

Physicochemical Mechanisms Controlling the Periodic Release of Flammable Gases from Hanford Tanks

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Hanford tanks contain more than 60 million gallons of high-level wastes produced by decades of extracting plutonium from irradiated uranium fuel. The wastes were concentrated to a thick slurry consistency by evaporation prior to storage to minimize space. The resulting concentrated waste properties introduced unanticipated, detrimental conditions affecting workers' and the public's health and safety and involving the release of potentially flammable gases. The released gases consist primarily of hydrogen, nitrous oxide, and ammonia.

Dilution and sluicing were initially proposed to mitigate the flammable gas safety conditions. As a result of evaluations, the mechanisms and conditions that are thought to control the accumulation and spontaneous release of flammable gases were identified and confirmed. The technical rationale was established for developing operational approaches to mitigate the periodic generation of flammable gases in existing tanks and to avoid any reoccurrence of this serious safety problem during future waste management activities. The chemistry of the two highest risk tanks was examined to test the potential for reversing the conditions causing gas buildup and the consequences of sluicing without appropriate chemical conditioning. The identified mechanisms apply equally to the remaining flammable gas tanks at Hanford as well as to other waste tanks in the DOE complex, particularly those at Savannah River. Passive means of mitigating the flammable gas condition require less than 1:1 dilution, and sluicing wastes from tank 106-C can be accomplished without creating a flammable gas condition.

Carbonate equilibria reactions and their effect on aluminum speciation are largely overlooked and provided the key for explaining the episodic release of flammable gases from tank wastes. The reaction of atmospheric carbon dioxide with a sodium hydroxide-rich waste solution produces carbonate precipitates. More importantly, this reaction lowers the pH of the waste and precipitates aluminum hydroxide as a gel. The wastes contain substantial amounts of complexing agents such as ethylene diamine tetraacetic acid (EDTA), hydroxy ethylene diamine triacetic acid (HEDTA), and their degradation products. These complexing agents stabilize the

aluminum hydroxide gel together with chromium, manganese and iron hydroxides, and oxyhydroxides under the resulting pH conditions. These complex species may coprecipitate and accumulate as a metastable layer in the middle and lower levels of the tank. The complexed aluminum hydroxide acts as a binding agent trapping other particulates in a microcrystalline mat. Microcrystalline particles such as sodium nitrite provide the structural strength for the mat.

Once the gas accumulation below the gel layer achieves a critical buoyancy sufficient to rupture the microcrystalline mat, a gas release event occurs. The cycle of gas buildup and release continues each time the buoyancy of the trapped gas exceeds the hydrostatic pressure and the gels' plasticity modulus. Stokes Law predicts a particle settling rate in the tank of less than 50 days, well within the historical periodicity of GREs.

Laboratory tests, forming the basis of a recent patent application, verify that large quantities of complexed aluminum hydroxide gel are produced by passing carbon dioxide through simulated waste solutions (Hohl, 1993) equivalent to those found in tank 101-SY. It was confirmed that a simple adjustment of pH will redissolve the gel, thereby reducing viscosity and safely facilitating continuous flammable gas release. Additional experiments were undertaken to provide a basis for understanding the role of complexed aluminum hydroxides in the $\text{CO}_2/\text{NaOH}/\text{Al}(\text{OH})_3$ (complexing agents)/ NaAlO_2 system.

This article examines a plausible mechanism for the periodic release of flammable gas and considerations for: (1) remediating existing flammable gas tanks through a combination of chemical treatment and mixer pumps; (2) diluting, combining, retrieving, and storing wastes; (3) preventing clogging of transfer lines; (4) sludge and soil washing; and (5) cribs, ponds, basins, and ground-water cleanup. This study provides a significant breakthrough for tank waste management by explaining key mechanisms controlling episodic release of flammable gases. The breakthrough provides the bases for removing the tanks classified as flammable gas from the watch-list and has broad operational applications with a potential for billions of dollars in cost savings.

Reactions due to radiolysis and heat continued within the tanks for as long as five decades, resulting in a waste product that is difficult to characterize.

Tank wastes at Hanford are some of the most complex mixed wastes known. Hanford operations used a wide variety of reagents to recover plutonium and other Transuranic Radioisotopes (TRUs) from irradiated fuel. The waste solutions from processing were saturated with respect to sodium nitrate and nitrite and contained a variety of surfactants, solvents, cleaning reagents such as sodium carbonate, and other process chemicals such as sodium hydroxide and aluminum. As a consequence, a complicated waste mix including large quantities of radioactive wastes, process reagents, and their decomposition products were transferred to storage tanks. Reactions due to radiolysis and heat continued within the tanks for as long as five decades, resulting in a waste product that is difficult to characterize. A considerable effort and its related literature have been compiled on the composition and physical-chemical characteristics of tank 101-SY (Herting et al., 1992a, 1992b; Reynolds, 1992; Pederson et al., 1993;

After the waste achieves thermal equilibrium with the tank environs, radioactive decay in the tank continues to liberate substantial quantities of heat.

Strachan, 1994). The aluminum chemistry of the tank wastes, which has been incompletely explored by previous workers (Barney, 1976; Reynolds and Herting, 1984; Stewart et al., 1994b), is the subject of this paper.

Hanford tank 101-SY is a double-shell tank that contains approximately 1.1 million (M) gallons of high-level radioactive waste from fuel reprocessing. The tank was filled with three substantial batches of waste (Herting et al., 1992a). The first batch, in April 1977, was 100 inches of typical double shell slurry (DSS) supersaturated with respect to sodium nitrite, sodium aluminate, and sodium carbonate. The second batch was 132 inches of organic complexant concentrate waste from B-Plant with substantial concentrations of the chelating agents, EDTA and HEDTA, their decomposed by-products, and strontium. In 1978, the tank was filled with two interim transfers from 106-SX and 111-U of 70 inches of organic-rich waste and was brought to level with 84 inches of DSS in 1980. Thus, the organic additions were sandwiched between the supersaturated salt solutions.

