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WHC-EP-0658

Moisture Monitoring of Ferrocyanide Tanks: An Evaluation of Methods and Tools

Prepared for the U.S. Department of Energy
Office of Environmental Restoration and
Waste Management

Westinghouse
Hanford Company Richland, Washington

Hanford Operations and Engineering Contractor for the
U.S. Department of Energy under Contract DE-AC06-87RL10930

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ID Number (include revision, volume, etc.): WHC-EP-0658

List attachments.: N/A

Date Release Required: 4/30/93

Title: Moisture Monitoring of Ferrocyanide Tanks: An Evaluation of Methods and Tools

Unclassified Category: UC-600

Impact Level: 4

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Title of Conference or Meeting: N/A

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	Yes	No
References Available to Intended Audience	[X]	[]
Transmit to DOE-HQ/Office of Scientific and Technical Information	[]	[X]

Author/Requestor (Printed/Signature): J. E. Meacham (signature) Date: 4/29/93

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WHC-EP-0658

UC-[redacted] 902

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Date Published
April 1993

Prepared for the U.S. Department of Energy
Office of Environmental Restoration and
Waste Management

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Richland, Washington 99352

Hanford Operations and Engineering Contractor for the
U.S. Department of Energy under Contract DE-AC06-87RL10930

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MOISTURE MONITORING OF FERROCYANIDE TANKS: AN EVALUATION OF METHODS AND TOOLS

J. E. Meacham
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ABSTRACT

This report reviews the strengths and limitations of moisture monitoring technologies that could be used for determining moisture concentration in Hanford Site single-shell ferrocyanide waste tanks. Two technologies (neutron diffusion and near-infrared spectroscopy) are being pursued as part of the ferrocyanide program. A third technology, Raman spectroscopy, is in development as a speciation tool at the Westinghouse Hanford Company 222-S Laboratory. The potential application of Raman spectroscopy to moisture monitoring is discussed.

Data on moisture retention are available from tank core samples, sludge modeling studies, and sludge simulant experiments. However, moisture monitoring remains necessary to confirm the that (1) sludges are not drying; and (2) predicted moisture trends are accurate. Effective moisture monitoring is a critical element in the unresolved safety question resolution strategy. After closure of the ferrocyanide unresolved safety question, the safety assessment may require moisture monitoring.

All of the moisture monitoring technologies discussed have strengths and limitations. The neutron probe has the potential for determining a vertical moisture profile, but is limited to the location and availability of Liquid Observation Wells. Experimentation with this system shows promise for yielding some form of moisture monitoring system in the near future.

The optical spectroscopy technologies have inherent limitations. Scattering and absorption limits interrogation to the tank waste surface. The nature of the waste surface makes it difficult for laser light to penetrate more than just a few millimeters in depth. The systems can also be affected by phenomena that influence the transmission of light, including reflectance and signal strength. However, the potential for added speciation of the waste makes the near-infrared and Raman spectroscopy systems worth investigating.

It is possible that no single technology may accomplish the level of moisture monitoring desired. If the moisture data obtained from either Liquid Observation Wells or surface scans is not sufficient, a combination of several technologies may be necessary to achieve a three-dimensional moisture profile of the ferrocyanide waste contained in waste storage tanks at the Hanford Site.

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LIST OF ACRONYMS

CASS	Computer Automated Surveillance System
CPAC	Center for Process Analytical Chemistry
LOW	Liquid Observation Well
NIR	Near-Infrared Spectroscopy
SST	Single-Shell Tank
USQ	Unreviewed Safety Question

1.0 INTRODUCTION

1.1 BACKGROUND

Radioactive wastes from defense operations have accumulated at the Hanford Site in underground waste tanks since the early 1940s. During the 1950s, additional tank storage space was required to support the Hanford Site defense mission. To obtain this additional storage volume within a short period of time, and without constructing additional storage tanks, Hanford Site scientists developed a process to scavenge radiocesium and other soluble radionuclides from tank waste liquids. The supernatant could then be disposed of to cribs, freeing tank space. In implementing this process, approximately 140 metric tons of ferrocyanide were added to 24 single-shell tanks (SSTs) in order to precipitate cesium nickel ferrocyanide.

Ferrocyanide is a complex of ferrous ion and cyanide that is considered nontoxic because it is stable in aqueous solutions. However, in the presence of oxidizing materials, such as nitrates/nitrites, near-stoichiometric amounts of ferrocyanide can be made to explode under special conditions in the laboratory by (1) heating it to high temperatures (above 285 °C); or (2) by an electrical spark of sufficient energy to heat the mixture. The explosive nature of ferrocyanide in the presence of an oxidizer has been known for decades, but the conditions under which the compound can undergo an uncontrolled exothermic reaction have not been thoroughly studied. Because the scavenging process involved precipitating ferrocyanide from solutions containing nitrate and nitrite, it is likely that an intimate mixture of ferrocyanides with nitrates and nitrites exists in some of the Hanford Site SSTs.

Efforts have been underway since the mid-1980s to evaluate the potential for a ferrocyanide explosion in the Hanford Site single-shell tanks (Burger 1989; Burger and Scheele 1988). In 1987, the final environmental impact statement for disposal of Hanford Site waste forms was issued (DOE 1987). The environmental impact statement projected that the bounding "worst-case" accident in a ferrocyanide tank would be an explosion resulting in a subsequent short-term radiation dose to the public of approximately 200 mrem.

A General Accounting Office study postulated a greater "worst-case" accident (Peach 1990), with independently-calculated doses one to two orders of magnitude greater than the 1987 DOE environmental impact statement. A special Hanford Site Ferrocyanide Task Team was commissioned in September 1990 to address all issues involving the ferrocyanide tanks, including the consequences of a potential accident. On October 9, 1990, Secretary of Energy James D. Watkins announced that a supplemental environmental impact statement would be prepared containing an updated analysis of safety questions for the Hanford Site single-shell tanks (including a ferrocyanide explosion).

Using process knowledge and historical records, 22* tanks were initially identified at the Hanford Site as containing 1,000 g-mole or more of ferrocyanide as the $Fe(CN)_6^{4-}$ radical. In October 1990, the ferrocyanide issue was declared an Unreviewed Safety Question (USQ) because the safety envelope for these tanks may no longer be bounded by the existing safety analysis report (Bergman 1986) and the 1987 DOE environmental impact statement. Work in and around any of the ferrocyanide tanks requires detailed planning, together with the preparation of supporting safety and environmental documentation, and approval by DOE management. These restrictions are prescribed by DOE orders for USQ issues, and significantly increase the time required to complete work or install equipment in the tanks.

