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FINAL REPORT

U.S. Department of Energy

Microstructural Properties of High Level Waste Concentrates and Gels with Raman and Infrared Spectroscopies

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Project Number: 54733

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Executive Summary:

Many high level waste (HLW) storage tanks at Hanford, WA and Savannah River, GA contain alkaline aluminate solutions arising from the dissolution of aluminum-clad spent nuclear fuel rods in concentrated alkali. Aluminates, along with hydroxide and high concentrations of nitrite and nitrate, came to be the dominant components of HLW from blending and evaporation of HLW supernatants over the past 40 years of plutonium production at Hanford and Savannah River. Waste processing steps at these sites often involve solutions that are supersaturated with aluminum species. Such solutions can occlude waste transfer pipelines via unwanted scale formation, gelling, and precipitation processes. While much is known about the bulk properties of alkaline aluminate solutions and a high degree of practical sophistication has evolved in handling them in HLW operations, the microscopic chemistry of these solutions is not well understood. Because aluminates serve to define many of the chemical and physical properties of HLW concentrates, several studies have addressed aluminate solubility in highly alkaline solutions with and without the presence of nitrate, nitrate, and other salts such as phosphate, EDTA, glycolate, citrate. More recent studies have focused on the spectroscopic properties of specific aluminate species in solution or in the solid state. Despite these studies, there remains a great deal of uncertainty about the speciation of aluminates in alkaline solutions. It has been suggested that water activity plays a crucial and previously unappreciated role in determining sodium aluminate solubility. The goal of this project was to establish clear connections between the bulk chemical and physical properties (bulk composition, pH, density, viscosity, relative humidity, water activity, gellation and precipitation processes) and microstructural properties (e.g., solvation, intermolecular and intramolecular interactions, ion-molecule interactions, ion-ion interactions) of alkaline aluminate wastes. The data was to be elucidated by detailed IR and Raman spectral measurements of alkaline aluminate solutions and precipitates. The key scientific insights derived from this project follow from an innovative correlation of regions the alkaline aluminate phase diagram with trends in microstructural properties via vibrational spectroscopy. With a better understanding of HLW based upon microstructural properties, the DOE will be better poised to safely store these wastes and will be able to better plan for their retrieval, pretreatment, and final disposal. It should be noted that bulk aluminate solution properties may change dramatically with relatively small changes in composition and temperature. This has direct consequences for safe storage, transport, and pretreatment conditions for these HLW materials.

The major research accomplishments of the project include:

- Successful correlation the microstructural vibrational spectroscopic properties of aluminate species with the alkaline aluminate phase diagram, a first.
- Development of a nitrite internal Raman standard method to provide an intensity baseline for quantitative comparisons of alkaline aluminate Raman spectra.
- Completion of a spectroscopic exploration of the role of water activity in the context of free vs bound water in alkaline aluminate solutions including correlations with bulk physical and chemical properties of the aluminate solutions.
- Completion and publication of a definitive single crystal polarized Raman study of the aluminate phase gibbsite.
- Completion of the first high-pressure, diamond-anvil-cell-based Raman studies of gibbsite and the related aluminosilicate dickite.

Research Objectives:

Background: Although aluminum species constitute a predominant proportion of tank wastes, the chemistry of aluminum in these alkaline solutions is inadequately understood. This is due, in part, to the extreme conditions of the HLW supernatant tank liquors. In REDOX waste, for example, the concentration of Al in HLW supernatants can exceed 1.5 M. In addition, the pH is often greater than 14, and the *individual* molar concentrations of Na^+, NO_3^-, and NO_2^- are in excess of 2 M. As a consequence of the high molar concentrations of Al^{3+}, Na^+, NO_2^-, and NO_3^-, the activity of water in these supernatant solutions is greatly decreased. The concentration of water in these solutions is in the range of 35-45 M, a significant reduction from the pure bulk water value of 55 M. On the molecular scale, there is not enough water present to satisfy the hydration requirements of the Na^+ and $Al(OH)_4^-$ ions in the alkaline aluminum solutions. Thus, most of the water present in the HLW supernatants is chemically "tied up" as hydrated water around the Na^+ and $Al(OH)_4^-$ ions, as well as structural water present in solid aluminate hydrates. The solution-solid phase behavior of the HLW supernatants can be thought of as a competition for water between ionic hydration and the structural water required for the aluminate hydrates. The role of water in these liquid waste concentrates emerges as a key determinant of which solid phases will form and ultimately control the viscosity and precipitation properties as well as the activities of the radionuclides of interest in HLWs.

Attempts to predict the various species of aluminum present in alkaline HLWs using chemical speciation models such as the Reynolds model based on equilibrium thermodynamics have met with little success (1). Sodium aluminate $Na_2Al_2O_3(OH)_2 \bullet 1.5H_2O$ is known experimentally to be a major solid phase component in alkaline HLWs. However, applications of chemical speciation models, such as the Environmental Simulation Program, have incorrectly predicted that much of the aluminum is present as a gibbsite phase (1). The current thermodynamic database does not adequately describe these extreme chemical compositions. As Reynolds (1) stressed, there is an ongoing need to develop an improved thermodynamic database to predict the chemical speciation of the HLW tank liquors. Recent progress has been made, however, by Sterner and co-workers (2), who have extended the Environmental Simulation Program to high base and aluminate concentrations using a combined approach of Raman spectroscopy and thermodynamic methods. Before this objective can be achieved, however, a more in-depth understanding of the chemical species present in these concentrated, caustic solutions and their interaction with water and other HLW constituents was needed—hence this project's the thrust toward microstructural characterization of these alkaline HLW simulants via vibrational spectroscopic methods. Furthermore, kinetic limitations on these reactions are expected to play a major role; true thermodynamic equilibrium is not expected in the short timeframe during precipitate formation. In addition to developing an improved understanding of the speciation of aluminum in alkaline solutions, this study also sought to establish correlations between the spectroscopically observed perturbations of the vibrational modes of water and aluminate solution composition.