The DSS was the by-product of evaporator operations in the Hanford 200 West area 242-S vacuum crystallizer which operated at temperatures over 120 degrees F. As the waste was transferred to the tank, the DSS waste was rapidly cooled by conduction through the floor and walls of the tank to approximately 110 degrees F, resulting in the massive precipitation of salts. The result was the formation of a stratified chemical system with a thick sludge layer on the bottom of the tank beneath a dense slurry. These bottom layers are often referred to as the nonconvective layer. A dense convective supernatant fluid rests on top of the slurry capped by a crust of waste salts. Since temperatures at the floor, walls, and surface of the waste arrived at a temperature of about 110 degrees F, it is hypothesized that salts found in the crust also coat the floor and walls of the tank.

After the waste achieves thermal equilibrium with the tank environs, radioactive decay in the tank continues to liberate substantial quantities of heat, establishing convection cells which have mixed and ultimately restratified the DSS and organic layers. The radiogenic processes are also responsible for the continued evolution of the waste chemistry. Part of the chemical phenomena in the tanks have been extensively studied (Melsel et al., 1993, 1991; Reynolds and Herting, 1984; Walker et al., 1992a) and can be summarized as follows:

- Radiolysis of water producing hydrogen and oxygen;
- Reduction-oxidation reactions involving (CrVI, CrIII) and (FeIII, FeII);
- Phase transitions from metastable to stable phases;
- Reduction reactions involving nitrates/nitrites to form a variety of reduction products including nitrous oxide, ammonia, and nitrogen gas; and
- Radiolysis of organics especially EDTA, HEDTA, citric and oxalic acids, and their by-products such as, acetate, glycine, and valine to form hydrogen and other hydrocarbons.

The gases produced largely by the radiolysis of water, reduction of nitrates, nitrites, and decomposition of organic compounds were histori-

cally released episodically at potentially flammable concentrations in the limited tank dome space. The dome space is approximately 40,000 cubic feet. The periodic releases also served to redistribute the solid microcrystalline particulates and disrupt thermal profiles established during the windows between gas release events (GRES). The episodic gas releases may achieve volumes approaching their lower flammability concentration limit for brief periods after the event (Babad et al., 1992c). Tank 101-SY is the only tank known to have experienced flammable gas releases that have temporarily exceeded the lower flammability concentration limit (McDuffie, 1994). Although the hazard is quickly mitigated through purging of the gases from the head space, the short-term hazard placed Hanford's tank 101-SY as the top safety concern in the DOE complex in 1990.

The mechanisms leading to the safety condition must be understood in order to satisfactorily address the concerns related to an Unreviewed Safety Question (USQ) under DOE Safety Order 5480.21. Tanks such as 101-SY are placed on the "watch-list" because of a USQ. In addition, resolving the USQ will provide a basis for removing the 25 tanks classified as flammable gas from the watch-list.

A number of promising interim mitigation schemes, especially mixer pumps (Stewart et al., 1994b; Fort et al., 1993), are being developed to facilitate a more uniform gas release rate (Benegas, 1992). Active methods of interim intervention through the deployment of a mixer pump in tank 101-SY have been determined to be fully successful (Stewart et al., 1994b). Active approaches, such as mixing or agitation through use of a sonic probe, are considered only as interim measures since the cause of episodic gas release is not yet well understood.

The successful development and deployment of a passive mitigation strategy requires a fundamental understanding of the physicochemical processes that govern the accumulation and periodic release of these gases. No passive in-tank mitigation approach has been developed yet to assure uniform release of these flammable gases. Dilution, incorrectly applied, could even exacerbate the problem (Stewart et al., 1994a). The flammable gas concern could be mitigated passively by simply increasing the tank dome space so as to assure that the flammability concentration limit is not reached. This would amount to lowering the tank level in tank 101-SY by about 25 percent. This study identifies and evaluates the fundamental mechanisms governing spontaneous, large-volume gas releases and, as a result, recommends a process for passive remediation (Alexander, 1994).

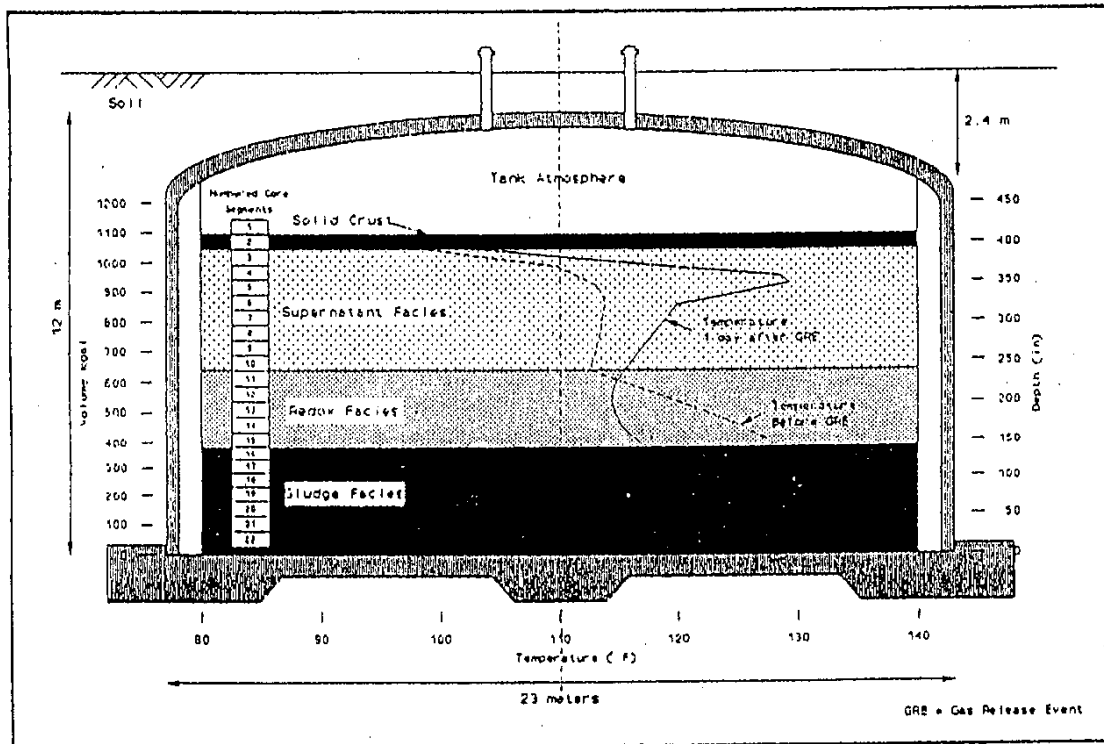
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LITHOFACIES MODEL

A lithofacies model is provided as a framework for discussions of the physicochemical processes governing the periodic release of flammable gas in the Hanford waste storage tanks. The stratification of tank 101-SY can be described in terms of four chemical lithofacies as shown in **Exhibit 1**: (1) a surface crust, (2) supernatant, (3) a redox front, and (4) sludge.