1.2 TECHNICAL JUSTIFICATION FOR MOISTURE MONITORING

A strategy for resolution of the ferrocyanide USQ was developed that involves demonstrating, on a tank-by-tank or tank farm basis, that waste tanks on the ferrocyanide Watch List do not present a credible risk for releasing radionuclides to the environment as a result of an uncontrolled reaction (Crowe et al. 1993). The technical basis for this determination will depend on the ability to demonstrate that the waste will not react under controlled conditions.

To maintain in situ safe storage, the waste must be kept in a non-reactive state. Three alternatives can bound safe storage in any given tank. It must be demonstrated that the contents of the tank are either (1) intrinsically safe--the waste contains an insignificant fuel inventory; (2) passively safe--the waste contains too low a fuel concentration to react; or (3) in a state of controlled safety--the waste is maintained in a condition that precludes a reaction.

If sufficient data are not available to assure that continued storage of the wastes is either intrinsically or passively safe, then the tank will need to be maintained under conditions of controlled safety. The key to applying such control is the development and demonstration of effective moisture and temperature monitoring. Experiments on ferrocyanide waste simulants have shown that propagating reactions can be prevented by the following three conditions, any one of which is sufficient to ensure safety:

- **Moisture content.** Water content greater than 12 wt% will suppress ferrocyanide propagating reactions at ferrocyanide concentrations up to 26 wt% (dry basis); this is the highest postulated initial ferrocyanide concentration.

- **Temperature.** Exothermic reactions will not initiate below 220 °C.

*Two more tanks potentially containing ferrocyanide were identified since the DOE responded to DNFSB Recommendation 90-7 in November 1990.

- **Low ferrocyanide concentration.** Ferrocyanide reactions will not propagate if the fuel concentration is below about 13 wt% (dry basis).

Moisture content is important because it acts as an inert diluent, and vaporization of water represents a large endotherm in postulated runaway reactions. It has been demonstrated that, for a stoichiometric mixture of ferrocyanide fuel and oxidant, 35 wt% water would limit temperature in the tank to boiling, approximately 120 °C (Fauske 1993). The total energy produced by the chemical reaction would be absorbed by the sensible and latent heat of the water present.

Ferrocyanide waste simulant studies and analyses of core samples from tanks 241-C-109 and -112 have demonstrated that the waste retains considerable water. The moisture content of ferrocyanide waste simulants centrifuged to 30 equivalent gravity years ranged from 48 to 67 wt% (Jeppson and Wong 1993). Analyses of core samples taken from actual ferrocyanide waste tanks have ranged from 40 to 60 wt% water (Cash et al. 1993b). Studies have concluded that moisture is held in the waste by capillary action, in gel form, and as chemical hydrates within the waste.

Although data on waste moisture content are available from (1) tank core samples; (2) sludge simulants; and (3) waste studies of moisture retention by ferrocyanide sludge, moisture monitoring remains necessary to confirm that sludges are not drying and that the predicted moisture trends are accurate. Moisture content of the waste is also a critical element in the USQ resolution strategy.

After closure of the ferrocyanide USQ, moisture monitoring will remain important. The safety analysis that is being prepared to resolve the USQ may require implementation of moisture monitoring or periodic surveillance. Under the current requirements of the Wyden Amendment (Public Law 101-510, Section 3137)* and increased environmental awareness, it will be important to maintain a "presence" in the tanks to preserve credibility. The public will require that the ferrocyanide tanks remain verifiably safe and that the tanks are not neglected while waste retrieval and remediation are implemented.

1.3 FOCUS AND SCOPE

This report identifies two moisture monitoring technologies currently under development; neutron diffusion and near-infrared spectroscopy. A third technology, Raman spectroscopy, is being developed as a speciation tool at the Westinghouse Hanford Company 222-S Laboratory, and its potential application to moisture monitoring is also discussed. The

*The Wyden Amendment requires the identification of Hanford Site single-shell or double-shell tanks that may have a serious potential for release of high-level waste due to uncontrolled increases of temperature or pressure. It further requires that monitoring in these tanks be installed as soon as practical.

most accurate moisture measurements of the ferrocyanide sludges to date have been achieved by direct analyses of core samples. Moisture analysis by core sampling has, however, been slow and expensive, taking up to six months and approximately one million dollars per SST. Core sampling would be an ineffective moisture monitoring technique because of timeliness and prohibitive costs; therefore, it is not discussed in this document.

The effect of ferrocyanide aging and energetics on continued in situ safe storage are outside the scope of this document. It is also important to note that temperature and moisture are not mutually exclusive parameters; that is, each can influence the other. This relationship and the impact of temperature on in situ safe storage is not discussed in this document, but has been addressed in other reports (Dickinson et al. 1993; Efferding 1992; Fauske 1992; Jeppson and Wong 1993). The role of moisture monitoring in the overall monitoring strategy for other (non-ferrocyanide) Hanford Site high-level waste tanks is also outside the scope of this report; however, this issue will be discussed in future documents.

Alternative and/or complementary methods for measuring single-shell waste tank moisture are described in Sections 2.1 through 2.3. Following the discussion of these methods, Section 3.0 provides overall conclusions resulting from this report. Several other options for moisture monitoring have been contemplated. A summary of the moisture monitoring technologies considered is presented in the Appendix to this report. Some of these technologies may be considered further as developments or more promising information becomes available.

2.0 MOISTURE MONITORING METHODS

Moisture monitoring technologies discussed in this section include neutron diffusion, near-infrared spectroscopy, and Raman spectroscopy. This section (1) describes each of the proposed measurement techniques; (2) provides a synopsis of the available information on the capabilities of each technique; and (3) discusses the strengths and limitations for each method. Where possible, solutions to the limitations are presented. A summary of the strengths and limitations of each technology is presented in Table 2-1.

Table 2-1. Strengths and Limitations of Proposed Moisture Monitoring Systems.

