# Postretrieval and Preclosure High-Level Radioactive Liquid Waste Tank Lay-up Using New Mex U-Mate$^{TM}$.

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## Abstract:

**The final long-term management challenge in the Department of Energy (DOE) is the safe and economic closure of underground tanks across the complex that were previously used to hold high level waste (HLW). The WVDP cannot immediately proceed with tank closure until NEPA determinations are made, therefore a tank lay-up strategy for 5 to15 years is needed. The goal of the lay-up is to place the tanks in a safe, stable, minimum-maintenance mode that does not compromise final closure options. A small team at the INEEL and U-Mate International Inc proposed a technical solution to support TFA's two basic needs (tank lay-up and grout formulation) using New Mex U-Mate. For tank lay-up, the team proposed several feet of a stabilizing material called New Mex U-Mate™ (NMUM) as furnished by U-Mate International, Inc. NMUM is a complex inorganic/organic material that offers excellent pH buffer control and heavy metal capture. This type of humate has a low salt content and a similar redox potential as the earth to which the tanks are exposed below ground. We expect with NMUM addition inside and outside (liquid suspension injected around the tank), tank corrosion will be reduced in lay-up. Using NMUM in a grout matrix is expected improve properties such as flowability and radionuclide retention. To validate the claims we made in regard to tank lay-up, we are working on a fast-paced research program that investigates the basic properties of NMUM mixed with HLW tank heels. The specific objectives of our current research are: 1) Mix various amounts of NMUM with surrogate tank waste while performance measures such as TCLP (toxicity characteristic leaching procedure), Kd, pH, and ion uptake are quantified. 2) Measure the instantaneous corrosion rate of a simulated steel tank before and after adding the NMUM in and around the tank. 3) Use NMUM as a co-feed to current grout formulations to ascertain whether improved properties are realized, such as flowability during grout placement and radionuclide retention. This research will demonstrate an innovative application of NMUM to technology needs associated with RCRA closure of DOE HLW tanks.**

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## I. Introduction:

**The final long-term management challenge in the Department of Energy (DOE) is the safe and economic closure of underground tanks across the complex that were previously used to hold high level waste (HLW). The cost to completely remove the tank and dispose of the tank material is prohibitive. This type of closure may add additional risk to both the workers and stakeholders. In the petrochemical industry, many old underground tanks are cleaned and then filled with sand or other inert material to provide a permanent closure method. To this end, we propose a method of HLW tank lay up using an organic/non organic material called New Mex U-Mate.**

**For example, the West Valley Demonstration Project personnel (WVDP) at the Oak Ridge National Laboratory (ORNL) have almost completed HLW retrieval and are ready for tank lay-up pending final NEPA approval for permanent closure. The tanks have approximately a 1-inch heel of water and other residuals that reside at the bottom of the tanks following cleaning. The tank lay-up is required to hold these tanks in a safe manner, as well as not jeopardizing the ability to fill the tanks with grout at a future date. The DOE is exploring three methods of tank lay up: 1) completely dry the tanks, 2) keep the liquid heel but add a corrosion inhibitor, and 3) add a stabilizing material inside the tank.**

**The DOE Tank Focused Area (TFA) has recently put a call for proposal to look at small-scale demonstration of alternative high-level waste (HLW) tank lay-up options. The ORNL tanks are 750,000-gallon carbon steel tanks and, at the point from which lay-up will proceed, will contain a small amount of insoluble solids residue and an estimated 5,000-gallon liquid heel. The WVDP cannot immediately proceed with tank closure until NEPA determinations are made, therefore a tank lay-up strategy for 5 to15 years is needed. The goal of the lay-up is to place the tanks in a safe, stable, minimum-maintenance mode that does not compromise final closure options.**

**With respect to final tank closure, the TFA is focusing on the use of a grout formulation such as technetium to reduce the mobility of key radionuclides. The specific grout formulation selected for a tank closure is based on the site-specific performance requirements across the DOE complex. To support future tank and site-specific selections of grout formulations for tank closures over the next several decades, the TFA desires to develop and document an improved science and performance understanding of tank closure grouts.**

**A small team at the INEEL and U-Mate International Inc proposed a technical solution to support TFA's two basic needs (tank lay-up and grout formulation) using New Mex U-Mate. For tank lay-up, the team proposed several feet of a stabilizing material called New**