The *surface crust facies* is characterized by a fractured mass of precipitated salts of sodium predominated by sodium nitrite, nitrate,

Exhibit 1. Lithofacies Model.



Source: Westinghouse Hanford Company reports (Hering et al., 1992a, 1992b, 1992c; Reynolds, 1992, 1993; Burke et al., 1993).

aluminate, and carbonates. The crust represents approximately 5 percent of the tank content weight or 55,000 gallons.

The *supernatant facies*, referred to in the literature as the convective layer, is primarily a saturated or supersaturated solution of the same salts constituting the crust. Chemical analyses of this layer indicate the presence of Al, Cr, Fe, Mn, and Zn hydroxides. Al(OH)_3 has been identified by X-ray analysis in the supernatant. The supernatant has a density of approximately 1.46 gm/cm^3 and a shear strength of less than 530 dynes/cm^2 at 32 degrees C.

The *redox facies* is defined on the basis of the Cr (VI, III) couple. Sodium nitrate, sodium nitrite, chromium phosphate, hydrated uranium phosphate, and calcium carbonate are identified by X-ray analyses. It is a transitional facies between oxidation reactions at the crust's surface and the water reduction layer producing hydrogen gas and is primarily located above the sludge facies. This redox layer correlates with the nonconvective slurry or pseudo-sludge layer referred to in the literature and shows a

Coprecipitation is commonly used to scavenge radioisotopes from solutions using metal hydroxide precipitation.

marked increase in solids when compared to the supernatant layer. The redox layer has a reported shear strength of 15,000 to 3000 dynes/cm² at 32 and 65 degrees C, respectively.

The *sludge facies* is characterized by relatively insoluble precipitates, such as iron and chromium oxides, and phosphates, clays, hydroxides, carbonates, and soluble salts in equilibrium with their ionic components such as sodium nitrate and sodium nitrite. These insoluble precipitates have incorporated, during their formation, radionuclides such as strontium and transuranics. Coprecipitation is commonly used to scavenge radioisotopes from solutions using metal hydroxide precipitation. This localization of radionuclides in settled particulates provides the heat engine and a concentrated source for radiolysis. This facies also contains organic compounds such as EDTA, HEDTA, oxalates, citrates, and their decomposition products. This facies has a reported shear strength of 116,000 to 4000 dynes/cm² at 32 and 65 degrees C, respectively. The layer corresponds to the nonconvective layer in the literature.

Exhibit 1 illustrates the stratification of Tank 101-SY and its thermal profiles before and approximately one day after the window C GRE. Before the window C GRE, the temperature profile is relatively constant at about 112 degrees F throughout the supernatant facies and rises abruptly at the redox-sludge interface and reaches a peak of approximately 130 degrees F in the sludge. One day after the window C GRE, a sharp increase is observed in the temperature near the 350-inch level to approximately 130 degrees F. This temperature profile following window C GRE is different than the one following window E GRE. The temperature is nearly isothermal throughout much of the tank following the window E GRE. The difference may be due to a more thorough mixing following window E, since the release during this window was much more forceful than window C. This is corroborated by chemical analyses of the tank wastes after these GREs. The chemical analyses also show a more uniform tank chemical distribution after window E than window C.

After a GRE, temperatures in the supernatant layer rise dramatically, corresponding to a turbulent upwelling of wastes from lower to higher elevations. One day after a GRE, the thermal profile appears mushroom-shaped. The thermal profile in three dimensions is a signature of radioactively "hotter" particulates and suspended waste, such as strontium carbonate, rafted by rapidly escaping gases to higher elevations in the tank. The thermal roll-over is accompanied by a substantial redistribution of hotter particulates and liquids from lower to higher levels in the tank. Immediately after a GRE, all but the bottom of the sludge facies is affected by the roll-over. In cases where the energy associated with the gas eruption is greatest, as in window E, the thermal profiles are vertical, that is the temperature is nearly uniform in the tank, corresponding to extensive mixing. In either case, after a GRE, the rafted particulates settle and the tank stratigraphy and the corresponding pre-GRE thermal profile return. Settling calculations using Stokes Law indicate that the micron-size particles (assuming a 4 micron mean) would settle through the supernatant layer in well under 50 days.

PHYSICO-CHEMICAL MECHANISMS

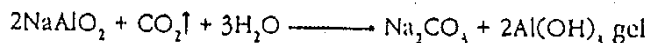
Physicochemical mechanisms leading to the buildup and periodic release of large volumes of flammable gases, up until now, have not been understood (Allemann, 1992a, 1992b; Ashby et al., 1994; Babad et al., 1992a, 1992b, 1992c, 1991; Burke et al., 1993; Strachan et al., 1993). As a consequence, approaches for the long-term, passive mitigation of flammable gas release have not been successfully implemented. Recent initiatives (Stewart et al., 1994a, Washington State Department of Ecology and U.S. Department of Energy, 1994) have focused on the dilution of the waste.

In order to effectively mitigate the safety concern, the authors conducted a number of investigations to isolate the governing physicochemical phenomenon using simulated waste. As a result, a sequence of five coupled mechanisms pivotal to episodic gas release has been identified.

The first mechanism is the absorption of atmospheric carbon dioxide with a typical NaOH-rich waste solution producing carbonate precipitates, analogous to the Solvay process; but more significantly, the atmospheric carbon dioxide lowers the pH of the waste solution in the upper level of the tank. This mechanism has been observed in similar waste tanks at Savannah River (Hobbs, 1991, 1986a, 1986b, 1985). At Savannah River, eight tanks with chemistry similar to those at Hanford were monitored for CO₂ absorption for a period of one year. Approximately 75 percent of all CO₂ entering the tank was absorbed. Hobbs found a direct correlation between CO₂ absorption and consumption of free hydroxide in the liquid waste phase. His direct in-tank measurements show a decrease of 2.5 pH units in 200 days, with an initial tank pH of 12.5. Hobbs also found that CO₂ absorption decreases substantially when either the free hydroxide concentration $\leq 0.1M$ or when the system approaches the carbonate-bicarbonate equilibrium pH.