METHOD	STRENGTHS	LIMITATIONS
Neutron Probe	Develops a vertical profile of moisture concentration. Much of the equipment required is already owned. Established technology for the well logging industry. Possible density analyses with the same probe.	Only 12 of 24 ferrocyanide tanks currently contain LOWs; more would have to be added. Probe only measures up to a 20 cm annular radius around the LOWs. Possible void spaces around the LOWs.
Infrared Scanning	Well established technology; off the shelf equipment available. Remote system with real-time analyses. Can develop a complete moisture map of a tank surface.	Limited to surface monitoring only. Equipment is sensitive to radiation fields. Optical reflectance off the waste surface or tank dome space humidity may limit sensitivity.
Raman	Strong speciation tool; may characterize waste in situ. When combined with a tunable laser, one probe could be used for both IR and Raman spectroscopy.	New unproven technology. Optical interferences in the tanks may limit application.

2.1 NEUTRON PROBE

2.1.1 Neutron Probe Concept

Moisture measurement using neutron diffusion is an established technology. The technique uses a neutron source and one or more neutron detectors. Fast neutrons are emitted from the source and are slowed or absorbed by the surrounding medium. Because hydrogen atoms are effective at slowing down neutrons, the detector countrate is a strong function of the moisture in the surrounding material.

The response of an active neutron probe to variations in the moisture content of the surrounding material depends primarily upon the distance between the detector and the neutron source. There are two methods for measuring moisture concentration around wells using neutron diffusion. The first method, the moisture gauge, has a short source-to-detector spacing, about 2 - 10 cm. The moisture gauge records an increase in countrate with an increase in the moisture concentration of the surrounding media.

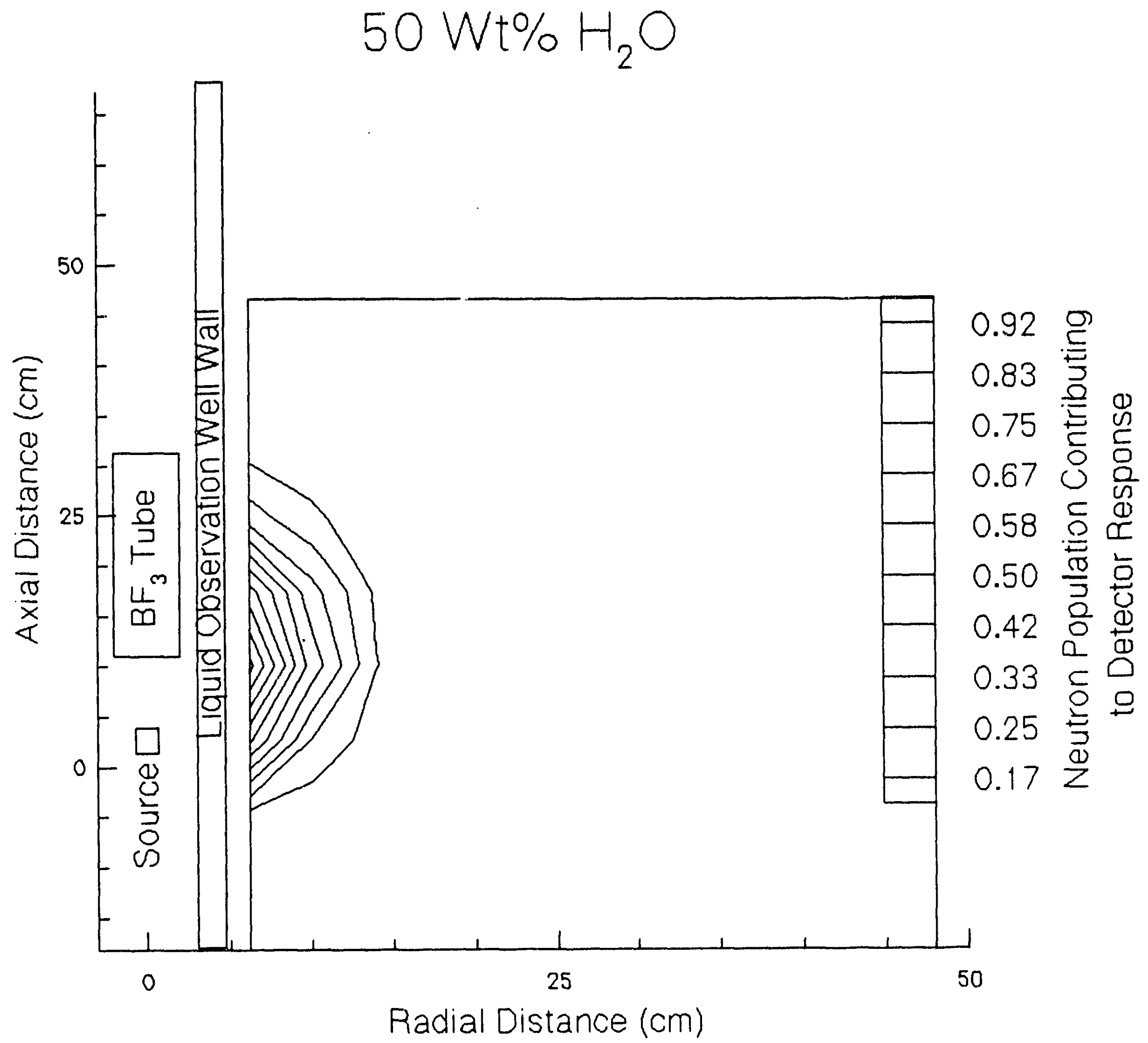
The second method, the neutron log, often has two detectors with longer source-to-detector spacing. For longer separation distances, the observed countrate decreases for increasing moisture concentration. The primary detector is placed approximately 50 cm from the neutron source, and the secondary detector is about 20 cm from the source. The secondary detector is used to correct the primary data for bore hole effects (Hearst 1993). The detectors may be wrapped with a thermal neutron absorber, such as cadmium, to avoid influences on the countrate by the presence of materials with high neutron capture cross section.

2.1.2 Neutron Probe Strengths and Limitations

Twelve of the twenty-four ferrocyanide tanks are equipped with a Liquid Observation Well (LOW) as a part of the single-shell tank leak detection system. Both a passive gamma probe and an active neutron probe can be deployed into the LOW using the drywell van. Measurements are recorded as a function of height, and the data are transferred to the Computer Automated Surveillance System (CASS) where an engineer analyzes the data to determine whether any changes have taken place in the liquid level.

Figure 2-1 shows the depth of investigation of the neutron probe to be approximately 10 cm beyond the wall of the LOW. For systems containing less than 50 wt% water, this depth of investigation is increased to 15 - 20 cm. An investigation of up to 20 cm is a great improvement over near-infrared and Raman spectroscopy, which can only interrogate the surface.