Many previous studies have added to the understanding of the aluminum species present in acidic solutions. However, this same level of understanding does not extend across the pH scale. Much remains to be learned about the structures and properties of the aluminum species in alkaline aluminate solutions. The dissolution of aluminum metal or aluminum hydroxide in caustic solution, the so called Bayer process, gives rise to the $Al(OH)_4^-$ species as the main aluminum-containing component of Bayer liquors. The tetrahedral structure of the $Al(OH)_4^-$ ion has been confirmed by electrical conductance (3), Raman (3,4), IR(4), and ^{27}Al NMR (4,5)

analyses. Although this anion has been shown to be the predominant species in alkaline solutions (4,6,7), there also exists spectroscopic evidence for the presence of other species in the alkaline aluminate solutions (3,5,8). A dimeric species $Al_2O(OH)_6^{2-}$ was suggested based upon comparisons between the Raman spectra of the solutions at high aluminum concentrations and the Raman spectrum of the potassium aluminate precipitate (4). The structure of the potassium aluminate includes discrete dimers of aluminate ions. These dimers are comprised of two apically linked tetrahedral Al units (9). The dimeric species in the alkaline sodium aluminate solution was believed to have the same structure as that of the crystal potassium aluminate precipitate (4,5). The ^{27}Al NMR data were also consistent with this structural interpretation given the similar coordination environments of the $Al(OH)_4^-$ and $Al_2O(OH)_6^{2-}$ anions (4,5).

Two main groups of precipitates are observed to form from aluminate solutions: (i) pseudo-boehmite, bayerite, and gibbsite, which have been suggested to crystallize initially as amorphous solids and then in the sequence pseudo-boehmite, bayerite, and gibbsite (10); and (ii) the products precipitated under very high aluminum and NaOH concentrations, $Na_2Al_2O_3(OH)_2 \bullet 1.5H_2O$ (monosodium aluminate MSA) (11,12) and $Na_6Al(OH)_6(NaOH)_3 \bullet 6H_2O$ (trisodium aluminate TSA) (13). The MSA consists of aluminum tetrahedra bonded in a plane with one hydroxide per aluminum sticking out of the plane (11,12). Aluminum tetrahedra are coupled into four- and eight-membered rings of polyhedra with the eight-membered ring forming vertical channels from plane to plane. The sodium ions and waters of hydration are all contained within these linear channels. This structure stands in sharp contrast to that of potassium aluminate (9), which consists discrete dimeric $AlO(OH)_6^{2-}$ units (vide supra). The TSA is an octahedrally-coordinated aluminum hydroxide ion whose trisodium salt forms as a comprised of of 1.5 equivalents of NaOH as well as 3 equivalents of water per $Al(OH)_6^{3-}$ unit (13). Currently, this is the only octahedral species found in the alkaline solutions beside acidic hydrolytic products (5).

General Objective—Correlate Phase Diagram with Microstructural Properties: For practical applications to the treatment of HLWs, it is important to know the transformation of species during the changes of sample compositions, especially the water content. However, most literature on the subject has focused on the structural discussions but not change of solid or solution species as the chemical composition of the solutions changes. Therefore, referencing of physical chemical, and microstructural properties of alkaline aluminates to the appropriate phase diagram (Na_2O-Al_2O_3-H_2O system) is critical. A change in the amount of any single component of this three-component mixture, such as loss of water by evaporation, can be represented as a straight-line trajectory on the phase diagram.

Methods and Results:

Methods

The primary microstructural probes employed in this project were derived from FTIR, Raman, and ^{27}Al NMR spectroscopy. Companion bulk property measurements included density, relative humidity, and composition. MicroRaman spectroscopy was used for all high-pressure diamond anvil cell based studies. The diamond anvil cells (DACs) were of the Merrill-Basset type and were set up with type IA diamonds. Ruby chips were used for pressure calibrations in the DACs. Spectral curve fitting and deconvolution studies were performed using the GRAMS spectral software analysis package. Raman band intensities in the alkaline aluminate solutions were calibrated with respect to an internal nitrite Raman intensity standard. Since the nitrite anion is essentially a non-coordinating species in alkaline aluminate solutions, its characteristic

Raman bands are not significantly affected by changes in the aluminate solutions. Relative humidities of the aluminate solutions were measured using a calibrated, NIST-traceable temperature-compensated capacitance-type relative humidity meter. Densities were measured using a temperature-compensated electronic density instrument. All aluminate samples were prepared quantitatively in such a way as to delineate precisely where each sample should be placed on the alkaline aluminate ternary phase diagram. The three apical points of this phase diagram correspond to sodium oxide, aluminum oxide, and water (*vide infra*). A spreadsheet was used to generate a list of starting quantities (sodium hydroxide, aluminum metal, water) needed to produce alkaline aluminate solutions at given desired final composition points on the ternary phase diagram.

