaOH Ratios

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Stoichiometric composition: 0.35 M NaOH				
Centrifuged Samples				
Varied Concentrations of Al(NO <sub>3</sub> ) <sub>3</sub>				
	Ppt Vol %	Ppt Characteristics	Conduct mmho	pH
100	20.0	White ppt	34.9	12.28
200	10.0	White ppt	40.3	3.70
300	5.0	White ppt	55.8	3.46
400	2.0	White ppt	68.3	3.32
500	0.0		77.0	3.22
600	0.0		85.6	3.08
700	0.0		95.4	2.90
800	0.0		99.0	2.75
900	0.0		105.2	2.63
000	0.0		107.2	2.50

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Table A2: Effects of Al/NaOH Ratios

Stoichiometric composition: 0.50 NaOH				
Varied Concentrations of Al(NO <sub>3</sub> ) <sub>3</sub>				
Standard Order of Addition:				
Al added to NaOH				
Al, M	Ppt Vol %	Ppt Characteristics	Conduct mmho	pH
0.100	0.0	Clear	48.5	12.57
0.150	20.0	White ppt	42.6	12.09
0.200	70.0	Gel	43.1	4.49
0.250	3.0	White ppt	51.2	3.67
0.300	5.0	White ppt	58.3	3.51
0.350	0.0	Clear	64.1	3.41
0.400	2.0	White ppt	70.2	3.27
0.450	1.0	White ppt	76.1	3.18
0.500	2.0	White ppt	81.6	3.11
0.100	0.0	Clear	44.5	12.37
0.150	25.0	White ppt	40.3	12.00
0.200	30.0	Gel	41.2	3.74
0.250	1.0	White ppt	50.3	3.48
0.300	1.0	White ppt	57.6	3.30
0.350	1.0	Clear	63.3	3.18
0.400	1.0	White ppt	70.4	3.04
0.450	1.0	White ppt	76.7	2.92
0.500	0.0	Clear	80.4	2.37
0.550	1.0	White ppt	85.1	3.04
0.600	1.0	White ppt	88.0	3.03
0.650	1.0	White ppt	92.9	2.94
0.700	1.0	White ppt	95.3	2.92
0.750	1.0	White ppt	98.2	2.87
0.800	1.0	White ppt	103.5	2.80
0.850	0.0	Clear	103.9	2.75
0.900	1.0	White ppt	105.4	2.63
0.950	1.0	White ppt	107.3	2.56
1.000	0.0	Clear	108.3	2.49

Table A3: Effects of Al/NaOH Ratios

Stoichiometric composition: 0.50 NaOH				
Varied Concentrations of Al(NO <sub>3</sub> ) <sub>3</sub>				
Inverted Order of Addition:				
NaOH added to Al Solution				
Al, M	Ppt Vol %	Ppt Characteristics	Conduct mmho	pH
0.150	18.0	White ppt	40.9	12.07
0.200	60.0	Gel	42.9	4.37
0.250	0.0	Clear	49.9	3.79
0.300	1.0	White ppt	57.4	3.69
0.350	0.0	Clear	64.1	3.58
0.400	1.0	White ppt	69.7	3.48
0.450	0.0	Clear	75.3	3.44
0.500	0.0	Clear	79.8	3.34
0.550	0.0	Clear	84.6	3.11
0.600	0.0	Clear	88.6	3.06
0.650	0.0	Clear	92.5	2.99
0.700	0.0	Clear	96.1	2.92
0.750	0.0	Clear	98.8	2.87
0.800	0.0	Clear	101.0	2.80
0.850	0.0	Clear	103.3	2.73
0.900	0.0	Clear	105.6	2.66
0.950	0.0	Clear	109.4	2.64
1.000	0.0	Clear	110.9	2.57

Table A4: Effects of Al/NaOH Ratios

Stoichiometric composition: 0.65 M NaOH				
Varied Concentrations of Al(NO <sub>3</sub> ) <sub>3</sub>				
Al, M	Ppt Vol %	Ppt Characteristics	Conduct mmho	pH
0.100	0.1	Clear	65.3	12.94
0.200	10.0		50.9	12.04
0.300	8.0		57.0	3.77
0.400	0.1		70.4	3.50
0.500	10.0		81.2	3.36
0.600	25.0		88.0	3.23
0.700	0.0		95.4	3.06
0.800	5.0		102.3	2.96
0.900	0.1		105.8	2.83
1.000	0.0		108.4	2.82