Figure 2-1. MCNP Calculated Source Neutron Population Density Reaching the Detector.



The existing neutron probe was designed to permit adjustment of the source-to-detector separation distance. The annular radius interrogated by the probe is a function of water concentration, source-to-detector separation, neutron source strength, and energy spectrum of the source neutrons. As the moisture concentration increases, the radius of investigation decreases. In the current configuration, the probe can detect moisture concentrations of 0 - 40 wt%. Experiments are being conducted with increased source-to-detector spacing using a stainless steel extender. This should substantially increase both the maximum annular radius investigated by the probe and the maximum detectable moisture concentration. A more intense neutron source and/or higher energy source neutrons would also increase the radius investigation.

The neutron probe can be utilized in two ways for moisture monitoring. The probe can be used to determine the axial moisture concentration profile along the length of the LOW. The probe would be lowered down the LOW at regular intervals to track possible trends in the moisture concentration of the waste. The probe could also be used as a threshold device. If a safe minimum moisture concentration is not met, appropriate personnel would be notified.

Either technique requires a properly benchmarked neutron probe computer model. The computer model is required to convert the neutron scan data from probe countrate to volume percent moisture. Weight percent moisture can be calculated using estimates or measurements of the waste density around the LOW.

There are a number of areas of concern that must be addressed for effective use of the neutron probe for measuring the moisture content of a tank. These include the following:

- Location of the LOWs in the tanks.
- Effects of water sluicing to install the LOWs.
- Conversion of volume percent to weight percent water using density information.

Only 12 of the 24 ferrocyanide tanks have LOWs, and these are generally located in risers close to the tank edges. There is a concern that waste located near a LOW is not representative of the entire tank. By deploying the neutron probes in a fixed-position 3.0 inch inside diameter LOW within a 75 foot diameter tank, a very small fraction of the total tank volume will be interrogated. However, recent results of experiments and hot spot modeling suggest that moisture monitoring in every location in the tanks may not be necessary (Fauske 1993; Dickinson et al. 1993). This work has concluded that localized dry out is incredible, and that the bulk of the tank contents would dry out first.

The LOWs were inserted through the hard saltcake by sluicing with water. A concern with neutron probe monitoring is the effect of water sluicing on the annular regions surrounding the LOWs. Sluicing may have disturbed significant quantities of waste around the LOWs, resulting in two undesirable effects: crystal growth on the LOW and void spaces. Voids around LOWs at the surface are evident in many in-tank photographs. When the water lance pierced the saltcake surface, a hole much larger than the LOW remained. If the interstitial liquid level is above the saltcake surface, the hole is filled with liquid. If it is below the saltcake surface, the hole is dry. The disturbances in the waste caused by water sluicing could affect the results of neutron probe measurements.

Crystal growth on the LOWs can exist both above and below the waste. Any crystal growth above the waste surface can be identified with photographs and by comparing neutron and gamma scans. Because ferrocyanide does not exist in these crystals, crystal growth above the waste surface would not hinder measurements. Crystal growth below the surface of the waste should not exclude moisture. Capillary forces in the waste would keep dry crystal pockets from forming.

The formation of void spaces around the LOWs during installation should prove to be a non-problem for moisture monitoring in the ferrocyanide regions. Ferrocyanide exists only in the sludge, not in the saltcake (Grigsby et al. 1992). Therefore, determining the moisture concentration in a hole in the saltcake around the LOW is not necessary. Below the saltcake layer, the water sluicing perturbed the sludge around the LOW. Analyses have shown that the ferrocyanide sludge is quite insoluble; thus, dissolution of the sludge around the LOW is unlikely. The sludge is comprised of small particles and is easily fluidized when mixed with water (Grigsby et al. 1992). Void spaces around the LOWs would be hydrodynamically unstable, and the sludge should flow back around the LOWs. The ferrocyanide tanks have not had waste transferred into them since the late 1970s and ample time has passed for equilibrium to be reached.

The presence of void spaces around the LOW could be checked using ultrasonic methods. However, preliminary experiments revealed excessive noise in the ultrasonic scans, and this technique does not appear to be promising (Stong 1986). Conditions around each LOW could also be checked by density measurements. The densities around the LOW would be compared to predicted process flowsheets or core sample analytical values to determine if liquid or void spaces exist as a result of sluicing.

The neutron probe, as presently configured, can only determine volume percent moisture. A density value for the waste is necessary to convert the volume percent data to equivalent wt% moisture values. Different approaches to arrive at a density value for the waste are possible. One approach is to determine the density precisely as a function of height along the LOW. Gamma-gamma tools are used in the well logging industry to perform this function. The application of a gamma-gamma tool could be complicated by the high gamma ray flux from the tank waste. This background gamma ray flux could be accounted for using a passive gamma probe measurement.

Another approach for obtaining density values would be to estimate the density value range using data from tank samples. Density values from several ferrocyanide tank waste samples have ranged from 1.3 g/cm^3 for supernate samples to 1.6 g/cm^3 for samples of waste solids. If higher density values are used to convert detector countrates to wt% water, then lower estimates are obtained for wt% water. Therefore, calculating the wt% water using the highest estimated density gives the lowest, most conservative wt% value.

An additional problem encountered using the neutron probe is the presence of boron in the fiberglass LOWs. Boron is an extremely efficient neutron absorber, and even a small amount can greatly affect probe response. Modeling efforts were performed using a boron content supplied by the original LOW vendor. However, modeling and benchmarking efforts have strongly suggested that this value is not accurate. An accurate value for the boron concentration is paramount to a successful modeling effort. Two techniques for boron determination are being pursued.

The Westinghouse Hanford Company Physical Analytical Laboratory is performing a full elemental analysis of a sample taken from a LOW. The results of this analysis should be valid for application in modeling efforts if the boron content is consistent both along the LOW length and among the other LOWs.

The neutron probe is being benchmarked for the computer model by immersing the probe directly into water without the LOW casing (Cash et al. 1993a). This removes all uncertainties in the system. With the probe model benchmarked for pure water, bias created by the LOW can be added to the model. Boron content can be adjusted until the calculations agree with experimental data.