The second mechanism is dependent on CO₂ absorption and applies to the waste in tank 101-SY as follows. The pH of the waste in tank 101-SY is stabilized well above the carbonate-bicarbonate pH buffer system. This is probably due to the presence of other metal hydroxides competing for or donating hydroxyl ions. The net result is that the partial pressure of atmospheric CO₂ maintains a constant driving force towards depletion of free hydroxide ions. The depletion of the free hydroxide ions, in turn, forces the precipitation of the insoluble aluminum and transition metal hydroxide species. These mechanisms are well understood as the basis for aluminum chemistry and its electrolytic production (Partington, 1926; Mellor, 1971; Cotton and Wilkinson, 1980; Pauling, 1988). The general reaction can be considered as:

The depletion of the free hydroxide ions forces the precipitation of the insoluble aluminum and transition metal hydroxide species.



The third mechanism is the simultaneous stabilization of the gel by the coordination between the aluminum in the gel and the nitrogen in complexing agents present in the waste. The phase shift by the absorption

of carbon dioxide results in the formation of a complex gel of aluminum, chromium, manganese and iron hydroxides, and oxyhydroxides that coprecipitate and accumulate as a metastable layer in the middle and lower levels of the tank.

The fourth mechanism is the formation of a self-healing microcrystalline mat bound by the complex gel. The complexed aluminum hydroxide gel acts as a binding agent in the microcrystalline mat. Microcrystalline particles (typically less than 12 microns), such as sodium nitrite, provide the structural strength for the mat.

The fifth mechanism is the accumulation of gas below the gel layer which achieves a critical buoyancy sufficient to rupture the microcrystalline mat, releasing flammable gases (McDuffie, 1994). The yield strength of the waste appears to substantially decrease after it has been vibrated, as is the case during a GRE. At shear rates of 700/second, strength recovery takes 300 hours (Stewart et al., 1994a). The thixotropic characteristic of gels accounts for the observed loss of shear strength and rapid strength recovery (Eschbach and Enderlin, 1993). The cycle of gas buildup and release continues each time the buoyancy of the trapped gas exceeds the hydrostatic pressure and the gels' plasticity modulus. Stokes Law predicts a settling rate of the particles in the tank in less than 50 days, well within the historical periodicity of GREs. Other workers report settling rates of 0.7 inches/hour for 12 micron size particles and 113 inches/hour for 150 micron size particles assuming a particulate density of 2.31 gm/cm³ and a convective-layer viscosity of 13 centipoise at 65 degrees C (Fort et al., 1994).

A number of experiments to evaluate the above phenomena was conducted at RMC Environmental Labs, West Plains, Missouri, using simulated tank wastes based on formulations provided by Westinghouse Hanford Company (WHC) (SIM-101-SY-92-A). The results of these experiments, their consequences, and the solution chemistry to prevent such sudden releases of gases due to gel formation are presented in this paper.

SCOPING EXPERIMENTS

The following experiments were designed to define the crucial physicochemical mechanisms controlling flammable gas release:

1. Carbon dioxide absorption experiments,
2. Formation of aluminum hydroxide gel,
3. Stabilization and reversibility of aluminum hydroxide,
4. Microcrystalline mat formation, and
5. GRE simulation.

Carbon Dioxide Absorption Experiments

Scoping experiments were conducted to simulate absorption of carbon dioxide by tank wastes from two sources: (1) circulating air above the crust surface, and (2) air introduced by air lift risers used in tank operations at Hanford to keep the waste mixed.

Several sets of experiments were carried out by dissolving a 2M quantity of sodium aluminate in a 2M sodium hydroxide solution. A 250-

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ml quantity of the above solution was placed in a reactor. The reactor was covered with a gas-tight lid with an inlet through which pure dry carbon dioxide was purged to create a carbon dioxide atmosphere, and it was kept at constant pressure. After reaching the desired pressure (1.1 atmospheres) the gas supply was cut off and the pressure changes inside were monitored by a closed tube manometer.

TRU processing transferred as much as 85 tons of sodium carbonate into the tanks such as 101-SY. Hence, additional scoping experiments were conducted where saturated sodium carbonate solutions (10 ml quantities) were added to 101-SY simulant solutions (100 ml) and stood overnight. In all of these cases, aluminum hydroxide was precipitated within 24 hours.

Formation of Aluminum Hydroxide Gel

The authors hypothesized that the absorption of carbon dioxide would lower pH and produce amorphous aluminum hydroxide. It was further thought that the amorphous phase plays an important role in GREs. During the carbon dioxide absorption experiments described above, a thin gelatinous precipitate was observed at the top of the solution. The thickness of the white gelatinous precipitate increased over a period of time. The growth of the gel was from the top to the bottom of the reactor. Simultaneously, the pressure of carbon dioxide substantially decreased within one hour, yielding a gel that covered the top layer of the solution. Secondly, the same solution in a different reactor was allowed to react with carbon dioxide gas where the gas was bubbled from the bottom microjet. In this case, the reaction was instantaneous. A gelatinous, white precipitate was formed inside the entire reactor, and the gel could not be poured out due to its gel-like constitution. In both experiments, a "leathery rind" identified as gibbsite was observed. All experiments were conducted at 110 degrees F.

Stabilization and Reversibility of Aluminum Hydroxide

In the above mentioned experiments, the gel underwent a rather rapid phase transition to the crystalline precipitate, gibbsite. Therefore, the temporary stability of the gel could not serve as a binding agent. Gibbsite would settle to the bottom of the tank and not play an important role in trapping gases. Therefore, additional experiments were conducted to determine whether other components in the tank sustained the stability of the amorphous aluminum hydroxide phase, a different binding agent was present, or our hypothesis should be abandoned.