Results

Ternary Na_2O-Al_2O_3-H_2O phase diagram

The axes of the phase diagram are weight percent Al_2O_3, Na_2O, and H_2O. In solution, the Al_2O_3 and Na_2O contents can be also be expressed as molar concentrations of $Al(OH)_4^-$ and Na^+, or excess hydroxide. The dominant controlling solid phases are gibbsite ($Al(OH)_3$), mono-sodium aluminate and tri-sodium aluminatte. In addition, boehmite can occur at temperatures of < 60° C (14). The phase boundaries for these solid phases are based on published solubility studies. These solid aluminate phases have been identified in structural and in spectroscopic studies of precipitates associated with concentrated sodium aluminate solutions (15).

Any change of a single component of this three component mixture, such as loss of water by evaporation, can be represented by a straight-line trajectory on the ternary diagram intersecting the 100% water vertex. With a NaOH:Al of 1:1, the trajectory lies in the gibbsite stability regime until water contents drop below 45 wt. % or so. At this point, the endpoint becomes that of monosodium aluminate, often referred to as the 1.25 hydrate. In other words, aluminate ion is not stable in solution unless there is excess NaOH present. Otherwise, $Al(OH)_3$ precipitates until the solution moves into the unsaturated regime shown on the diagram. In addition, the phase diagram shows that precipitation can occur *upon dilution* depending on upon the location in phase space by intercepting the gibbsite phase boundary.

Of particular interest in this investigation is the behavior of the caustic sodium aluminate species in solution close to the phase boundaries. Although useful spectroscopic information has been reported on concentrated aluminate solutions (16,17,18), there is insufficient solution composition data to tie these spectra to specific composition points on the aluminate phase diagram. In this study, the aluminate phase diagram was used to prepare sodium aluminate solutions based on these phase boundaries. In addition, other key physiochemical properties of the aluminate solutions can be mapped onto the phase diagram including water activity (obtainable, in principle, by measuring the relative humidity above each aluminate solution), and density of each solution.

Raman and IR spectra of sodium aluminate solutions

The dominant vibrational features in $Al(OH)_4^-$ solution are the strong water ν(OH) and deformation bands, the aluminate bands in the 500 - 950 cm^{-1} region, and the vibrational bands of the reference standard NO_2^-. In the Raman spectrum, the aluminate bands occur at 532, 619, and 692 cm^{-1}. IR-active vibrations associated with aluminate species include the 727 and 893 cm^{-1} bands. In addition to the aluminate bands, these spectra also contain contributions from water, excess hydroxide, and the reference nitrite anion.

Many of the HLW slurries contain molar concentrations of both nitrate and nitrite (3). In this study, the concentration of aqueous sodium nitrite was fixed at 0.5 M and the vibrational modes of the nitrite anion were used as an internal standard. In the Raman spectrum, the nitrite bands occur at 814 and 1325 cm^{-1}, which are assigned to the ν_2 and ν_1 modes of NO_2^-, respectively. The IR-active nitrite band, assigned to the ν_3 vibration, occurs at 1250 cm^{-1}.

Of special interest in this study are the IR- and Raman-active vibrations in the HOH bending region of water, and in the OH stretching region from 2700 to 3800 cm^{-1}. The H-O-H bending mode of H_2O has a band position 1663 cm^{-1} in both the IR and Raman. In the OH stretching region, Raman-active vibrational bands occur at 3250, 3398, and 3605 cm^{-1}. The 3250 and 3398 cm^{-1} bands are also present in the IR spectrum and have been assigned as the first overtone of the H-O-H bending vibration of water, and the asymmetric OH stretching vibration of water (19), respectively. The 3605 cm^{-1} (Raman) and 3671 cm^{-1} (IR) bands are associated with the high concentrations of "free" hydroxide. In addition, the IR spectra of some concentrated sodium aluminate (CSA) solutions exhibit a band at 2740 cm^{-1}.

A more detailed analysis of the aluminate and water / hydroxide bands will be presented below. However, the complementary nature of Raman and IR spectroscopy to the study of CSA solutions can be illustrated. Raman spectroscopy provides a sensitive method to study the speciation of aluminates in solution. In addition, because of the high molar concentrations of Na^+, OH^-, and $Al(OH)_4^-$, the water molecules contained in these CSA solutions are expected to be perturbed by their "close" proximity to these ionic constituents. The water vibrations are predominant features in both the Raman and IR spectra of the CSA solutions. The intensity of the H-O-H bending vibration of water is very weak in the Raman spectrum. This band is very intense in the IR spectrum, however, due to a difference in selection rules between IR and Raman spectroscopy.

Raman and IR spectra in the Al-O stretching region (500 - 950 cm^{-1})

Raman spectra of the 1, 3 and 5 M aluminate solutions exhibit aluminate bands occurring at 537, 620, and 692 cm^{-1}. Also contained in these spectra is the ν_2 band of nitrite which, along with the ν_3 band at 1275 cm^{-1}, is employed as an internal standard. The Raman intensities of the 537, 620 and 692 cm^{-1} bands are normalized to the 1325 cm^{-1} band of nitrite (ν_1 mode). The intensities of the 537 and 692 cm^{-1} bands increase disproportionately relative to that of the 620 cm^{-1} band. When the solution concentration of Al is 1 M, the 620 cm^{-1} band accounts for > 80% of the total Raman intensity present from the Al-O stretching bands. In contrast, the 620 cm^{-1} band represents < 50% of the total Raman intensity when the Al concentration is 5 M (Figure 5b). These results are in agreement with Raman and IR studies of sodium aluminate solutions (17,20,21).