Table A5: Effects of Al/NaOH Ratios

Stoichiometric composition: 0.75 NaOH; Centrifuged Samples Varied Concentrations of Al(NO <sub>3</sub> ) <sub>3</sub>				
Al, M	Ppt Vol %	Ppt Characteristics	Conduct mmho	pH
0.100	1.0	White ppt	92.7	13.08
0.150	1.0	White ppt	70.3	12.85
0.200	2.5	White ppt	72.7	12.71
0.250	11.9	White ppt	62.4	11.77
0.300	30.9	White ppt	61.1	4.45
0.350	1.0	White ppt	69.8	3.81
0.400	1.0	White ppt	74.6	3.62
0.450	1.0	White ppt	81.9	3.48
0.500	1.0	White ppt	85.1	3.39
0.550	1.0	White ppt	91.2	3.30
0.600	1.0	White ppt	95.2	3.23
0.650	1.0	White ppt	98.3	3.20
0.700	1.0	White ppt	103.6	3.10
0.800	1.0	White ppt	108.4	2.97
0.900	1.0	White ppt	112.8	2.89
1.000	1.0	White ppt	114.3	2.77



Table A6: Effects of Al/NaOH Ratios

Stoichiometric composition: 0.75M NaOH; Centrifuged Samples Varied Concentrations of Al(NO <sub>3</sub> ) <sub>3</sub> ; Duplicate Samples				
Al, M	Ppt Vol %	Ppt Characteristics	Conduct mmho	pH
0.100	0.0		77.3	13.17
0.150	0.0		56.3	13.00
0.200	3.8	White ppt	55.6	12.74
0.250	49.0	White ppt	50.0	10.61
0.300	65.0	Colloid	52.2	5.96
0.350	0.0		59.1	4.00
0.400	0.0		65.2	3.84
0.450	0.0		69.7	3.73
0.500	0.0		74.6	3.66
0.550	0.0		79.4	3.55
0.700	0.0		89.0	3.32
1.000	0.0		100.5	2.87

Table A7: Effects of Al/NaOH Ratios

Stoichiometric composition: 0.75 M NaOH; Centrifuged Samples Varied Concentrations of Al(NO <sub>3</sub> ) <sub>3</sub> ; Duplicate Samples				
Al, M	Ppt Vol %	Ppt Characteristics	Conduct mmho	pH
0.100	0.0		77.0	12.84
0.150	0.0		56.2	12.74
0.200	5.0	White ppt	53.7	12.54
0.250	43.0	White ppt	49.4	8.24
0.300	55.0	Colloid	51.2	4.30
0.350	0.0		57.7	3.75

Table A8: Effects of Al/NaOH Ratios

Stoichiometric composition: 0.85 M NaOH				
Varied Concentrations of Al(NO <sub>3</sub> ) <sub>3</sub>				
Al, M	Ppt Vol %	Ppt Characteristics	Conduct mmho	pH
0.100	0.0	Clear	110.4	13.04
0.200	2.0	White ppt	68.0	12.77
0.300	7.0	White ppt	57.8	6.28
0.400	1.0	White ppt	69.6	4.19
0.500	0.0	Clear	84.2	3.69
0.600	0.0	Clear	92.2	3.51
0.800	0.0	Clear	111.6	3.22
0.900	0.0	Clear	113.3	2.97
1.000	0.0	Clear	116.9	2.83

Table A9: Effects of Al/NaOH Ratios

Stoichiometric composition:				
1.00 M NaOH, 0.3 M NaNO <sub>3</sub>				
Varied Concentrations of Al(NO <sub>3</sub> ) <sub>3</sub>				
Al, M	Ppt Vol %	Ppt Characteristics	Conduct mmho	pH
0.100	0.0	Clear	127.0	13.08
0.200	1.3	Yellow haze	89.1	12.93
0.250	3.8	White solid	89.3	12.88
0.300	8.1	White solid	82.6	12.57
0.350	100.0	Gel		
0.400	97.4	Gel		
0.450	40.0	Gel with colloid		
0.500	2.5	Flakes	89.5	3.65
0.550	0.6	Flakes	93.4	3.46
0.600	2.5	Flakes	96.3	3.39
0.650	10.0	Flakes	95.0	3.32
0.700	2.5	Flakes	100.6	3.25
0.800	2.5	Flakes	105.5	3.10
0.900	2.5	Flakes	109.1	2.98
1.000	1.3	Flakes	110.5	2.85

Table A10: Effects of Al/NaOH Ratios

Stoichiometric composition: 1.00 M NaOH, 0.6 M NaNO <sub>3</sub> Varied Concentrations of Al(NO <sub>3</sub> ) <sub>3</sub>				
Al, M	Ppt Vol %	Ppt Characteristics	Conduct mmho	pH
0.100	0.0	Clear	134.6	12.99
0.200	1.7	Yellow haze	100.7	12.91
0.250	3.8	White solid	99.4	12.88
0.300	20.0	White solid	95.2	12.57
0.350	100.0	Gel		
0.400	97.0	Gel with colloid		
0.450	73.4	Flakes		
0.500	0.4	Flakes	93.1	3.59
0.550	1.7	Flakes	102.0	3.44
0.600	2.5	Flakes	104.6	3.34
0.650	3.8	Flakes	106.0	3.28
0.700	2.5	Flakes	107.5	3.19
0.800	2.5	Flakes	111.5	3.07
0.900	2.5	Flakes	113.7	3.05
1.000	1.7	Flakes	114.8	2.82