Aluminum hydroxide was generated by bubbling carbon dioxide through two sets of 101-SY simulants, one as a blank and one spiked with 0.2 M/L of EDTA. The time for the phase change of the amorphous aluminum hydroxide to gibbsite occurred within several hours. This phase change occurred with the precipitation of the floating gelatinous aluminum hydroxide to a white crystalline powder at the bottom of the reaction vessel. When substantial quantities of carbon dioxide were used, the reaction became irreversible (i.e., the $Al(OH)_3$ precipitate remained as a precipitate). Furthermore, when this precipitate was held at 110 degrees F for prolonged periods it became insoluble, even in a large excess of

The temporary stability of the gel could not serve as a binding agent.

Exhibit 2. By-Products of EDTA and HEDTA in 101-SY Simulant.

EDTA	glycine	aminoglycolic acid
HEDTA	ethyl amine	propyl amine
Valine	methyl amine	isopropyl amine

NaOH, indicating that the transformation from the gel to the insoluble crystalline form, gibbsite, is difficult to reverse.

The same experiment was carried out using 101-SY with the complexing agents, HEDTA and EDTA. The aluminum hydroxide in the presence of complexing agents did not transform into the crystalline gibbsite in time periods in excess of five weeks. By titrating the precipitates with and without complexing agents with NaOH, we found that the stabilized gel went back into solution between 2.2 to 2.5 M/L of NaOH. However, when sonicated, the gel dispersed into the medium (peptization).

The organics in the simulant were characterized using gas chromatography and mass spectrometry. EDTA, HEDTA, and a number of their by-products were observed. The compounds are listed in **Exhibit 2**. Other degradation products have been determined using ¹³C-labeling (Pederson and Strachan, 1993).

Microcrystalline Mat Formation

The nature of the microcrystalline mat is hypothesized to play the critical role in trapping flammable gases. Therefore, an examination of the mat in simulated waste (SIM-101-SY-92-A) was conducted.

A stereo-microscopic examination of microcrystalline mat structure reveals rosettes of prismatic crystals of sodium nitrite distributed throughout the amorphous organo-aluminum hydroxide matrix. The prismatic sodium nitrite crystals appear to reinforce the mat. In addition, cubic crystals of sodium nitrate are scattered throughout the matrix.

Gas Release Event (GRE) Simulation

In order to compare the effectiveness of the microcrystalline mat to trap gases with that of agglomerated crystals of sodium nitrite/sodium nitrate, the following experiments were conducted.

Experiments consisted of bubbling hydrogen from the bottom of the reactors containing 2M NaAlO₂, 2M NaOH, and 2M Al(OH)₃ gel saturated with sodium nitrite and sodium nitrate. Since the rate of ascent of hydrogen gas (buoyancy) is proportional to the viscosity of the liquid at a given temperature, all three reactors were kept at the same temperature. The travel time was recorded for the ascent of the bubble to a constant height using electronic timers. The length of the path was 100 cm. The rates of hydrogen gas ascent for the 100-cm column are presented in **Exhibit 3**.

A second set of experiments was conducted on a 4-liter capacity reactor and filled with solution C (**Exhibit 3**). A glass jet was placed at the bottom

Exhibit 3. Migration of Hydrogen Gas through NaOH/NaAlO₂/Al(OH)₃ Systems.

Reference	Solution Composition	Migration time (seconds)
A	Saturated Nitrate/Nitrite Solution in 2M NaOH	4.77
B	Reference A plus 2M NaAlO ₂	5.16
C	Reference A plus 2M NaAlO ₂ and Al(OH) ₃	indefinite

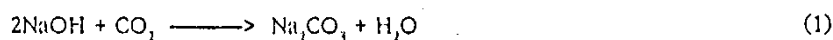
(column height=100 cm)

of the reactor, and pure hydrogen was bubbled through the jet through metering devices at the rate of 0.1 ml/min. The top of the reactor was sealed tightly with an open tube manometer to measure the pressure of the hydrogen whenever the gel layer was broken. Varying thicknesses of the Al(OH)₃ gel were developed by carefully reacting pure dilute HCl with the NaAlO₂ solution until the desired thickness of the gel was created. For confirmation, the experiment was repeated several times by varying the thicknesses of the gel. All of the experiments were carried out using freshly formed gels at 110 degrees F. A plot comparing gel thickness with gas pressure at breakthrough is presented in **Exhibit 4**.

EXPERIMENTAL RESULTS AND DISCUSSION

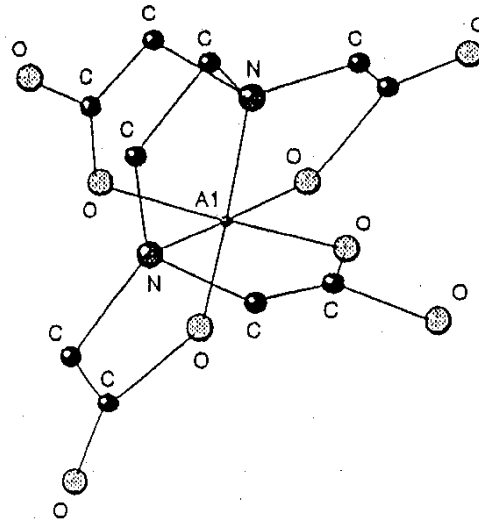
Our experiments verify that the formation of carbonate can be attributed to the absorption of atmospheric carbon dioxide and the subsequent instantaneous reaction with sodium and other alkaline earth metal hydroxides. Examination of the tank history revealed that the tank was aerated for a long period of time introducing additional carbon dioxide directly into the waste solution. Other reactions in the tank supplied secondary sources of carbon dioxide such as the decomposition of oxalates. During the filling of tank 101-SY, large quantities of sodium carbonate were transferred to the tank forcing saturation to supersaturation from inception.