Moolenaar and coworkers (21) were among the first to assign the 537 and 692 cm^{-1} bands to a dimeric hydroxide ion $[(OH)_3AlOAl(OH)_3]^{2-}$ species (21):

$$2\ Al(OH)_4^- \leftrightarrow (OH)_3\text{-}Al\text{-}O\text{-}Al\text{-}(OH)_3^{2-} + H_2O. \qquad (1)$$

Their interpretation was based on a comparison of the Raman spectrum observed at high aluminate concentration with that of solid sodium aluminate, assuming its crystal structure to be similar to that of known potassium aluminate (22). However, they could not rule out the possibility that the new species was some other form of aluminate, such as a dehydrated monomer

$$Al(OH)_4^- \leftrightarrow OAl(OH)_2^- + H_2O, \qquad (2)$$

which presumably could dehydrate even further to form AlO_2^-. Note that the formation of each of these species is linearly dependent on water activity and the sequence represents a two-step mechanism for reaction. If aluminate does indeed dimerize in concentrated alkaline solution as per reaction (1), it should, in principle, also form higher oligomers as well, such as

$$(OH)_3\text{-Al-}[\text{O-Al}(OH)_2\text{-O}]_n\text{-Al-}(OH)_3^{-n+2}. \qquad (3)$$

An earlier Raman study (13) had assigned these bands to a proposed linear AlO_2^- species. To date, no direct (i.e., spectroscopic) evidence has been reported to support the existence of the AlO_2^- species. However, this species has been invoked in a recent modeling study (1). Subsequent Raman and FTIR studies, however, have supported the assignment of the new bands to the aluminate dimer species (14,23). However, Watling et al. have argued recently that more complex aluminate polymers and oligomers may be present in addition to the $Al(OH)_4^-$ and $[(OH)_3AlOAl(OH)_3]^{2-}$ species (15).

The measured Raman depolarization ratios for the 537, 620, and 692 cm^{-1} aluminate bands are 0.04, 0.01 and 0.17, respectively. The depolarization ratio can be used to distinguish totally and non-totally symmetric vibrations. For totally symmetric vibrations, the depolarization ratio has a value close to zero. Assignment of the 620 cm^{-1} band to the totally symmetric Al-O vibration of the monomeric $Al(OH)_4^-$ species is confirmed by the very small depolarization value of 0.01 in agreement with recently reported values (15). The larger depolarization ratios of 0.04 and 0.17 for the 537 and 692 cm^{-1} bands indicate that these vibrational modes have lower symmetry. This supports their assignment to a dimeric-polymeric species in solution.

Additional support for the presence of these monomeric and dimeric species comes from a recent theoretical study of aluminate species in alkaline solution (14). In dilute solution, the calculations suggested that the tetrahedrally coordinated $Al(OH)_4^-$ species was favored energetically on the basis of *ab initio* calculations. At high concentrations of aluminate, the dimeric doubly hydroxyl-bridged species $[(OH)_3Al(OH)_2Al(OH)_3^{2-}]$ was favored. In these theoretical studies, both water molecules and the coordinated hydroxyl groups played a critical role in determining the stability of the aluminate structures in solution. In fact, one of the key theoretical limitations at present is the ability to include solvent effects in a meaningful way. They concluded that further work is now needed to examine the effects of water and sodium ions explicitly within a quantum mechanical framework (14).

Raman and IR spectra of the ν_2 mode of water (H-O-H bend)

Despite the large number of experimental and theoretical studies of alkaline aluminate solutions and their precipitates, the role of water and of coordinated hydroxide ions in aqueous solution has largely been ignored. Prior vibrational studies of concentrated alkaline aluminate solutions have focused exclusively on the Raman- and IR-active aluminate bands in the 500 - 950 cm^{-1} region. The vibrational modes of water and hydroxide in the H-O-H bending region and O-H stretching region have received little, if any, attention. As indicated earlier, all of the proposed dimerization reactions involve the release of water. Furthermore, these reactions all involve hydroxyl groups coordinated directly to aluminum ions. Finally, the activity of water present in these concentrated alkaline aluminate solutions is significantly lowered by the high ionic concentrations of sodium, aluminate, and excess hydroxide.