Moisture monitoring for any of the twelve ferrocyanide tanks not equipped with LOWs will require the installation of a LOW. Alternative installation methods, which do not create severe void spaces, should be considered. Saltcake drilling techniques being developed for thermocouple tree installation utilize a low-water volume, high-pressure drill head. This results in less disturbance of the waste around the thermocouple tree. To correct the boron problem, LOWs with well known properties (such as carbon steel) can be installed. A carbon steel LOW would greatly increase the probe's moisture detection capabilities.

2.2 NEAR-INFRARED

2.2.1 Near-Infrared Spectroscopy Concept

Another method for measuring moisture in the tanks is by determining water content at the waste surface. Surface monitoring may be acceptable for determining a minimum moisture content for the entire tank. Waste near the surface would tend to be more dry than waste beneath the surface. Ferrocyanide sludge and saltcake (mostly alkaline double-shell tank evaporator bottoms or aluminum decladding waste) contained in the SSTs consist of small particles (predominantly 5 microns in diameter). High capillary forces in the sludges would favor a drier-top wet-bottom moisture gradient.

Experiments recently performed on ferrocyanide simulant sludge revealed that the sludge retains moisture when dewatered by centrifugation on filters at several gravities. Even at 50 gravities of centrifugal force, the sludge retained over 40 wt% moisture. This suggests that even in the event of a leak in a SST, the sludge below the saltcake surface would remain wet.

A method for evaluating the moisture content of the surface is near-infrared spectroscopy* (NIR). NIR is an important new analytical technique with a demonstrated capability to perform simultaneous multi-component determinations on irregular solids (Williams and Norris 1987). Infrared light in this spectrum is absorbed mainly from combinations of carbon-hydrogen, nitrogen-hydrogen, and oxygen-hydrogen bond vibrational motions. Because the frequency of a vibration is dependent on the details of the associated chemical bonds, the patterns of absorption provide a unique fingerprint that defines a particular molecule with some degree of certainty. However, compared to the mid-infrared, the absorption bands are much weaker. This results in lower absorption coefficients for NIR.

The lower absorption coefficients mean that thicker samples can be interrogated which are easier to handle and provide less sampling error. In many cases the log of the inverse of the diffuse reflectance is found to be linear with analyte concentration; this "pseudo Beer's law" behavior makes the data very easy to use. In this region of the spectrum work can be performed directly with solid samples. There are many cases where the analysis can proceed directly on undisturbed objects in situ.

A contract was recently established with the Center for Process Analytical Chemistry (CPAC) at the University of Washington. CPAC will investigate the potential for using a NIR system to remotely analyze the moisture content of the surface materials in ferrocyanide waste tanks.

2.2.2 Near-Infrared Spectroscopy Strengths and Limitations

There are several successful commercial applications of surface NIR moisture measurement technology. The food industry is using this technology to measure moisture content in cookie dough, flour, and food grains (Rubenthaler and Pomeranz 1987; Kelly et al. 1989). CPAC has been involved in some of these areas, providing moisture related spectroscopy studies and demonstrations of concept feasibility. There have been recent advances in infrared component technologies that support the pursuit of an in situ NIR system.

The initial CPAC work will provide a feasibility assessment for determining waste tank surface moisture with spectroscopic measurements. Experiments will be completed with a saltcake surrogate that demonstrates the principle of this technology and its feasibility for use with tank wastes. Data will be used to produce a conceptual design for implementing the technology within a hot cell and within a waste tank. An advantage of the NIR system is the capability to provide near real-time moisture determinations of extruded core samples or the tank waste surface.

* Wavelength 1100-2500 nm

NIR moisture monitoring has several advantages. Calibration of the instrument is straightforward, and may not require the extensive modeling necessary for the neutron probe. Moisture monitoring of non-homogenous cookie dough with NIR has proved quite successful. Once the NIR system was calibrated to account for the existence of chocolate chips, walnuts, and other ingredients, accurate moisture determination was possible irrespective of surface geometry and cookie dough composition.

A NIR system would not have the radial limitations that exist with the neutron probe and core sampling. A near-infrared camera system could be fastened on a rotating mount and inserted into a riser. The camera could sweep the surface of the tank to develop a moisture contour plot similar to those generated for infrared mapping of surface temperature. The system would perform a contour sweep at regular intervals to trace moisture trends.

If a NIR camera system is not feasible, similar results could be achieved by mounting a NIR probe on a robotic arm. However, this option could be expensive. One robotic system would probably have to serve several tanks, making this option labor intensive and more costly. Moving the instrument among tanks would increase worker exposure to radiation.

The wide use of infrared/near-infrared technology provides its greatest advantage when compared to the other alternatives. Most of the NIR components are readily available; however, the engineering required to implement a NIR system might be extensive. NIR also holds potential for limited speciation of the ferrocyanide tank contents. Speciation of organics and other molecules present in the waste may be possible using the absorption information. The system should also delineate between chemically bound and free water. The combination of these data with information from other sensors, such as Raman and atomic emission spectroscopy, would greatly expand the knowledge base of tank waste materials.

There are several limitations that will have to be weighed or resolved before a NIR system is implemented. These include the following:

- Optical reflectance off the waste surface or tank dome space humidity (mist).
- Results that are limited to surface interrogation only.
- Equipment sensitivity to radiation.

Optical systems can be affected by disturbances that affect the transmission of light. One concern is that if the system is installed at an outside riser, the camera would have to scan over 60 - 70 ft to reach the opposite side of the tank. The near-infrared wave band is particularly sensitive to moisture, and water vapor in the tank dome space could stop the scan from reaching the desired point. The extreme angle caused by this distance might cause the NIR scan to bounce off the surface, similar to a stone skipping on water. This would eliminate much of the NIR information from reaching the camera, resulting in a poor analysis. CPAC will be reaching a go/no-go decision to determine if these optical challenges can be overcome. Ultimately, NIR may have to be used in conjunction with other technologies to develop a three-dimensional moisture profile.

Scattering and absorption will limit optical instrumentation to surface applications. The strong water absorption and the variability of the waste optical properties make it very difficult to penetrate a depth of more than just a few millimeters. Therefore, infrared and NIR interrogation are limited to the surface. A possible solution to this would be the use of cone penetrometer techniques for insertion of spectroscopy-based probes deeper into the waste.