The absorption of carbon dioxide by strong alkaline solutions is a well-understood phenomenon. Extensive work has been done in this area, and a U.S. patent has been issued (Hobbs, 1991) dealing with carbon dioxide intake at the Savannah River waste tanks. Our experiments on carbon dioxide absorption by NaAlO₂/NaOH only reaffirm these findings. These reactions can be visualized as:

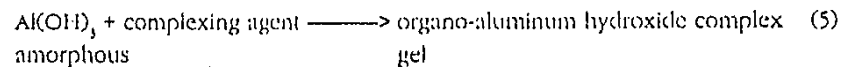


The precipitation of carbonates ultimately depletes NaOH in the tank. The depletion of NaOH by carbon dioxide, in turn, lowers the available hydroxyl

Exhibit 5. The Structure of the Complex between Tripositive Aluminum and the Anion of EDTA.



the presence of chelating agents stabilize the amorphous (gel) form of aluminum hydroxide. Therefore, the presence of organic compounds such as EDTA, HEDTA, valine, glycine, oxalates, and surfactants in waste tanks can stabilize the amorphous aluminum hydroxide by complexation:



The aluminum hydroxide concentration in the wastes is at supersaturation due to evaporator dewatering. That is, NaAlO_2 and Al(OH)_3 are in equilibrium with their solid phases. Thus, the equilibrium is poised towards precipitation with even the slightest change in the OH concentration. As noted above, free hydroxide ion is continuously consumed by CO_2 .

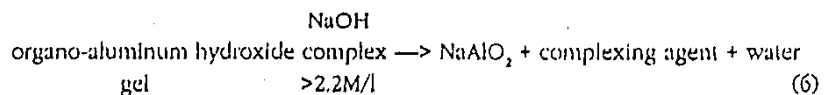
The stability of the organo-aluminum hydroxide complex gel in a tank environment allows it to serve as the binding agent for a variety of precipitates including sodium nitrite, sodium nitrate, aluminates, carbonates, and hydroxides. The complex exhibits the typical properties of gels including high viscosity and thixotropism, essential properties of a binding agent. **Exhibit 5** shows an aluminum-EDTA complex. This complex structure is isomorphous to the tripositive cobalt complex previously reported (Pauling, 1988). Reported concentrations of organics (>2 weight percentage), aluminum (>3 weight percentage), and hydroxyl ions (>2.4 weight percentage) (Herting et al., 1992) in tank 101-SY are favorable to

**Chemical methods
are being considered
to passively mitigate
GREs.**

gel formation according to our experiments. After a GRE, the mat begins to re-form in a few days. Settling calculations indicate that the largest particles would settle in hours, and the 12 micron fraction would settle within two weeks. This is consistent with the time observed for the nonconvective phase to regain its initial shear strength after a GRE. The amorphous aluminum hydroxide is stabilized and reinforced by the complexing agents present and by the sodium nitrite crystals. The net result is that the released gases continuously build up pressure until the gas pressure exceeds the elasticity modulus of the gel. The observed GREs have reoccurred every 100 to 150 days since about 1981.

In order to mitigate a GRE, the microcrystalline mat must be broken down either mechanically or chemically. Primary mechanical means of disrupting the mat include mixer pumps and sonic probes. The mixer pump has been successfully demonstrated as a mitigative measure in tank 101-SY (Stewart et al., 1994b). Preliminary experimental work with sonification of the gel confirms that a sonic probe could also mitigate GREs. Based on our observations, mechanical agitation will liquify the gel due to its thixotropic character and reduce the overall viscosity of the waste. Either approach will promote continuous gas release and prevent GREs.

Chemical methods are being considered to passively mitigate GREs. These methods include dilution with water or 2M NaOH (Stewart et al., 1994a). Stewart et al. conclude that dilution with water alone may require unacceptably large quantities because the dilution would be accompanied by a shift in the aluminum hydroxide-aluminate boundary. In addition, water dilution, carried to an extreme, could accelerate tank corrosion (Divine et al., 1985). Our work demonstrates that organic complexants react with the aluminum hydroxide and expand its stability field. A series of organo-aluminum hydroxide gel species is stable at higher hydroxide concentrations than the inorganic system. We define stabilities up to 2.5M OH for the complexed form as compared to 1.6M OH for an inorganic system saturated in the major sodium salt components (Barney, 1976). Our experimental results provided above confirm that the organo-aluminum hydroxide complex gel solubility is readily reversible at NaOH concentrations near than 2.2 molar in 101-SY simulants (SIM-101-SY-92A):



Equation (6) provides a strategy for passively mitigating GREs while ensuring waste minimization. Its application is referred to as the Alexander Process.

APPLICATIONS

The passive mitigation process described above and simplified in equation (6) has a wide range of applications including: (1) remediating existing flammable gas tanks through a combination of chemical treatment and mixer pumps; (2) diluting, combining, retrieving, and storing wastes;

- (3) preventing clogging of transfer lines; (4) sludge and soil washing; and
- (5) cleaning up cribs, ponds, basins, and ground water.

Passive Mitigation of Flammable Gas Tanks

Several passive mitigation approaches can be taken to remove flammable gas tanks from the watch-list.

1. Dissolve the gel, thereby destroying the mat, and allow continuous release of gas;
2. Lower the tank volume by about 35 percent to assure that gas pressures in the dome space never exceed the lower safety limit for flammable gas concentrations;
3. Ventilation; or
4. A combination of the above.