H-O-H bending region of concentrated alkaline aluminate solutions

Raman and IR transmission spectra showing the HOH bend and NO_2 stretching vibrations of 1, 3 and 5 M aluminate solutions were measured. Using nitrite as an internal standard, the IR and Raman spectra were fit using two bands at 1663 cm^{-1} and 1580 cm^{-1}. The use of these two bands was based on a recent Raman study of water (24) where two components were clearly resolved in the H-O-H bending region. In water, the position of the higher frequency band occurs at 1640 cm^{-1} and is assigned to the ν_2 mode of partially hydrogen-bonded water. The 1581 cm^{-1} band was assigned the ν_2 mode of water molecules that are in a "fully" hydrogen-bonded configuration. According to Pimentel and McClellan (25), however, the energy of the ν_2 band of water is expected to increase as hydrogen bonding increases, which would argue against this assignment. What is clear, however, is that two components are present in the ν_2 region. The intensity of the higher frequency component at about 1663 cm^{-1} decreases sharply as a function of the relative partial pressure of water and intercepts the *x*-axis at a relative humidity of about 30%. This analysis suggests that two types of water are present in the sodium aluminate solutions. The 1663 cm^{-1} band corresponds to the "free" water and the lower frequency component is tentatively assigned to water "constrained" water molecules. As the aluminate concentration increases, the intensity of the 1663 cm^{-1} band is strongly decreased relative to that of the 1580 cm^{-1} band.

The intensity of the ν_2 band of water at 1663 cm^{-1} was normalized to the intensity of the ν_1 mode of nitrite at 1325 cm^{-1} in the Raman spectra and to the intensity of the ν_3 mode of nitrite at 1250 cm^{-1} in the IR. Unlike the OH stretching region, which contains contributions from both hydroxide and water, the only contribution to the 1600 - 1700 cm^{-1} region (H-O-H bend; ν_2 mode) is from water itself. The Raman and IR intensities of the ν_2 band of water decrease in a linear fashion as the molarity of water is decreased. More importantly, the intensity of this band is highly correlated to the molar concentration of water, the density of the aluminate solution, and to the water vapor pressure above the solution (i.e., relative humidity).

The position of the ν_2 band of water in the IR and Raman spectra of the alkaline aluminate solutions ranges from 1655 cm^{-1} at 1 M to 1663 cm^{-1} at 5 M. These values compare to a position of 1643.5 cm^{-1} in IR spectrum of bulk water (19). As hydrogen bonding increases, the OH stretching bands shift to lower frequencies and the HOH bending band shifts to higher frequency (25). The 20 cm^{-1} blue-shift of the HOH bending band from that of bulk water reflects an overall increase in the extent of hydrogen bonding present in the alkaline aluminate solutions. Because of the broad, overlapping bands in the IR spectra of the alkaline aluminate solutions, a shift in position of the ν(OH) bands is not resolved. An increase in hydrogen bonding is consistent with the high concentrations of aluminate, excess hydroxide, and Na^+ in these alkaline aluminate solutions.

ν(OH) region of concentrated alkaline aluminate solutions

The ν(OH) region contains spectral contributions from water, excess hydroxide, and hydroxide coordinated to aluminum (e.g., $Al(OH)_4^-$). Overall, the spectra in the ν (OH) region are similar with bands at 3608, 3393, and 3250 cm^{-1}, and a low frequency shoulder centered at about 3000 cm^{-1}. The intensity of the 3608 cm^{-1} band increases with increasing excess hydroxide concentration as does the low frequency shoulder at about 3000 cm^{-1}. The total Raman intensities in the ν (OH) region along with Raman and IR intensities of the ν (HOH) (ν_2 mode at 1663 cm^{-1}) can be plotted as a function of H_2O molarity. Unlike the ν_2 band of H_2O, the total

Raman intensity in the ν (OH) region shows a slight decrease with decreasing molarity of H_2O and has a large positive intercept. The large positive intercept at zero H_2O molarity reflects the large amount of excess hydroxide and hydroxide coordinated to aluminum.

One of the unique features of concentrated alkaline solutions is the Raman-active band at 3608 cm^{-1}. This band has been assigned to the ν (OH) vibration of free hydroxide. A more careful analysis of this band in future studies may provide access to the role of sodium ions in the aluminate solutions.

High pressure Raman investigations of solid aluminate and related aluminosilicate species

The work of Johnston et al, who recently published definitive single crystal polarized Raman studies of the solid aluminate species gibbsite (26) and the related aluminosilicate species dickite (27), set the stage for high-pressure diamond-anvil-cell-based Raman investigations of these two compounds. These pressure-dependent Raman investigations focused on the rich OH stretching regions of the two minerals. In both gibbsite and dickite, a number of Raman active OH bands in the 3300 – 3700 cm^{-1} region, corresponding to distinct OH sites, are observed. Preliminary high-pressure investigations in the OH region of gibbsite reveal the following trends. The Raman OH bands shift to higher energies upon pressurization. A phase change occurs around 23 kbar with the appearance of new bands and disappearance of some old bands. The depressurization cycle following a maximum pressure of 60 kbar exhibits hysteresis when compared to the pressurization cycle. While the original, unpressurized Raman spectrum is essentially recovered at the end of the pressurization cycle, some small but distinct changes are apparent in the pressure-cycled gibbsite sample. The OH-1 internal dickite Raman band appearing at 3623 cm^{-1} at ambient pressure first red shifts to 3618 cm^{-1} at 19 kbar then blue shifts and broadens from 19 –55 kbar. At 55 kbar, the band maximum appears at 3645 cm^{-1}. This meandering pressure shift can be interpreted as evidence for a phase transition in dickite that occurs in the ambient-to-19 kbar pressure regime. The more external OH-2, OH-3, and OH-4 bands of dickite exhibit complex pressure responses. These high-pressure studies represent an important generalization and extension of the original aluminate project into an exciting and relevant new arena. The studies on these solids provide the requisite foundation to look at pressure as a perturbation in aluminate solutions.