One drawback of an NIR camera is the limited life caused by gamma radiation exposure to the semiconductor components within the scanner. Based upon an average radiation level within the SSTs of 150 R/h, the useful life of an infrared camera may be limited to approximately 100 hours (Efferding 1993). Possible solutions may be (1) to provide more shielding; or (2) to have a system stored in the riser that could be deployed periodically. Radiation resistant infrared components are not as well developed as those for the optical wavelength regions. Current NIR optical fibers, which would be usable for remote applications, have high absorptions. These fibers are fragile and expensive compared with conventional silicate fibers. Radiation resistant probes and optical fibers are being developed as more radiological applications are required; however, dependence on a technological break-through is tenuous at best.

2.3 RAMAN

2.3.1 Raman Spectroscopy Concept

Raman is a vibrational form of spectroscopy that provides information complementary to infrared spectroscopy on molecules. Unlike infrared spectra, which result from direct absorption of infrared light, Raman spectra are the result of inelastic light scattering. Therefore, there is no wavelength dependence on the source of excitation radiation. Instead, the light frequencies shifted from the source frequency are observed. This shift provides a unique fingerprint that defines a particular compound. The resultant spectra are obtainable with laser excitation ranging from the ultraviolet to the near infrared. This makes Raman based techniques ideally suited for application with fiber optics, since the source frequency can be tuned into favorable light transmission ranges for various materials.

The use of fiber optics to deliver radiation to and collect scattered radiation from a remote sample is a key element in the use of Raman spectroscopy for rapid, routine measurements. A probe consists of a bundle of several optic fibers, typically 200 microns in diameter, surrounding a single excitation fiber. The excitation fiber carries the laser energy, and the surrounding fibers transmit the scattered light back to the detector. Much of the success of the Raman measurements, particularly with strongly scattering samples, depends on the filter selection. The filter must reject the scattered laser radiation while transmitting the longer wavelength Raman scattering radiation.

2.3.2 Raman Spectroscopy Strengths and Limitations

The greatest strength provided by a Raman spectroscopy system is its broader application for speciation. With the advent of the tunable laser, several spectra of light can be generated and channeled through the fiber optic cables. A Raman probe has the potential for utilizing both Raman and near-infrared wavelength light. One probe could perform both functions, making it a powerful tool for speciation of the tank contents. Raman speciation requires a less focused beam than the NIR. This would allow interrogation of a larger area, and could lead to a more accurate analysis.

Because Raman is an optical system, it has many of the same optical advantages and limitations encountered by NIR. Raman is relatively insensitive to water; however, with the advent of a tunable laser, several spectra of light can be generated for speciation, including those bands more sensitive to water. Raman is a relatively new technology and does not yet have the extensive use of either NIR or neutron diffusion. Therefore, a Raman system may be more expensive to develop for all the ferrocyanide tanks.

Raman spectroscopy does not lend itself to the camera technology that NIR affords. The sample being investigated must be in close proximity to the Raman probe. Therefore, a robotic arm may be required to utilize Raman in situ. As described earlier for the NIR system, a robotic arm might prove expensive. However, Raman does hold promise as a hot cell analytical tool. Samples could be brought to the instrument and optical conditions in a hot cell could be more readily controlled.

Raman is a relatively new technology and there are presently uncertainties about the applicability of Raman surface moisture mapping. The Raman system would supply real-time speciation information that could be a real asset for hot cell analyses of core samples. Of all the methods discussed, Raman has the largest potential for speciation as well as measuring moisture content.

3.0 CONCLUSIONS

All of the moisture monitoring systems have strengths and limitations that have been discussed in this report. The neutron probe has the potential for determining a vertical moisture profile, but the technique is limited to the location and availability of LOWs. Experimentation with this system shows promise for yielding a usable moisture monitoring system in the near future.

The optical NIR and Raman systems have inherent limitations. Scattering and absorption limits interrogation to the tank waste surface. The nature of the waste surface makes it difficult for laser light to penetrate more than just a few millimeters in depth. It will be necessary to demonstrate that the wastes are wetter at the bottom of the tank than the top. The systems can also be affected by phenomena that influence the transmission of light, including reflectance and signal strength. However, the potential for added speciation of the waste make the NIR and Raman systems worth investigating.

Finally, it may be that a single technology cannot accomplish the level of moisture monitoring that is desired. A combination of several technologies may be necessary, and development is underway on the three different technologies discussed in this report.

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APPENDIX

SUMMARY OF TECHNOLOGIES CONCEPTUALIZED FOR MOISTURE MONITORING OF FERROCYANIDE TANKS

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MINUTES FROM FERROCYANIDE MOISTURE MONITORING WORKSHOP CONDUCTED FEBRUARY 19, 1992 RICHLAND WA

Purpose and Objectives: Gary Dukelow

Gary described the basic purpose of the meeting: to assist in the decision making process for potentially undertaking a limited number of development/ design options leading to a system capable of measuring the water moisture content of the ferrocyanide tanks. During the day we would discuss the alternatives on the agenda and evaluate these alternatives individually and provide them to Ed Sheen/Gary to provide a basis for proceeding further. Funding limitations would preclude pursuing all alternative concepts.

Technical Background on Need: Bob Cash

Bob presented information on why moisture monitoring is needed for the ferrocyanide tanks. A phase type diagram was presented showing a propagation limit line for the reactive/unreactive limit. This triangle has weight percent of water as the triangle base. Fuel (ferrocyanide) and oxidizer (nitrate/nitrite) form the other two legs. Tank safety will require monitoring both temperature and moisture.

Neutron Well Logging moisture monitoring techniques: Joe Hearst

Joe presented fundamental information regarding the technique of using the slowing down of neutrons by hydrogen and detection of these neutrons as a means of determining water content of the hydrogen bearing media. Joe discussed the differences in the tank safety application and the more common well logging done in industry; for example, the LOW is dry inside and well bore holes are normally water filled. He cautioned the literature assumes water filled holes unless otherwise stated. Joe indicated current research is underway for NMR based systems but they probably do not apply to the tank problem because of probe size. Also, Neutron die-away based approaches require a pulsed neutron source electronic package that would probably be longer than the tank depth.

Some of the important conclusions were as follows:

- We should find out how much density matters and correct for it for our case.
- We should use a field verifier to assure consistency of the data.
- We should use epithermal neutrons to avoid chemical effects by shielding the BF3 tube detector.

- Choose the source to detector spacing for the tank safety application.

- Build a calibration facility.

Discussion: Tank homogeneity, importance of adequate calibration facilities, and importance of identifying weight or volume percent moisture were discussed. Also availability of easy source-detector spacing on the existing probe was mentioned.

