**SELECTION OF AT-TANK ANALYSIS EQUIPMENT FOR DETERMINING
COMPLETION OF MIXING AND PARTICLE CONCENTRATION IN HANFORD
WASTE TANKS**

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Introduction

Under the Hanford Site Tank Waste Remediation System (TWRS) privatization strategy, the U.S. Department of Energy (DOE) requires the Project Hanford Management Contract (PHMC) Team to supply tank wastes to the Privatization Contractor for separation/treatment and immobilization (vitrification). Three low-activity waste (LAW) envelopes represent the range of liquid wastes in the large underground waste-storage tanks at the Hanford Site. The PHMC Team also is expected to supply high-level waste (HLW) envelope, which is an aqueous slurry of insoluble suspended solids (sludge).

The Privatization contract contains specification limits that define acceptable concentrations and ranges for chemical, physical and radiological parameters for each of the waste envelopes. Before waste is transferred to the Privatization Contractor's processing facility, the DOE must verify that the waste is within those parameters.

The PHMC Team is expected to transfer tank waste from Hanford's 200 Areas into a 1 million-gallon staging tank prior to transfer to the Privatization Contractor's waste processing facility. The staging tank will contain two airless 300-horsepower mixer pumps, and a sampling apparatus, developed by AEA Technology Engineering Services, Inc (AEA), which will allow contract-verifying waste samples to be drawn from different tank depths.

Laboratory analyses of highly radioactive mixed waste are very expensive, expose personnel and equipment to radiation, and require considerable time and expertise to perform. Therefore, the PHMC Team desires to ensure that all samples collected are representative of the entire tank contents and all results are contractually and technically acceptable. The PHMC also desires to reach a steady state in the staging tank as quickly as possible because delays by the DOE in transferring waste to the Privatization Contractor could mean monetary penalties as large as \$1 million per day.

Ideally, the staging tank should achieve a state of complete homogenization of liquid and solid components before and during acquisition of all contract-verifying samples. However, no rapid, at-tank mean exists to determine if sufficient mixing has been achieved and if it is a steady state or cyclical process. In addition, a rapid, at-tank determination of suspended particle concentration is desired. If the contract specification limit for suspended solids is exceeded, it may be necessary to allow the tank to settle or take corrective action. This could lead to costly delays in transferring the waste.

Therefore, development of an at-tank analysis system to determine completion of mixing and particle concentration is necessary. At-tank analysis is a formidable task because the waste is highly radioactive and caustic, and it contains near-saturated levels of dissolved species that can crystallize or precipitate. In addition, the actual form of chemicals and relative distribution of those forms in the waste is not well understood (e.g., a chemical species can exist as a neutral molecule, an ionized molecule, a molecular complex, etc.).

To ensure safe and efficient process-engineering operations, equipment used in the staging tank environment must be rugged, reliable, and easy to install and operate. User interfaces must

clearly present data in a manner that is easily understood and utilized. Ideally, the equipment must require little or no maintenance or continuing calibration.

This document will describe the functions and requirements of the at-tank analysis system concept developed by the Robotics Technology Development Program (RTDP) and Berkeley Instruments. It will discuss commercially available at-tank analysis equipment, and compare those that meet the stated functions and requirements. This is followed by a discussion of the considerations used in the selection of instrumentation for the concept design, and an overall description of the proposed at-tank analysis system.

Function of the At-Tank Analysis System

The primary function of the at-tank analysis system is to determine if the tank has achieved a "steady-state" mixing condition (i.e., are the solid and liquid tank components homogenized or as mixed as possible). This determination will be made by examining analytical results produced by the at-tank analysis system from samples that are obtained by the nested, fixed-depth fluidic sampler being developed by AEA. By comparing sample results from different tank depths or over the course of time, a determination can be made as to whether the tank is sufficiently mixed. For the Hanford waste tanks, a number of different chemical, physical and radiological parameters can be used as indicators of homogeneity—these are discussed later.

A secondary function of the at-tank analysis system is to address suspended solids and settling issues. This second function is addressed by measuring suspended solids or turbidity, for which several commercial instruments are available operating in reflectance or transmission modes. These instruments can be readily modified such that sapphire and stainless steel (or other suitable alloys such as Hastaloy) are the only materials that are exposed to the sample. The seal between the sapphire and the metal can be either a braze (soft weld) or an elastomer.

A third possible function of the at-tank analysis system is to identify important chemical components that may be approaching upper Privatization Contract specification limits. However, a conservative analysis by Hanford statisticians and scientists indicated that no chemicals are near the contract specification limits¹. Therefore, no need has been identified, to date, that requires the measurement of individual chemical components using the at-tank analysis system.

¹ Meeting Minutes from "Nested, Fixed-Depth Sampler Real Time Analysis Status Meeting," 5/19/98.