Table A11: Effects of Al/NaOH Ratios

Stoichiometric composition: 1.00 M NaOH, 0.9 M NaNO <sub>3</sub> Varied Concentrations of Al(NO <sub>3</sub> ) <sub>3</sub>				
Al, M	Ppt Vol %	Ppt Characteristics	Conduct mmho	pH
0.100	0.0	Clear	142.5	13.20
0.200	0.6	Yellow haze	109.9	12.93
0.250	5.0	White solid	112.8	12.90
0.300	35.0	White solid	103.6	12.32
0.350	100.0	Gel		
0.400	97.0	Gel		
0.450	40.0	Gel with colloid		
0.500	7.5	Flakes	107.5	3.55
0.550	2.5	Flakes	111.2	3.44
0.600	3.8	Flakes	112.5	3.32
0.650	2.5	Flakes	113.8	3.28
0.700	4.9	Flakes	115.7	3.23
0.800	3.8	Flakes	116.6	3.09
0.900	2.5	Flakes	117.6	2.96
1.000	1.0	Flakes	119.9	2.83

Table N1: Behavior in Nd, Al and NaOH Mixtures

Stoichiometric composition: 0.0333 M Nd					
Varied Concentrations of NaOH					
NaOH, M	Super % Trns	Ppt Vol %	Precipitate Characteristics	mmho/cm	pH
0.000	76	0.0	Clear	7.8	3.07
0.016	67	0.0	Colloid	7.7	5.61
0.033	51	0.0	Colloid	7.4	5.96
0.049	40	0.0	Colloid	7.3	6.26
0.065	23	0.0	Colloid	7.2	6.40
0.081	99	20.8	Purple solid	7.6	6.64
0.098	100	18.8	Purple solid	8.7	10.21
0.130	100	21.9	Purple solid	14.6	11.96
0.163	100	21.9	Purple solid	20.3	12.29
0.195	100	20.8	Purple solid	25.8	12.36
0.228	100	19.8	Purple solid	31.2	12.48
0.260	100	21.9	Purple solid	37.6	12.57
0.293	100	20.8	Purple solid	42.6	12.61
0.325	100	18.8	Purple solid	48.3	12.65
0.358	100	20.8	Purple solid	54.5	12.74
0.390	100	22.9	Purple solid	58.7	12.79
0.423	100	26.0	Purple solid	65.5	12.81
0.455	100	20.8	Purple solid	69.8	12.84
0.488	100	27.1	Purple solid	75.8	12.88
0.520	100	20.8	Purple solid	79.9	12.92
0.553	100	20.8	Purple solid	85.3	12.95
0.585	100	20.8	Purple solid	90.2	12.99
0.618	100	21.9	Purple solid	95.2	13.00
0.650	100	19.8	Purple solid	99.9	13.04

Table N2: Behavior in Nd, Al and NaOH Mixtures

Stoichiometric composition: 0.04 M Nd, 0.2 M Al					
Varied Concentrations of NaOH					
NaOH, M	Super % Trns	Ppt Vol %	Precipitate Characteristics	mmho/cm	pH
0.439		1.0	Purple viscous colloid	45.0	3.96
0.488		93.3	White, amorp solid	42.4	4.39
0.536		95.2	White, amorp solid	43.3	5.40
0.561		95.2	White, amorp solid	43.4	5.96
0.585		89.5	White, amorp solid	45.2	6.22
0.600		91.4	White, amorp solid	45.2	6.49
0.614		93.3	White, amorp solid	44.7	6.71
0.634		97.1	White gel	45.6	7.01
0.648		99.0	White gel	44.5	7.93
0.663		100.0	White gel	46.1	8.75
0.683		100.0	White gel	48.7	9.87
0.697		100.0	White gel	50.4	11.32
0.712		86.7	White solid	50.6	11.54
0.731		82.9	White solid	52.6	12.22
0.746		70.5	White solid	54.9	12.45
0.761		68.6	White solid	56.5	12.56
0.780		66.7	White solid	58.5	12.66
0.804		66.7	White solid	60.6	12.75
0.829		64.8	White solid	63.5	12.86
0.853		64.8	Purple solid	65.8	12.93
0.878		64.8	Purple solid	67.5	12.95
0.926		64.8	Purple solid	66.2	12.93
0.975		62.9	Purple solid	68.8	13.00
1.024		61.0	Purple solid	75.0	13.11
1.073		55.2	Purple solid	81.2	13.20
1.121		53.3	Purple solid	86.6	13.29
1.170		51.4	Purple solid	92.9	13.40