Brief description of the existing system: Fred Stong

Fred provided descriptions of the existing in-tank and soil moisture neutron probes. He also showed some of the typical data obtained with these tools and described the differences between them. The purpose of the in-tank measurements is to provide data that, when combined with gamma and ultrasonic probe data, can be used in assigning interstitial liquid levels to tanks with LOWs. These are fiberglass drywells installed within some of the single shell tanks. The in-tank neutron probe is 22.4 inches long, including the removable neutron source. The outside diameter is 2.8 inch maximum, thus providing 0.2 inches of clearance to the LOW wall. The detector is a BF-3 tube that was specially fabricated for high gamma rejection, has 8.1 inches of active length, and is 1.5 inch in diameter.

The fill gas is enriched to 96% with a fill pressure of 25 cm-hg. The tube contains carbon to reduce gamma-induced neutron pulse degradation. Neutron sensitivity is approximately 6 cps in a uniform flux of 1 neutron/sq.cm/second. The custom electronics provides a very high resolution pulse height spectrum sufficient to eliminate gamma background counts.

Discussion: The logging cable is a single conductor 1/8 in diameter steel jacketed. The neutron source is 1.5 Ci 241AM/Be. Source to detector spacing can easily be changed, with fabrication of a new spacer for the source-holder. Changing source-to-detector spacing could provide the same data as for dual detector systems. Fred indicated there had been resistance in the field surveillance to accepting results of decreasing countrate with increasing moisture. Fred believes some sample of original LOW material might be on site to permit material analysis. Low voltage (24 Vdc) is sent down the logging cable; a dc-dc high voltage converter and preamplifier are also located in the probe.

Recent computer studies of existing system: Hans Toffer

Hans described the results of some preliminary computer modeling studies using the MCNP code with the existing system. Gamma scans were also considered in combination with the neutron scans. For these computer analyses, the detector was divided into 3 parts and the neutron countrate computed for each part as well as the total for various weight fractions of water in the surrounding medium. Hans discussed both using the extension feature that was designed into the probe and using two different spacers to extend the radius of investigation, or moisture range. Data was presented on the computed density effects and it was mentioned the technique was not very sensitive to expected density variation. Computed effect of boron in the LOW wall material on the detected neutron countrate was presented, as well as a number of photos of tank interiors and scan results.

Recommendations included the following:

- Perform analyses of tank features.
- Consider detector source spacing.
- Combine gamma and neutron scans observed to give moisture and density estimates.
- Consider any new neutron probe (with computer analyses).
- Neutron scans of top surface with some sort of swinging arm might be useful in helping indicate tank homogeneity.

Discussion: It was mentioned that one tank had three LOWs and this might provide data on homogeneity. In general the LOWs do not have large cavities, as shown in the photos in the vicinity of salt wells. There was general agreement on the need to vary source detector spacing, with one suggestion of modulating it with a motor drive.

Moisture Measurement - Electromagnetic Induction Method: Ronald L. Hockey

Ron described electrical resistivity logging as a standard well logging practice to combine with other logs. Resistivity measurements, in conjunction with temperature, porosity, and water resistivity, can be used to obtain water saturation values. He discussed basic electrical resistivity concepts, ionic conduction, water saturation, and other factors that affect the resistivity of a saltcake or sludge. He mentioned the induction coils could be deployed in either direct contact with the waste or through LOWs with nonmetallic walls. Resistivity of a saltcake or sludge is affected by ion concentration of free water, temperature, porosity, water saturation, and transport properties (such as geometry and linkage of pore spaces). Resistivity may be sensitive to chemical constituents if their electrical resistivity differs sufficiently from surrounding material and the spatial separation is sufficient. Calibration would be performed on material with similar electrical properties.
The radius of investigation could be from 6 inches to 12 ft as a function of frequency.

Discussion: The issues of inhomogeneity and permeability were discussed. The need for temperature measurement and possible differences between measured temperature in an LOW and the actual waste was also discussed. Ron described that electrically the measured value is the resistance, R, term of the coil complex impedance $Z = R + jX$ (X is the inductive reactance). Concern in calibrating out the various things that affect the output signal were expressed by several contributors. Effects of magnetic permeability due to ferrous materials potentially in the probe range were considered.

Moisture Measurements Requirements/Restrictions, Design Thoughts, and four Conceptual Techniques: Gloria A. Bennett

Gloria first presented some considerations on measurement requirements/restrictions: (1) technique should avoid dependence on chemical complexity of waste; (2) technique should minimize number of variables that influence measurement; (3) resulting instrument will be transportable, tank to tank; and (4) maximize simplicity of measurement.

Some design thoughts presented were to (1) try to use existing commercial or easily modifiable tool; (2) try to capitalize on equipment already installed/available; and (3) use front end data transfer such that the probe can stay in tank and vans move between data acquisition leads. Gloria then described 4 ideas for measuring the moisture. These were (1) a pair of linear arrays of direct contact resistance electrodes; (2) a transmit-receive pair of transducers embedded in waste material; (3) an embedded, evacuated air sampling sensor containing humidity, temperature, and supplemental electrodes; and (4) an embedded salt cylinder encased in semipermeable membrane with a fiber optic strain wrapping.

Discussion: The problem of radiation hardening was mentioned for in-tank sensors and any fiber optics. The difficulty of inserting any in-tank sensors was mentioned. The dependence of readings on sodium hydroxide and nitrates for the humidity based approach was mentioned. Problems of thermal compensation, long term drift and strain sensitivity for the fiber optic approach were discussed.

Spectroscopy Based Moisture Monitoring: Steve Mech

Steve described a technique for measuring moisture that would utilize infrared surface characterization. The technique would capitalize on multiple absorption bands for water, and complements Raman scattering techniques being developed for chemical speciation. His recommendation is for a feature test using existing tools and simulants to establish technical feasibility.

Discussion: Some discussion of cone penetrometer techniques for insertion of spectroscopy based probes was conducted. A cone penetrometer would avoid possible creation of disturbed tank contents such as might be present in water or steam based insertion. The cone penetrometer potentially raises concerns of system weight on the tank and assurance of not penetrating the tank bottom.

Spectroscopy/fiber-optic based approaches: Lloyd Burgess

Lloyd described activities completed at CPAC directed toward measuring the moisture in commercial cookies. This technique quantified both bound and unbound moisture by using a harmonic of NIR (near infrared) spectroscopy. He indicated that the frequencies were comparable to Raman spectra and had developed sufficient chemometrics (signal interpretation algorithms) to illustrate viability for the NIR technique.