Requirements for the At-Tank Analysis System

The PHMC Team desires an analysis system that is at-tank and in-line. The system cannot remove, extract, or process a sample. Several additional requirements are imposed on the system related to tank farm operations and environmental and waste regulations. These requirements limit the types of analytical measurement equipment that can be considered and are summarized in Table 1, Design Requirements for At-Tank Analysis System and Associated Equipment.

Table 1. Design Requirements for At-Tank Analysis System and Associated Equipment

<u>Requirement</u>	<u>Solution or Approach</u>
1. Interface at-tank analysis system with sampler (NOTE: analysis system <i>must</i> be presented with a representative and homogeneous sample from the sampler)	<ul style="list-style-type: none"> ◆ Use a 1-in. tap upstream of sampling needle ◆ Control sampler pumps and valves during analysis system operation ◆ Provide a flushing solution for the at-tank analysis system loop
2. Explosion proof	<ul style="list-style-type: none"> ◆ Use intrinsically safe probes, suitable NEMA enclosure, remote electronics
3. Resistant to high radiation fields	<ul style="list-style-type: none"> ◆ Use radiation resistant materials (withstand > 750 R/hour)
4. Withstand 15-20% NaOH, pH of 12-14+, and function for all waste envelopes (A, B, C)	<ul style="list-style-type: none"> ◆ Use caustic resistant materials: stainless steel, Hastaloy, sapphire; ensure functionality with high Al (env. A), Cs (env. B), and complexant (env. C) waste.
5. Double containment housing	<ul style="list-style-type: none"> ◆ Use double containment
6. Waste compatibility/reactivity	<ul style="list-style-type: none"> ◆ Meet tank farm waste compatibility and reactivity requirements
7. Meet NQA-I requirements	<ul style="list-style-type: none"> ◆ Conform to all documentation, quality, and program requirements
8. Operable in severe weather (heat, cold, wind, snow, rain)	<ul style="list-style-type: none"> ◆ Use environmental enclosure
9. No introduction of chemicals into the waste stream	<ul style="list-style-type: none"> ◆ Do not consider analyzers or probes that release buffers or leach chemicals
10. No cross-contamination of samples or interference with other measurement or sampling equipment	<ul style="list-style-type: none"> ◆ Design such that if analysis system loop fails or plugs, sampler is not impacted
11. Operable by a chemical technician (no advanced training or data interpretation required)	<ul style="list-style-type: none"> ◆ Use simple at-tank display and control panel ◆ Integrate all sensor data output into single display/interface screen
12. Minimal or no maintenance; no clogging/precipitation	<ul style="list-style-type: none"> ◆ Use only "hardened" equipment (caustic and radiation resistant); heat-trace system
13. Minimal or no calibration	<ul style="list-style-type: none"> ◆ Do not consider equipment that relies on frequent calibration
14. Easy to replace or remove (minimal time required, minimal personnel exposure)	<ul style="list-style-type: none"> ◆ Use pipe taps or connections that are easy and safe to handle, install, and remove; provide option for redundant analysis loop; provide ability to remove one probe or all probes
15. Data archiving and remote data transmission	<ul style="list-style-type: none"> ◆ Use at-tank data storage/backup; ensure data ports available for remote transmission

Available At-Tank Analysis Equipment

Equipment currently under development and prototype technologies were not considered because of the critical function of the at-tank analysis system and the difficulty in assessing emerging technologies. For these reasons, only commercially available equipment have been considered. However, the progress of the following DOE programs will be monitored for potential future guidance or consideration for inclusion in the at-tank analysis system:

- "Comparative Testing of Pipeline Slurry Monitors," Tom Hylton, Principal Investigator (PI), Oak Ridge National Laboratory, Technical Task Plan (TTP) OR17C231.
- "Current Practice of Environmental Characterization and Monitoring Technologies," Stephan Weeks, PI, Special Technologies Laboratory, TTP NV07C264.
- "Integrated Raman pOH Sensor for In-Tank Monitoring," Job Bello, PI, EIC Laboratories, Inc., TTP NV08C231.
- "Ultrasonic Sensors for *In Situ* Monitoring of Physical Properties," Shuh-Haw Sheen, PI, Argonne National Laboratory, TTP CH26C217.

Existing process analysis equipment such as wet-chemical analyzers (utilizing colorimetry, electrodes, and titrations) and X-ray fluorescence spectroscopy (XRF) offer the greatest analytical power and flexibility for quantitative measurement of multiple chemical species. While process analyzers could likely measure samples with little or no pretreatment, XRF requires removal of significant levels of interfering radioactive species² such as Cs¹³⁷. Although these techniques require only a few milliliters of sample and produce only milliliters of dilute effluent (typically non-hazardous), they were rejected based on the above-mentioned requirements.