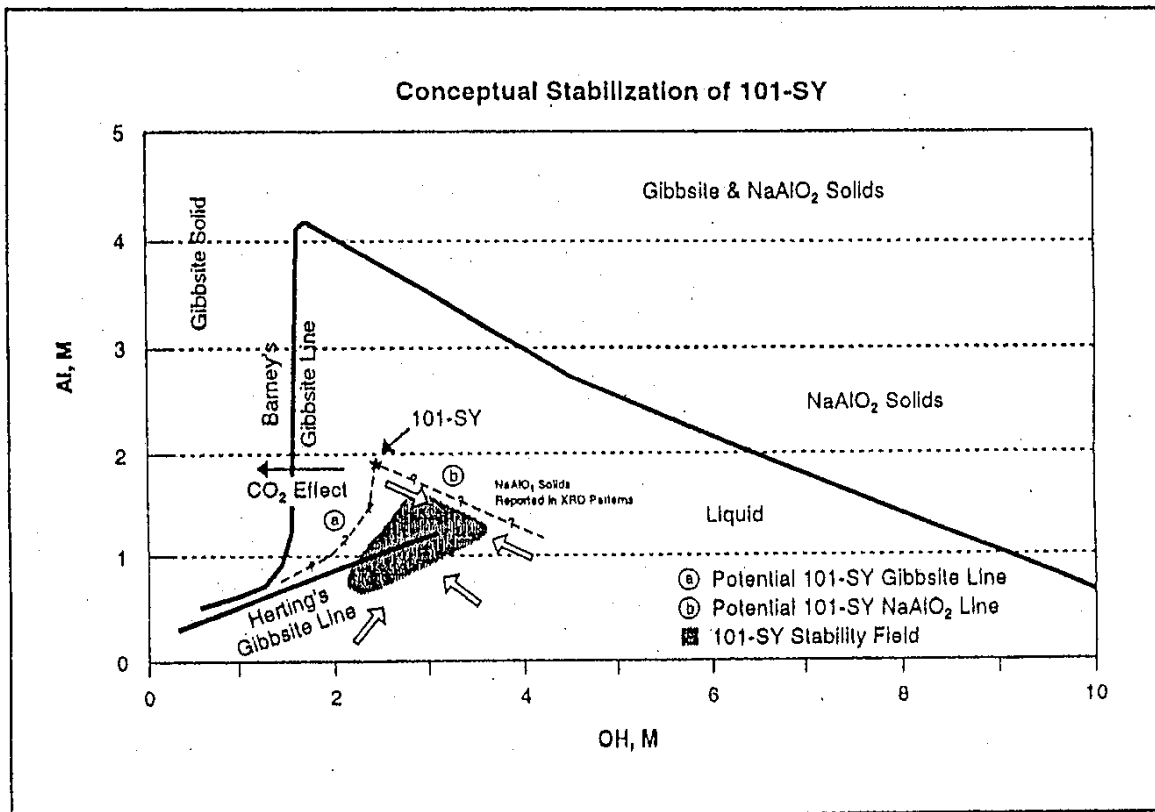
Conceptual approaches for destroying the microcrystalline mat can be defined by examining the equilibria of the $\text{CO}_2/\text{NaOH}/\text{Al}(\text{OH})_3$ (complexing agent)/ NaAlO_2 system. Exhibit 6 shows that the aluminate/aluminum hydroxide composition in tank 101-SY is to the right of the univariant curve (Barney, 1976). X-ray diffraction data confirm the presence of NaAlO_2 in tank 101-SY and also confirm that the phase boundary for liquid/ NaAlO_2 solids passes through 101-SY (as indicated by "b" in Exhibit 6), likely with the same slope as that previously determined (Barney, 1976). Experiments, described above, to locate the position of the univariant curve aluminate/gibbsite, indicate that the aluminate/organo-aluminum hydroxide complex univariant curve also passes through the composition of 101-SY for the Al/OH plot (as indicated by "a" in Exhibit 6). The combined results suggest that 101-SY was driven to or near the invariant point by the evaporator.

Therefore, given that CO_2 reactions in the existing tank will drive the system to produce more gel, a pH adjustment is required. A target stability field for this adjustment is indicated in Exhibit 6. Diluting the waste without raising pH with NaOH could force precipitation of aluminum hydroxide, creating a potentially worse condition. If the pH drops to even lower values, tank corrosion could accelerate.

The recommended passive approach for mitigating flammable gas conditions in Hanford tanks is to lower the tank below the level at which flammable concentrations could accumulate. In particular, for cases such as tank 101-SY where episodic releases are known to occur, dissolve the gel by appropriate additions of caustic solutions. This approach would provide defense in-depth since dissolution of the mat would allow continuous passive evolution of gas. However, should gas ever be released episodically, it would always be below the safety limit for flammable concentrations. Until pH is adjusted, mixer pumps should be used as an interim preventive measure in double shell tanks that periodically release large concentrations of flammable gas. For many single shell tanks, the head space is currently adequate to avoid flammable gas concentrations. This is supported by the fact that only tank 101-SY has ever exceeded the

Diluting the waste without raising pH with NaOH could force precipitation of aluminum hydroxide, creating a potentially worse condition.

Exhibit 6. Conceptual Stabilization of Flammable Gas Tanks.



lower flammability concentration limit. Historical data on flammable gas volumes should be reviewed for all tanks on the watch-list. Therefore, after review, it is likely that most of these tanks can be taken off the list. The likely outcome of the review is that only tank 101-SY will require mitigation. Finally, the flammable gas condition in tank 101-SY can be mitigated with less than the total volume of an additional double shell tank.

Retrieval by Sluicing Contents of Tank 106-C

Tank 106-C is a prime candidate for retrieval because this waste is classified not only as transuranic and high-level, but also as high-heat because of the radioactive decay of strontium. Historically, water has been added to the tank to provide evaporative cooling of the waste and to prevent the sludge from drying out. In the absence of these water additions, the heat load in Tank 106-C may exceed allowable temperature limits with the potential for structural damage to the tank. The tank is currently classified as sound, but there is a concern that should the tank start leaking,

continued water additions could result in an increased amount of waste released to the environment.

Specifically, this action would accomplish the following (NEPA Services, WHC, 1994):

Remove at least 75 percent of the high-heat waste, and thus reduce the tank heat load to less than 11.72 kilowatts (Kw) (40,000 British thermal units (Btu) per hour). Water additions could then be stopped, and the tank removed from the safety "watch-list."

Past-practice sluicing is proposed to be accomplished by transferring waste from Tank 106-C to the receiver tank, Tank 241-AY-102 (Tank AY-102), an underground double shell tank (DST). Two transfer lines would connect the tanks. One line would carry the slurry (sluiced waste) to the DST, and the other would carry the supernate liquid from the DST, which would be used to mobilize the waste in Tank 106-C and facilitate pumping and waste transfer. The supernatant in tank AY-102 would be pumped out prior to sluicing to provide adequate receiving space. Supernatant from Tank 241-AY-101 then would be pumped to Tank AY-102 and used as a compatible sluicing agent.