**Mex U-Mate™ (NMUM) as furnished by U-Mate International, Inc. NMUM is a complex inorganic/organic material that offers excellent pH buffer control and heavy metal capture. This type of humate has a low salt content and a similar redox potential as the earth to which the tanks are exposed below ground. We expect with NMUM addition inside and outside (liquid suspension injected around the tank), tank corrosion will be reduced in lay-up. Using NMUM in a grout matrix is expected improve properties such as flowability and radionuclide retention.**

**The specific objectives of our current research are:**

1) **Mix various amounts of NMUM with surrogate tank waste while performance measures such as TCLP (toxicity characteristic leaching procedure), Kd, pH, and ion uptake are quantified.**
2) **Measure the instantaneous corrosion rate of a simulated steel tank before and after adding the NMUM in and around the tank.**
3) **Use NMUM as a co-feed to current grout formulations to ascertain whether improved properties are realized, such as flowability during grout placement and radionuclide retention.**

## II. Technical Background:

**U-Mate International Inc., produces granular humates (organic material consisting of humic substances) at its Gallup, New Mexico facility. Typically, NMUM is used as a fertilizer. This research will demonstrate an innovative application of NMUM to technology needs associated with RCRA closure of DOE HLW tanks.**

**U-Mate International Inc. is a privately held Arizona corporation organized in 1997 to explore and encourage the active use of organic compounds as soil additives and for exploratory and permanent uses as vehicles for soil and environmental remediation. The company has an active mining site in Gallup, New Mexico, with known reserves totaling approximately ten million tons of high-grade humates with low sodium content. The company produces high-grade humates with high humic and fulvic organic acid concentrations and sells the product under the registered trademark of "New-Mex U-Mate™."**

**As the DOE considers in-situ tank lay-up and final closure, the focus should be to ensure that the material used to lay-up and close the tank is in harmony with the environment in which it will reside for eternity. To that end, using NMUM would allow the use of humic and fulvic substances, the most widely distributed natural products on the surface of the earth. Humic substances are found in soils, sediments, and subsurface mining strata and within water resources. These substances have the greatest single influence on all physical, chemical, and biologic conditions on earth.**

**Humic acids are complex aggregates of dark brown, amorphous, high-molecular-weight substances united by general principle of structure but with some distinctions depending on their origins. As chemical functions, they contain carboxylic, phenolic, amino, and**

quinone groups with aromatic nucleuses of low degree of condensation incorporated by parts of non-aromatic character. The presence of aromatic nucleuses with mobile p-type electrons and various functional groups allow humic acids ionic exchange, complex formation, and oxidizing-reduction reactions.

Humic acids are colloids and behave somewhat like clays, even though the nomenclature suggests that they are acids. When the cation exchange sites on the humic molecule are filled predominately with hydrogen cations, the material is considered to be an acid and is named accordingly. However, it has no great effect on pH because the acid is insoluble in water. When the predominant cation on the exchange sites is other then hydrogen, the material is called humate. The humates of monovalent alkali metals (e.g., sodium, and potassium) are soluble in water, but humates of multivalent metals (e.g., calcium, magnesium, and iron) as well heavy metals are insoluble. Apart from their effect on the solubility of materials and their absorption by clays, the different cations have little effect on the humic molecules. The composition of NMUM is given in Table 1.

Table 1. Typical NMUM Composition.

| | |
|---|---|
| Organic Matter | 81% |
| Humic Acid (Fulvic and Humic) | 60%-72% |
| Fulvic | 40% |
| PH (soil) | 5.4ppm |
| Cation Exchange | 84.1% |
| Nitrate ($NO_3$) | 80ppm |
| Phosphate ($P_2O_2$) | 5500ppm |
| Potash ($K_2O$) | 500ppm |
| Al | 10,000-12,000ppm |
| Ca | 10,700-37,500ppm |
| Cu | 0-11ppm |
| Fe | 10,200-10,600ppm |
| K | 400ppm |
| Mg | 2200ppm |
| Mn | 13ppm |
| N | 11,900ppm |
| Na | 1500ppm |
| P | 2400ppm |
| S | 2000ppm |
| Zn | 35ppm |
| Cd | 0.01ppm |
| Cr | 0.06ppm |
| Pb | 0.01ppm |
| Ni | 0.15ppm |
| As | 3.8ppm |
| Cl | 900ppm |
| Se | 208ppm |