Table N3: Behavior in Nd, Al and NaOH Mixtures

Stoichiometric composition: 0.033 M Nd, 0.2 M Al					
Varied Concentrations of NaOH					
NaOH, M	Super % Trns	Ppt Vol %	Precipitate Characteristics	mmho/cm	pH
0.131	74	0.0	Colloid	43.2	3.46
0.261	74	0.0	Colloid	44.1	3.61
0.392	74	0.1	Colloid	45.2	3.78
0.523	N/A	99.0	Gel	43.0	5.96
0.653	N/A	100.0	Gel	45.8	8.57
0.784	100	53.1	White, amorph	61.1	12.48
0.915	100	56.3	Purple, amorph	65.2	12.68
1.045	100	61.5	Purple, amorph	79.5	12.97
1.176	100	62.5	Purple, amorph	97.4	13.11
1.307	100	56.3	Purple, amorph	113	13.20
1.437	100	44.8	Purple, amorph	129	13.29
1.568	100	41.7	Purple, amorph	143	13.36
1.699	100	40.6	Purple, amorph	158	13.38
1.829	100	39.6	Purple, amorph	171	13.43
1.960	100	38.5	Purple, amorph	184	13.44
2.091	100	37.5	Purple, amorph	195	13.47
2.221	100	34.4	Purple, amorph	207	13.51
2.352	100	34.4	Purple, amorph	218	13.58
2.483	100	34.4	Purple, amorph	230	13.61
2.613	100	33.3	Purple, amorph	240	13.63
2.744	100	31.3	Purple, amorph	248	13.65
2.875	100	27.1	Purple, amorph	285	13.67

Table N4: Behavior in Nd, Al and NaOH Mixtures

Stoichiometric composition: 0.033 M Nd, 0.333 M Al					
Varied Concentrations of NaOH					
NaOH, M	Super % Trns	Ppt Vol %	Precipitate Characteristics	mmho/cm	pH
0.132	72	0.0	Clear	62.0	2.62
0.263	73	0.0	Clear	63.8	2.80
0.395	73	0.0	Clear	64.7	2.87
0.527	73	0.0	Clear	65.0	3.00
0.658	73	2.1	Slight haze	66.1	3.14
0.790	68	35.4	Colloid	66.6	3.46
0.922	N/A	94.8	White gel	61.0	5.13
1.053	N/A	100.0	Purple gel	66.0	7.68
1.185	92	58.3	White solid	83.0	12.02
1.317	100	51.0	White solid	95.8	12.45
1.448	100	59.0	Purple amorph	103.1	12.61
1.580	100	50.0	Purple amorph	99.5	12.57

Table N5: Behavior in Nd, Al and NaOH Mixtures

Stoichiometric composition: 0.133 M Nd,					
Varied Concentrations of NaOH					
NaOH, M	Super % Trns	Ppt Vol %	Precipitate Characteristics	mmho/cm	pH
0.033		10.0	Purple ppt	14.4	6.74
0.067		20.0	Purple ppt	14.6	6.83
0.134		39.0	Purple ppt	14.8	6.91
0.167		24.0	Purple ppt	15.3	7.21
0.234		27.0	Purple ppt	22.9	12.48



Table N6: Behavior in Nd, Al and NaOH Mixtures

Stoichiometric composition: 0.033 M Nd, 0.333 M Al					
Varied Concentrations of NaOH					
NaOH, M	Super % Trns	Ppt Vol %	Precipitate Characteristics	mmho/cm	pH
0.031	73	0.0	Clear	55.6	2.76
0.063	73	0.0	Clear	55.7	2.94
0.094	73	0.0	Clear	56.8	3.05
0.125	73	0.0	Clear	56.8	3.12
0.153	73	0.0	Clear	57.4	3.14
0.188	73	0.0	Clear	57.5	3.17
0.219	73	0.0	Clear	57.8	3.23
0.250	73	0.0	Clear	58.4	3.24
0.281	73	0.0	Clear	58.2	3.25
0.313	73	0.0	Clear	58.4	3.28
0.344	73	0.0	Clear	58.9	3.30
0.375	73	0.0	Clear	59.4	3.32
0.406	73	0.0	Clear	59.7	3.35
0.438	73	0.0	Clear	59.8	3.37
0.469	73	0.0	Clear	60.7	3.37
0.500	73	0.0	Clear	60.0	3.41
0.531	73	0.0	Clear	59.9	3.43
0.563	73	0.0	Clear	60.4	3.46
0.594	73	0.0	Clear	60.9	3.48
0.625	73	0.0	Clear	61.3	3.53
0.656	73	0.0	Clear	62.1	3.57
0.688	73	0.0	Colloid		