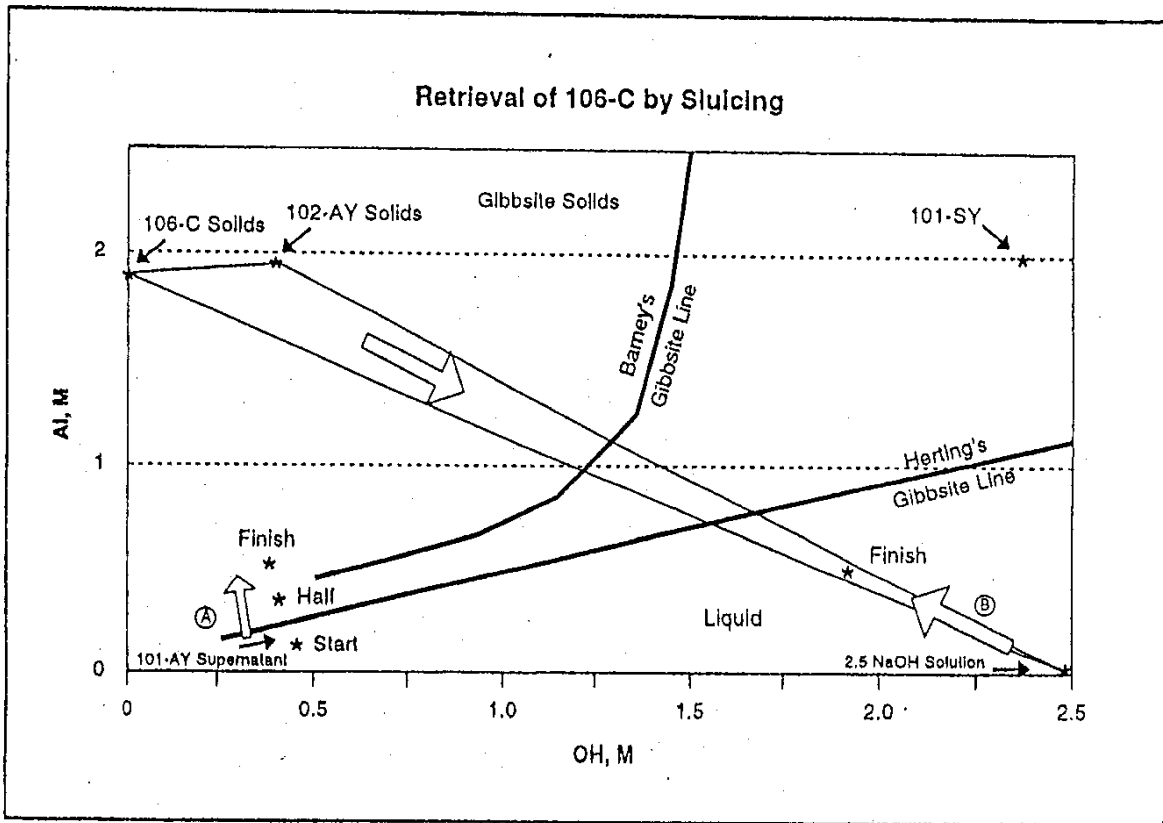
Based on the theoretical and experimental observations presented above, the compositions of the sluicing operation, as proposed, would proceed along the reaction path in Exhibit 7. Without caustic additions, the resulting sluicing path begins with the supernatant in the liquid field and soon crosses into the gel field. Therefore, use of 101 AY supernatant as a sluicing fluid would require a basic adjustment. As illustrated in Exhibit 7, any number of starting fluids could successfully accomplish the sluicing action without ending up in the gel field. We recommend experimentally defining the relevant isopleth to the unique compositions being mixed before selecting the optimum solution composition. Our estimates indicate that approximately 2.5M NaOH will bring about total dissolution of aluminum hydroxide species in 106-C as NaAlO_2 . This value provides a significant safety margin for the prevention of gel formation. Independent calculations by WHC using the Environmental Simulation Program (ESP) suggest caustic leaching with greater than 2.2M NaOH and appear to confirm our recommendation. The recovered waste would allow sufficient dome space to further eliminate the possibility of a flammable gas condition.

The recovered waste would allow sufficient dome space to further eliminate the possibility of a flammable gas condition.

Preventing Clogging of Transfer Lines

The Hanford 200 West and 200 East tank farms are connected by a piping system for waste transfer. The current cross-site transfer system has six main pipelines, four of which have clogged. Much of the transfer was accomplished by maintaining temperatures high enough to keep the majority of salts in solution. However, clogging was common during past transfers. It is apparent that the organo-aluminum hydroxide complexes could plug lines and severely reduce their performance and even present a hazard. Consideration needs to be given to pH adjustments of the waste streams to prevent gel formation and subsequent pipe clogging.

Exhibit 7. Retrieval of Wastes from 106-C by Sluicing.



Sludge and Soil

Sludge washing is accompanied by a rapid drop in pH for Savannah River wastes (Hobbs et al., 1992; Walker and Hobbs, 1992b; Hobbs, 1991). Washing with sodium hydroxide has been recommended as an alternative to sodium nitrite with the benefit of inhibiting corrosion (Hobbs, 1992a). The use of a sodium hydroxide wash can be included in pretreatment schemes, for example, following an acid wash by making use of equation (6) above and the Alexander Process.

Cribs, Ponds, Basins, and Ground-Water Treatment

The Alexander Process can also be applied to treatment of contaminated water (supernatant) in cribs, ponds, basins, and ground water at Hanford and other sites where radionuclides and hazardous metals are dissolved. After introducing the complex appropriately, filtering it out of the system after it has sequestered target nuclides and hazardous metals, one can dissolve the complex in a reactor vessel releasing the nuclides

for further treatment and disposal. The Alexander Process is particularly compatible for applications at Hanford and Savannah River because the end products are caustic and can be returned to the tank farms.

CONCLUSIONS AND RECOMMENDATIONS

The GREs in the Hanford tanks are controlled by the sodium aluminate/ organo-aluminum hydroxide complex equilibrium. By controlling the free hydroxide ion concentration and by adding appropriate stabilizing agents, one can redissolve the gel. The presence of feather-like crystals of sodium nitrite appears to reinforce the self-healing organo-aluminum hydroxide complex gel. Mechanical devices, such as mixer pumps in conjunction with proper aluminum chemistry, can permanently remediate the problem. The redissolution process has numerous applications for radioactive waste cleanup in transfer lines, tanks, evaporators, cribs, ponds, and ground water. This study provides a significant breakthrough for tank waste management by explaining key mechanisms controlling episodic release of flammable gases which have broad operational applications with a potential for billions of dollars in cost savings. ■

By controlling the free hydroxide ion concentration and by adding appropriate stabilizing agents, one can redissolve the gel.

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