Humic acid has an approximate chemical formula of $C_{74}H_{46}O_{38}N_4$ and a molecular weight ranging from 20,000 to 40,000. The chemical structure is presented in Figure 1. The unique properties of humic acids include large molecular surfaces and its availability of many multifunctional sites. They have low water solubility at neutral and acidic pH. They are soluble at high pH > 10 and produce dark brown solutions. Humic acid immobilizes

**heavy metals from water solutions by adsorption and complexation. These complexes are very strong and eventually metals become incorporated into humic acid molecules by multiple chemical bonds.**

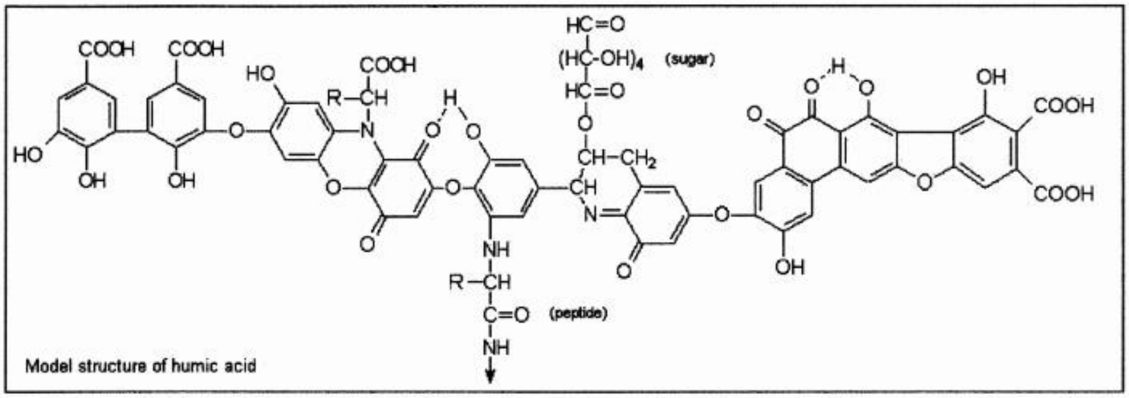

Figure 1. Chemical Structure for Humic Acid

**Fulvic acid has an approximate chemical formula of $C_{27}H_{26}O_{18}N_2$ and molecular weight ranging from 3,000 to 6,000. The chemical structure is pictured in Figure 2. The unique properties of fulvic acids include relatively high water solubility resulting in yellow to brown solution. Most salts of fulvic acids have very low water solubility. In addition, fulvic acids produce complexes with most of the heavy metals, thus also immobilizing them.**

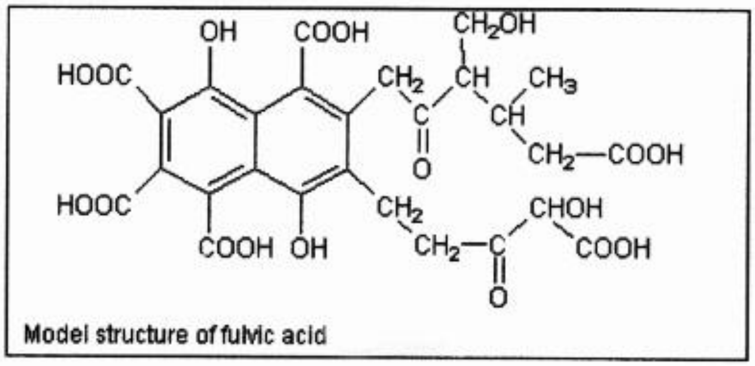

Figure 2. Chemical Structure of Fulvic Acid

**Since fulvic acids are believed to be transferred over time into humic acids, metals precipitated as fulvic acid salts are eventually incorporated into bigger molecules of humic acids that prevent their leaching from humic substances.**

**Within humic and fulvic compounds are a variety of functional groups, including carboxyl, phenolic hydroxyl, aliphatic or alcoholic hydroxyl, enolic hydroxyl, carbonyl, quinone, and amino groups. These groups provide reactive sites for the safe lay-up of tank waste. Additional chelation is the major mechanism of reaction between humic acids and heavy metals that are present in the tanks, and the acids provide an excellent sorption surface. The literature shows (Buckau 1998 and Buckau 1999) that many radioactive elements present in the HLW storage tanks are capable of reacting with**

**humic substances and thus forming organo-metal complexes of different adsorptive stability and solubility.**

## III. Specific Technical Approaches For Validation

### A. Tank Lay-up with Stabilizing Material

**To validate the claims we made in regard to tank lay-up, we are working out a fast paced research program that investigate the basic properties of NMUM mixed with HLW tank heels. We anticipate that this research plan will allow others in the TFA community to evaluate this concept as technically sound and economically feasible. To that end we have outlined the research plan that we are proposing.**