Discussion: This work confirms the proposed technique discussed by Steve Mech. Some discussion of cone penetrometer and auger based insertion techniques ensued. Radiation damage potential for fiber optic and other components was also discussed. It was mentioned that Gary Dukelow, Bob Cash, Harry Babad, and Carl Schroeder would be visiting CPAC later in the week.

Ultrasonic approach: Ed Sheen

Ed described the ultrasonic probe used in current surveillance activities that operates through the LOW wall. This probe does not penetrate the tank waste with ultrasound, and Ed was not optimistic that ultrasonic measurements could be made considering the very high attenuation numbers heard from the hydrogen tank mitigation activities.

Discussion: The group was somewhat uncertain about the attenuation of sound to expect in the ferrocyanide tanks, and the group felt that documentation would be needed for this attenuation with respect to frequency to effectively consider any possibility of sonic/ultrasonic tomography or moisture measurement. The possibility of microwave measurements was also discussed, and Carl would possibly discuss this later at CPAC in Seattle with a knowledgeable electrical engineering professor (later on 2/25/92, Carl indicated he learned at that meeting the high conductivity was a very large problem for this approach).

RESULTS OF INDIVIDUAL EVALUATIONS OF THE VARIOUS MEASUREMENT METHODS

The results are in random order on the evaluation form, 13 participants completed the forms.

Meets the requirements? (Moisture range, accuracy, penetration, frequency of measurements) Yes / No response or NA = not able to judge:

(a) Eddy Current Probe	Yes 7%	No 78%	NA 14%
(b) New Neutron Probe	Yes 86%	No 0%	NA 14%
(c) Conductivity based direct contact	Yes 0%	No 62%	NA 38%

(d)&(f) Spectroscopy (d & f combined)	Yes 50%	No 14%	NA 36%
(e) Microwave	Yes 0%	No 64%	NA 36%
(g) Up-date existing probe	Yes 50%	No 21%	NA 29%
(h) Ultrasound	Yes 0%	No 56%	NA 9%

Ability to meet the 15 important considerations that were identified. Individuals ratings are reported here as 100% = capable of meeting the consideration or favorable (some evaluators used 0 to 5 and some used yes/no for this part as well, thus a 100% here means 5, all items judged as yes, or all items a +).

(a) Eddy current probe	61%
(b) New neutron probe	78%
(c) Conductivity Based direct contact	47%
(d)&(f) Spectroscopy	54%
(e) Microwave	46%
(g) Up-date existing probe	82%
(h) Ultrasound	58%

COMMENTS SUBMITTED BY INDIVIDUALS ON OR WITH THE EVALUATION FORMS:

(a) Eddy current probe

- Needs core sample and lots of data analysis
- Ground work not yet done
- Has large radius of investigation which is good
- Hard or impossible to interpret the results
- The eddy current method may have some promise. The possible large volume of this method has real interest, but the work has not been done and the potential is unknown and probably not good.

Related comment:

- "My vote is for the electrical polarization method, from a dry casing, provided that a frequency can be found which is sensitive only to the water molecule and not other chemical/molecular bonds also. This will include both bound and free water. The depth of investigation can be adjusted by shaping of the field coils and the search/pickup coil. If the waste is 6 feet deep, a zone of interrogation in the shape of a torus with approximate 6-foot radius can be obtained. Closer coil separations give correspondingly smaller volumes of interrogation."

(b) New neutron probe

- Neutron probe may have a problem using a water filled hole. However this method has a big advantage over others because it can be used through a steel casing.
- Probably best overall (from current information).
- I don't think one method by itself can do everything. For moisture measurement only, I would combine a neutron probe with an eddy current probe.
- It appears the new neutron probe and the spectroscopy technique could be used to complement each other.
- Recommend proceeding with the existing technology and minimize the requirements.
- The neutron method seems to be the only one developed into a usable system. It also can make use of past data. The method should be optimized for our needs and conditions.
- Established method; needs more calibration for density and chemical sensitivity.
- The FTIR spectroscopy sounds interesting, but I don't think that it is achievable in a useful time frame. I think the existing probe should be adapted (source extension, etc) to provide some answers in the near time frame. A new probe could be developed from this work if warranted.

(c) Conductivity based direct contact

- Highly questionable approach.
- Direct conductivity probes or humidity measuring devices as proposed by LANL will be subject to the chemistry of the salt/sludge, sodium hydroxide content will strongly influence the % RH out of the material. These techniques may have some value as detectors of change.

(d)&(f) Spectroscopy

- IR looks good for chemical separation, but I believe it must ultimately be used in conjunction with another method to measure tank moisture. Limited field of view.
- Must use penetrometer to be really effective.
- Could be used in conjunction with neutron probe.
- It appears the neutron probe and the spectroscopy technique could be used to complement each other.
- Calibration facility required.
- Demonstrated technology
- Survivability in the tank environment?
- If chemical identification of waste constituents is also a desired objective, then the spectroscopic methods are the preferred route. If the penetrometer method is not suitable for inserting "windows" then an auger drill can be used to go through the crust. Both techniques are proposed here in the tanks. A hollow-stem auger can be used to route light beams facing into the waste, with scanning and detection electronics on the surface.

(e) Microwave

- Inadequate discussion; should possibly consider a large volume sample.

(g) Up-date existing neutron probe

- We should definitely try this as a quick inexpensive method that may give adequate results.
- Existing neutron system should be modified per Crowe calculations to improve linearity.
- See new probe comments.

(h) Ultrasonic

- Ultrasonics may be able to measure velocity and locate boundaries of different layers as long as the frequency remains below 200 HZ. This frequency is too low to image anything.
- Inadequate discussion. Attenuation? Image possibility. Possible sample size.

Telephone-conference with Richard Lanza, MIT, and Ed Sheen, WHC, 2/24/92:

Dick is concerned on the whole issue of tomography and tank homogeneity. We need to look carefully at the attenuation of sound as a function of frequency. Sonic tomography may offer promise in resolving the tank homogeneity issue. With respect to what we can do now; he indicated strongly we should proceed on the near term with the established neutron technology where we have the experience and tools. The other approaches are farther removed. IR is at best a surface effect. We might be able to insert and leave in-place small guide tubes placed by auger or other drill. Dick would like to see the ultrasonic attenuation data.

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