Relevance, Impact and Technology Transfer:

a. *How does this new scientific knowledge focus on critical DOE environmental management problems?* The correlation of microstructural alkaline aluminate HLW properties via spectroscopy with bulk properties of HLWs opens up critical new avenues for understanding and better working with HLWs. For example, microstructural characteristics derived from can be used to detect and predict the onset of unwanted precipitation processes in HLWs.
b. *How will the new scientific knowledge that is generated by this project improve technologies and cleanup approaches to significantly reduce future costs, schedules, and risks to meet DOE compliance requirements?* Microstructural, spectroscopically-based investigations of HLWs building upon this project's fundamental studies point to the possibility of rapid monitoring and feedback of HLW conditions in real time. For example, fiber-optic cable based Raman spectroscopy can be employed to monitor HLW tank contents, analyze real time flow conditions HLW pipelines, and to warn of impending problems. Also important is the potential to utilize the microstructural paradigm as a basis for designing newer, more

efficient, less costly, less time-consuming, and more environmentally friendly options for alkaline aluminate HLW treatment, minimization, and storage in the future.

c. *To what extent does the new scientific knowledge bridge the gap between broad fundamental research that has wide-ranging applications and the timeliness to meet needs-drivenn applied technology and development?* The project's fundamental design was based upon the "bridging-the-gap" concept that the microstructural and bulk properties of alkaline aluminate HLWs should be correlated in a systematic fashion. Needs-driven applied technology as applied to alkaline aluminate HLWs will, of necessity, focus on controlling bulk properties. This project gives a microstructural, spectroscopically-based rationale for monitoring and controlling bulk alkaline aluminate HLW properties in the interest of environmental preservation.

d. *What is the project's impact on individuals, laboratories, departments, and institutions? Will the results be used? If so, how will they be used, by whom, and when?* The project greatly enhanced LANL's capability to connect its spectroscopic expertise at the microstructural level to a HLW problem in which bulk HLW properties need to be better understood. Specifically, the project served to establish clear connections between vibrational spectroscopic observables and specific points on the alkaline aluminate ternary phase diagram. Diamond anvil cell expertise for high-pressure vibrational spectroscopic studies of aluminate materials developed for this project has been disseminated to LANL CST-4 and to the laboratories of the university collaborators at Purdue University and Eastern New Mexico University.

e. *Are larger scale trials warranted? What difference has the project made? Now that the project is complete, what new capacity, equipment or expertise has been developed?* The project provides a sound, spectroscopically-based foundation for a deeper understanding of alkaline aluminate HLWs. With this deeper understanding comes the potential to handle these HLWs at an unprecedented level of speed, safety, and sophistication while significantly reducing undesirable environmental impacts and minimizing costs. A logical, practically-focused extension of this project would be to carry out *in situ* vibrational spectroscopic probes of real alkaline aluminate HLWs at Hanford and Savannah River (e.g., via a fiber optic cable Raman system) and map these results onto the ternary alkaline aluminate phase diagram. With this data, informed predictions of the future behavior of the HLW could be made and, if necessary, an intervention strategy could be implemented to modify this behavior to constrain it to an environmentally desirable outcome.

f. *How have the scientific capabilities of collaborating scientists been improved?* Both of the university research groups collaborating on the project enhanced their scientific capabilities significantly. Professor Johnston and his students at Purdue University learned high-pressure diamond anvil cell technology and now have the expertise to incorporate it as a regular component of their spectroscopic measurement arsenal. Professor Kenney and his students at Eastern New Mexico University learned how to extend the diamond anvil cell techniques they have developed for electronic spectroscopy to include the vibrational spectroscopic regime. They also acquired much valuable experience and expertise in setting up Raman experiments and Raman imaging systems.

g. *How has this research advanced our understanding in the area?* The key advances in the scientific understanding derived from the project are: (a) the formulation of a spectroscopically based model of the roles of bound vs. free water in elucidating alkaline aluminate chemistry at the microstructural level, (b) establishing connections between the

bulk aluminate properties in the macroscopic regime as summarized by the ternary phase diagram and the microscopic spectroscopic properties of aluminate solutions and precipitates, and (c) a spectroscopic characterization of the pressure responses of selected aluminate species.

h. *What additional scientific or other hurdles must be overcome before the results of this project can be successfully applied to DOE Environmental Management problems?* The project results are sufficiently well refined and sufficiently complete in their present form to be of considerable value in addressing problems associated with alkaline aluminate HLWs. The additional studies recommended in the Future Work section (*vide infra*) would make the study even more valuable in a practical context to address DOE concerns.

i. *Have any other government agencies or private enterprises expressed interest in the project?* Yes.

Project Productivity:

The project schedule was modified to accommodate a change of PI in year three of the project. The original project PI, Dr. Stephen F. Agnew, took a leave of absence from Los Alamos National Laboratory in February 1999. Dr. Jon R. Schoonover took over Dr. Angew's duties as project PI with provisions for Dr. Agnew to remain within the project loop as a consultant. Project schedule modifications also arose from problems with the Raman laser system and problems in aluminate sample relative humidity measurements during the high humidity summer months in Los Alamos.