**To validate the previous work in this area, the INEEL will collaborate with U-Mate International Inc. and will obtain surrogate tank heel compositions from ORNL. NMUM will be added to the surrogate liquid. During the mixing in an evacuated container, any off gassing will be measured and captured for postmixing composition evaluation. The mixture will then be evaluated for retention of radioactive simulates. Table 2 summarizes the parameters that will be measured during and after mixing.**

**Table 2. INEEL NMUM mixing and measurements.**

| Action | Property | Technique | Material |
|---|---|---|---|
| Premixing | | | |
| | Bulk density | | Heel, NMUM |
| | PH | Dissolving | NMUM |
| | Trace Metals | NAA | Heel, NMUM |
| | Humic acid | Gravimetric/ Spectroscopic | NMUM |
| | Fulvic | Gravimetric/ Spectroscopic | NMUM |
| | Total Organic Carbon (TOC) | Combustion infrared method | NMUM |
| During Mixing | | | |
| | Released Gas | Summa* | Headspace |
| | Temperature | Immersed Tc | Mixture |
| | PH | Immersed probe | Mixture |
| | Level Swell | Direct measurement | |
| | Color change | Observation | |
| Postmixing** | | | |
| | Trace metal | TCLP, NAA | Leachate |
| | Bulk density | Direct | Solid |
| | Ion capture | Ion Chromatography | Leachate |
| | TOTAL Organic Carbon (TOC) | Combustion infrared method | Leachate |

***An evacuated canister that is then analyzed by a GC-Mass Spectrometer**
****Two months after mixing**

**Mixtures of NMUM with the surrogate table waste will start with 10% free liquid and increase until there is no free liquid. We seek to find the optimal mixing ratio of NMUM to**

**liquid, based on the performance indices of heat released, ionic capture and TCLP release rates. To obtain a base case, we will run clay and zeolite mixtures concurrently with these experiments. This will allow the TFA to review our work and techniques. By analyzing the content of organic carbon and humic substances (humic and fulvic acids) we can also determine the stability of heal-NMUM mixture. Analysis of ions will also provide data on this product stability.**

**Mixing NMUM with WVDP tank heels will expose the organic material to radiation from the decay or the radionuclides present. A determination as to the radiation exposure being detrimental to the humates' exposure to ionization radiation will be performed. Performing long-term exposures with radioisotopes will meet current TFA needs. Therefore, to perform a scoping look at possible detrimental effects, the samples produced during the mixing phase of our research the mixtures will be exposed to high flux x-rays using the facilities at the Idaho Accelerator Center in Pocatello, Idaho where they have various sized linear accelerators are available.**

**The samples will be exposed to a flux simulating the exposure over 50 years if used in a waste tank application. The planned sample irradiation will be performed inside an evacuated cylinder, and the gas release rate and constituents will be measured by GC-mass spectrometry to determine constituents present. After irradiation, a portion of the samples will be run through the same post-mixing matrix as was out lined in Table 2. This will determine any radiation effects that my result in deployment during tank lay-up.**

## B. Tank Corrosion

**Another need of the TFA is to mitigate corrosion of the tanks during the lay-up period. Most of the corrosion is occurring from the outside in. We think that to mitigate the corrosion by adding NNUM inside and outside the tank the corrosion potential would be reduced. The NMUM would be added to the out side of the tank by injecting a slurry solution of the material in water.**

**To validate this approach a series of corrosion tests are proposed in our research in the experimental apparatus pictured in Figure 3.**