Similarly, analysis equipment that would create a waste stream such as inductively coupled plasma-atomic emission spectroscopy (ICP-AES) and atomic absorption spectroscopy were not considered.

After the stated functions and requirements were imposed on the instrument selection process, only a few devices remained as possible candidates for inclusion in the at-tank analysis system.

Table 2, Commercially Available In-Line and Non-Invasive Chemical, Physical and Radiological Parameter Monitoring Probes, lists robust analysis equipment that can measure chemical species, physical properties and radiological properties relevant to the functions defined above. All of the equipment listed can be mounted directly in a pipe through a tap, as a part of a pipeline, or externally on a pipe. The list is not exhaustive, but represents the vast majority of robust analysis methods that do not require the removal, extraction, or processing of a sample.

² Two well-developed technologies at PNNL provide a means to address the removal of radioactive isotopes prior to XRF analysis. Silicotitanates, as well as other chelating and ion exchange compounds, are known to remove specific radioisotopes. These compounds are commercially available in a micro-bead form. The second enabling technology at PNNL is a miniaturized "renewable column" that has been under development by several groups within the last 5 years. The renewable column allows milligram quantities of micro-beads to be trapped, while allowing non-radioactive liquid to pass to an instrument such as an XRF. At the end of every cycle, the used micro-beads are flushed to waste and a new batch of micro-beads is introduced, thus avoiding cross-contamination and fouling.

Table 2. Commercially Available In-Line and Non-Invasive Chemical, Physical and Radiological Parameter Monitoring Probes.

SPECIFICATIONS ANALYSIS	TEMPERATURE RATING	PRESSURE RATING	MAXIMUM FLOW-RATE	LINE SIZE & WETTED PARTS	OTHER FEATURES
CONDUCTIVITY (total ionic content)	0 to 120° C max	250 psi	---	3-in. tee; glass filled PEEK or Noryl	electrodeless; response time: 0.5 second to 90% of value
BULK DENSITY (solids density + liquid density)	-240 to 204° C (-400 to 400° F)	1450 psig (100 bar)	3,200lb/min for 1 to 2-in. i.d. pipe	1/8-, 1/4-, 1/2-, 1-, 2-, 3- in.; 316 SS	no flow path restriction; secondary containment housing;
REFRACTIVE INDEX (a measure of liquid only density)	100 to 150° C	145 psi (1 MPa)	---	1-in. NPT; sapphire prism, stainless steel or Hastaloy body, seal	includes temperature measurement; “not affected by color, turbidity, solids or flow rate”; “no recalibration required”; instrument located remote from measurement head
GAMMA RADIATION (Cs ¹³⁷ activity)	---	N/A	---	GM tube selection based on 1-in. i.d. pipe	self-contained; can mount on analysis system or on sampler
OPTICAL SPECTROSCOPY - NEAR-INFRARED - RAMAN - ULTRAVIOLET/VISIBLE	100° C using EPDM seal; >150°C: braze seal Other proprietary sealing techniques exist, which may raise this limit.	150 psi, depending on measurement cell or probe configuration	---	Sapphire optics, stainless steel or Hastaloy body, seal (gasket or braze)	in-line probe, conventional flow-cell, or windowless flow-cell; all instruments can be placed remote from the sampling location; relative method complexity: Raman>near-infrared> ultraviolet/visible
PARTICLE SIZE DISTRIBUTION (does not include total suspended solids concentration)	150° C	150 psig (10 bars)	2 meters/second	1/4-in.- 48-in.; sapphire, stainless steel or Hastaloy body, gasket	“special coating” on sapphire window for chemical and radiation resistance
SUSPENDED SOLIDS CONCENTRATION	0 to 100° C, EPDM seal 150° C with braze	150 psig (10 bars)	---	1/2-in., 1-in. NPT, 1 1/2- in., 2-in. R.F. flanges; 316 stainless steel or Hastaloy body, sapphire, seal	separation from electronics: 300 ft.; explosion-proof NEMA 7, Class 1, Group D, Div.1; optional self- cleaning window jets

--- = Not determined

Table 2 (cont.). Commercially Available In-Line and Non-Invasive Chemical, Physical and Radiological Parameter Monitoring Probes.