Personnel Supported:

The project provided postdoctoral support at Los Alamos National Laboratory for Dr. Curtis Westerfield, now at Komag, Inc. Mr. Rob Corbin was also supported at LANL for technical assistance on the project. University faculty collaborators supported included Professor Cliff T. Johnston from Purdue University and Professor John W. Kenney, III from Eastern New Mexico University. Professor Johnston's student Mr. Shan-Li Wang and Professor Kenney's students Ms. Melissa Summers and Ms. Bobbi Torres also were supported to carry out summer research activities on the project at LANL.

Publications:

Professor Johnston's single crystal Raman study on gibbsite (accepted for publication *in Am. Mineralogist*) is a major outcome of this project (26). Professors Kenney and Johnston, together with their students, have collaborated on two diamond-anvil-cell-based high-pressure Raman investigations of aluminate or aluminate-like species (gibbsite and dickite) that are being prepared for publication in the near future. A summative project manuscript on aluminate speciation and aluminate/water interactions as elucidated by vibrational spectroscopy is being prepared for publication in *Environmental Science and Technology*.

Interactions:

a. Presentations at Scientific Meetings: Former PI Steve Angew gave a presentation titled "IR and Raman Studies of High Level Waste Concentrates" at the 52nd Northwest Regional ACS Meeting in Moscow, ID, June 18-21, 1997. Profesor Cliff Johnston gave an overview presentation of the project at the CMST-CP annual review conference in Gaithersburg, MD on

March 11, 1999 titled "Microstructural Properties of High Level Waste Concentrates and Gels with Raman and Infrared Spectroscopies".

c. Long Term Collaboration Initiated: This project stimulated a long term collaborative research relationship in higih pressure vibrational spectroscopy between the two university collaborators on the project, Professor Johnston at Purdue University and Professor Kenney at Eastern New Mexico University.

Transitions:

N/A

Patents:

No patents were filed or awarded for this project.

Future Work:

The successes and challenges of present project point clearly to a number of opportunities for significant new work in the future.

Refinements in Existing Procedures and Experiments: In the course of the present project it became apparent that certain refinements in what was already being done would give rise to more accurate, reproducible experimental results. Relative humidity measurements on aluminate solutions require great care. A capacitance-type relative humidity meter was employed in all work reported in this study. Meter hysteresis, long equilibration times, lack of agreement between identical NIST calibrated meters, and dependence of relative humidity readings on the distance of the probe above the solution are problems that have been encountered with the capacitance method. An alternative worth investigating in subsequent studies is an absolute water vapor pressure measurement above freeze-pump-thaw degassed aluminate solutions. Another alternative is to measure water vapor content above aluminate solutions by quantitative IR absorption spectroscopy through a known cell pathlength. These alternatives are proposed as ways to circumvent the hysteresis/non-reproducibility problems encountered with the capacitance method. If the capacitance method is retained in future humidity studies, comparisons between meters and a reproducible measurement protocol are essential prerequisites. In future work, it is recommended that relative humidity, density, and spectroscopic measurements be taken on samples thermostatted to the same temperature. The present "room temperature" experimental protocol represents a range of temperatures between ~18 - 27° C depending upon the day and the location of the specific experiment or measurement.

Role of Carbonate: Further study is needed to address the critical role of the carbonate anion CO_3^{2-}, a known constituent of aluminate tank wastes derived from atmospheric CO_2 absorption, in perturbing alkaline aluminate speciation and precipitation processes. A number of important questions come to mind. To what extent does carbonate displace hydroxy anions bound to aluminates? How does the presence of carbonate affect alkaline aluminate monomer/dimer/ oligomer equilibria? Are alumino-carbonate species present in alkaline aluminate solutions?

Can these be detected and identified spectroscopically? Do alumino-carbonate precipitates form from alkaline aluminate solutions exposed to atmospheric CO_2? How much CO_2 must be dissolved in an alkaline aluminate solution to give rise to significant chemical perturbations? Does unintentional atmospheric CO_2 absorption in laboratory aluminate solutions during preparation and use constitute a significant problem? Careful vibrational spectroscopic investigations of known alumino-carbonate solid phases are needed to set the stage for spectroscopic investigations of aluminate solutions containing carbonate. Studies based upon isotopically labeled CO_2 absorption by alkaline aluminates are potentially valuable in sorting out the vibrational spectroscopic assignments of alumino-carbonate species in the solution phase and in the solid state. The use of $^{13}C/^{18}O$ labeled CO_2 (and also $^{13}C/^{18}O$ labeled Na_2CO_3) opens up the intriguing possibility of using ^{13}C and/or ^{18}O NMR together with the more traditional ^{27}Al NMR to investigate alumino-carbonate speciation in alkaline aluminate solutions.

Role of Nitrate: The nitrate anion is employed as an internal Raman scattering standard in the present study. Nitrite is assumed to be non-coordinating with respect to aluminate species. It would be worthwhile to test whether or not nitrite does indeed behave as a good standard. Such a test could be performed by systematically decreasing the nitrate concentration in the aluminate solutions and extrapolating the results to the limit $[NO_2^-] = 0$.

Temperature Effects: All of the spectroscopic measurements and companion physical property measurements in the present study were performed on aluminate solutions at or very near 25°C. Much can be learned by carrying out these studies as a function of temperature. Experimentally, the changes required for temperature-dependent studies are extremely modest: equipping the Raman instrument with a thermostatted solution cell holder and changing the temperature at which relative humidity and density measurements are performed to match the spectroscopic cuvette temperature. Careful elucidation of the aluminate monomer/dimer equilibrium constant as a function of temperature and extraction of an enthalpy value via a van't Hoff analysis represent obvious future goals. A much more complex but extremely worthwhile goal is the characterization of the phase and precipitation behavior of aluminate solutions as a function of temperature via spectroscopic probes at the microstructural level.