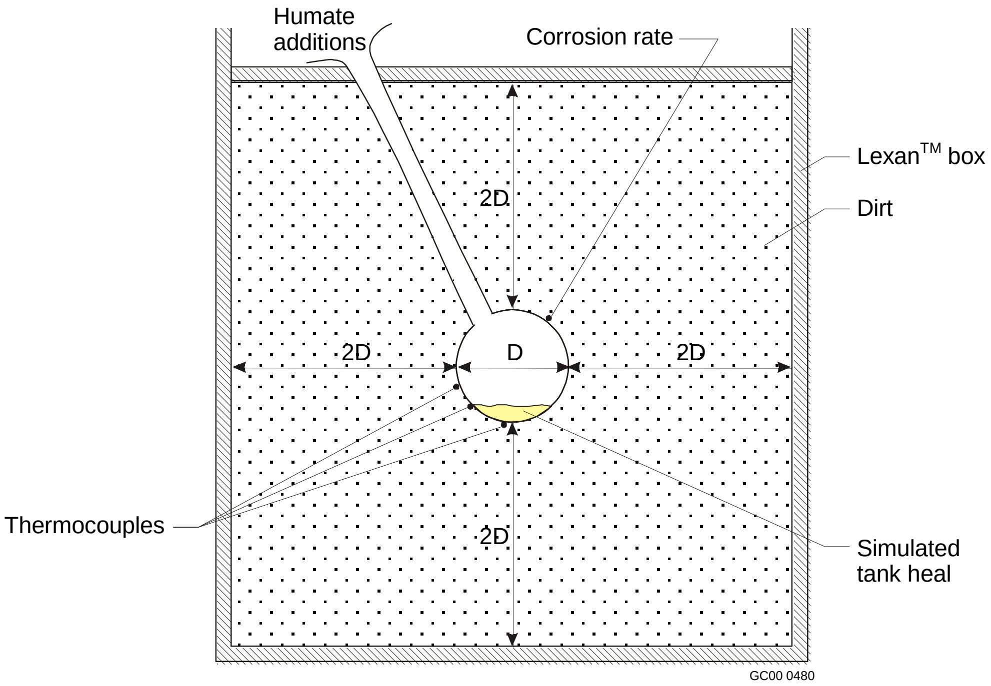

Figure 3. Corrosion Apparatus Picture (not to scale).

**The concept is to measure the instantaneous corrosion rate inside and outside of the tank. This measurement will be made using an instantaneous corrosion probe, which measures the current in a system. The corrosion rate will be measured (on the inside and outside walls) in the test apparatus using the same material as the tanks at ORNL. Investigated soil environment will be created from actual samples of soil collected from tank storage areas (TSAs) or similar. The surrogate material will be placed inside the simulated tanks that in turn will be placed in four different soils yet to be determined (the goals is to get a variety of soil compositions so that these results will be valid across the DOE complex).**

**Four simulated tanks will be used for each soil sample. Three will be exposed on various soil/NMUM mixtures. One will be kept as control in the original soil. The instantaneous corrosion rate will be measured for each soil with various doses of NMUM (inside and outside the tank). Thus, the instantaneous corrosion rate will be correlated with doses of NMUM added. The same variables will be repeated at least three times during the studies (at the beginning, at 1 month, and at 4 months) in order to investigate exposure time on instantaneous corrosion rate.**

### C. Grout Formulations

**We believe that adding NMUM to grout formulation will help the performance goals of grout, namely, reduced heat of hydration, better flow during placement, less water bleed during curing, and flexibility for a variety of waste types (including both alkaline and acidic), and strength.** Research in this area is designed to validate our claims by preparing grout formulations at the INEEL using prepared waste surrogates as published in the open

**literature. After mixing the formulations with the addition of NMUM, the INEEL will performance test the resultant grout waste forms, which will include:**

- **a) performing Kd measurements for alpha emitters, technetium, cesium, and strontium (simulates will be used for all radionuclides)**
- **b) performing TCLP measurements for RCRA metals**
- **c) measuring leachability indices**
- **d) assessing the impact of grout formulations on the solubility of technetium and chromium.**

**The performance goals will be achieved by properly selecting dry-blend additives such as cement types, fly ash, clays, slags, suspension agents, sorbents, etc. To provide the technical community comparative data, we will prepare two formulations using fly ash and clays.**

## IV Summary

**In summary, we are proposing to the technical community a broad approach to determine whether NMUM could be used as a tank lay-up method and investigate the impact on grouting (If grouting is going to be the final step in tank disposal). . - This type of remediation step offers a safe, cost effective way to provide lay-up for these tanks.**

**U-Mate International Inc. in addition to its mining operations, has been in the forefront of developing procedures and proprietary products using humates particularly with respect to soil and environmental remediation.**

## V References:

**Buckau G. (editor). "Effects of Humic Substances on Migration of Radionuclides: Complexation and Transport of Actinides," First Technical Progress Report, Karlsruhe, August 1998.**

**Buckau G. (editor). Effects of Humic Substances on Migration of Radionuclides: Complexation and Transport of Actinides, Second Technical Progress Report, Karlsruhe, June 1999.**