High Pressure Effects: The present project included high pressure DAC-based Raman spectroscopic investigations of the phase and structural behavior of gibbsite, a key solid component of the ternary aluminate phase diagram. The six distinct OH vibrations in gibbsite display unique, site-dependent band intensities and energies. Work is now in progress to characterize the pressure responses of these six hydroxyl vibrations. High-pressure vibrational spectroscopic studies on a related crystal, dickite, which also displays several distinct hydroxyl structural environments, are complete and being prepared for publication. DAC-based vibrational studies on the other solid aluminate phases (monosodium aluminate and trisodium aluminate) constitute the logical next step for future high-pressure investigations. Also important for future studies are high-pressure investigations of aluminate solution phases. It is possible, in principle, to construct a ternary aluminate phase diagram as a function of pressure in which the solution and solid constituents are identified and quantitated by vibrational spectroscopic methods. A pressure-dependent aluminate phase diagram could have significant potential practical applications in advancing the understanding of complex aluminate processes involving pressure. Examples include shock wave compressions associated with valve closures

in alkaline aluminate liquid waste tank pumping systems, pressure from the buildup of trapped encapsulated gases in liquid wastes and slurries via radiochemical processes, and high pressures associated with deeply buried wastes subjected to geological pressure gradients.

Aluminate Thin Film Solution Evaporation Studies: FTIR spectroscopy was employed in the present study to monitor composition and speciation changes in thin films of aluminate solutions over time as these films lost water to evaporation. The film thickness, temperature, and density were not monitored in these studies. Future thin film evaporation experiments should include a provision for monitoring these three key physical properties in real time as the spectra are measured. This would allow the evaporation spectra to be correlated with aluminate concentrations at specific points in the ternary alkaline aluminate phase diagram. For example, film thickness changes over time could be monitored by interference the laser interference fringe method used in matrix isolation spectroscopy (28). Both thickness and density information could be obtained, in principle, by suspending the sample in the FTIR beam path (e.g., a thin ZnSe window onto which a thin film of aluminate is spread) from a quartz microbalance (29) so that water loss could be monitored quantitatively while thickness was measured interferometrically.

Effects of Other Cationic Species: The present study focused exclusively on alkaline aluminate solutions in which the metal cation present is sodium, Na^+. Further studies of aluminate solutions containing other cations with different hydration energies (e.g., Li^+, K^+, Rb^+, Cs^+, Sr^{2+}, NH_4^+, $N(CH_3)_4^+$) would be of great interest as these cations are expected to alter the nature of the competition for water by aluminate vs. cation and thereby affect aluminate speciation. It is known, for example, that K^+ stabilizes the aluminate dimer relative to the monomer. Such studies would be of considerable importance in elucidating the behaviors of the radionuclides $^{137}Cs^+$ and $^{90}Sr^{2+}$ in alkaline aluminate solutions. Cations with low hydration energies can organize the aluminate solutions by acting as structure directing species. Precipitation of higher aluminate oligomers by large bulky cations (e.g., $N(CH_3)_4^+$) is another worthwhile goal for subsequent studies on alkaline aluminate solutions.

Raman Depolarization Ratio Studies: Raman depolarization ratio trends in aluminate, water, and hydroxide bands are complex and not easily related to the species present in alkaline aluminate solutions. Depolarization ratio changes in the aluminate monomer/dimer bands observed in the present study may point to the formation of species with differing symmetries but more work needs to be done before any definitive assignments can be made. A more comprehensive investigation of aluminate depolarization ratios in future studies may lead to a much better understanding of microstructural properties of aluminate solutions. This investigation should include a combined experimental/theoretical effort aimed at elucidating the effects of cations and coordinated water molecules on the depolarization ratios of anionic aluminate species.

Simulations and Modeling of Aluminate Species and Solutions: Recent theoretical work by Gale and coworkers on ab initio aluminate simulations, while interesting and significant, focused only on the modeling of individual aluminate species and some highly simplified interactions between these species, water molecules, and cations (14). More realistic simulations that seek to model the complex interspecies interactions in solution are needed. A good alkaline aluminate solution model must consider not only the interactions and equilibria between aluminate species themselves but also the effects of the water hydration sphere(s) around these aluminates. Much

more work needs to be done in modeling the interactions in aluminate solutions involving cationic species (e.g., Na^+ or, more generally, M^{z+} cation hydration effects and structure directing properties). Finally, the modeling of aluminate precipitation processes is important.

Long Term Alkaline Aluminate Precipitation Studies: When allowed to stand for a long period of time (several months), some aluminate solutions prepared for solution-phase spectroscopic and bulk physical property measurements have been observed to form precipitates. A long-term study is needed in which aluminate solutions are prepared, allowed to sit, but monitored on a regular basis to look for precipitate formation. Follow up studies on those solutions in which precipitation occurs should include (a) identification and analysis of the precipitates by micro XRF and microRaman spectroscopies and (b) remeasurement of solution phase properties so that quantitative comparisons can be made to the solution properties measured shortly after preparation.

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