SPECIFICATIONS ANALYSIS	MEASUREMENT RANGE	INTERFERENCES	POTENTIAL PROBLEMS	MODEL, MANUFACTURER, COST
CONDUCTIVITY	selectable	unknown	fouling; 3-in. line size requirement	electrodeless conductivity; Lisle-Metrix Ltd., Toronto, Ontario, Canada, 416-249-9151, ~\$10,000
BULK DENSITY	flow accuracy $\pm 0.10\%$ of flow rate; density accuracy: ± 0.0005 g/cc ($\sim 0.1\%$); repeatability: $\pm 0.05\%$; range: <1.0 to >5.0	none known	triangular-shaped flow-path blockage (although flow is not restricted by the design)	CMF100, ELITE Mass Flow and Density Meter; Micro Motion Inc. Boulder CO 800-760-8119 ~\$10,000
REFRACTIVE INDEX (N_D = ratio of sample refractive index to sapphire prism refractive index; a unitless ratio)	different ranges selectable from 1.32 to 1.53 standard repeatability: $\pm 0.0002 N_D$ (0.1%); accuracy: $\pm 0.0004 N_D$	none known	sapphire prism fouling; seal failure; must customize to extend range and CCD must be shielded and coupled to sapphire fiber-optic imaging conduit	REFRAC DS Rosemount Analytical, Inc. Irvine, CA 949-863-1181 ~\$15,000 ~\$7,000 for additional measurement heads
GAMMA RADIATION	$\sim \pm 2\%$ precision; range modified using detector selection/shielding	other radioactive sources/waste	large range may require two detector configurations	various: e.g., TSA Systems, Ltd. Longmont, CO 303-651-6147 ~\$10,000
OPTICAL SPECTROSCOPY - NEAR-INFRARED - RAMAN - ULTRAVIOLET/VISIBLE	(matrix/species dependent) >0.1 -1% of C-H, O-H, N-H species. e.g., organic carbon, water content, EDTA >0.1 -1% of molecular anions. e.g., NO_3 , NO_2 , $\text{Al}(\text{OH})_4$, SO_4 , PO_4 ppm sensitivity for molecular species and organics. e.g., NO_3 , NO_2 , oil and grease.	drift of light source, detector spectral (peak overlap) chemical (complexation) physical (bubbles)	most optical measurements would be semi-quantitative and only provide relative (not absolute) concentration estimates window fouling; seal leakage/failure complexity of data interpretation UV/VIS: low selectivity	various manufacturers of rugged fiber-optic probes and spectrometers windowless flow-cell: Sigrist Process-Photometer (Lisle-Metrix Ltd., Toronto, Ontario, Canada, 416-249-9151) NIR and Raman: ~\$40-80k UV/VIS: ~20-50k
PARTICLE SIZE DISTRIBUTION	0.5 micron to 2 mm size	bubbles	window fouling; seal leakage/failure	Lasentec, Redmond, WA 425-881-7117; ~\$80k
SUSPENDED SOLIDS CONCENTRATION	0.05% to 8% by wt; pathlengths available: 0.2 to 5.7 cm (giving different measurement ranges)	highly opaque or high solids will give over-range result	window fouling; seal leakage/failure	various: e.g., Monitek Technologies, Inc. Hayward, CA 800-458-4454 ~\$15,000

Comparison of At-Tank Analysis Equipment

Any chemical or radiological species or physical property can be used to determine tank homogeneity provided the following are met:

- The parameter must be present and measurable (above the instrument detection limit) in all of the tanks.
- The parameter must have sufficient differences in level (or concentration) among tanks to be used as an indicator of completion of mixing.
- The parameter must display sufficient differences in level (or concentration) at different depths within an unmixed or partially mixed tank to be used as an indicator of completion of mixing.
- The instrument must have sufficient precision to discriminate differences in the level or concentration of the parameter.

The problem of determining completion of tank mixing is similar to asking, "how different (or alike) are measurements at different depths or at different times?" This is different than trying to *accurately* measure a parameter. To address the problem of tank mixing, relative measurements can be made. However, it is important that the measurement instrument have sufficient precision (repeatability or reproducibility) to discriminate among different levels. One measure of the "discriminating power" of an instrument can be estimated as follows:

- Compute the range of the parameter of interest (standard deviation of the mean can be used). Range is the difference between the highest sample value and the lowest sample value within a tank or among tanks.
- Determine the repeatability of the measurement instrument. The repeatability is usually given as a $\pm$ value or as a standard deviation (one sigma).
- Divide the range by the repeatability. This number ("discriminating power") represents the number of distinctive levels or concentrations that can be determined using that technique (in that particular waste type).

Therefore, in addition to the measured parameter having a suitable level and range, the measurement equipment must 1) be capable of meeting the primary analysis functions, 2) meet the imposed requirements, and 3) have a high discriminating power.

Typical measurement ranges and repeatability for selected at-tank analysis equipment are given in Table 3. Sensitivity levels (minimum detection limit) and measuring range are dependent on the sample matrix (physical and chemical properties), species to be measured, and degree of sample homogenization. Manufacturer's technical specifications or best estimates, where indicated, are given. Conductivity is not included because it is likely the least useful measurement technique, requires a large (3-in.) pipe mounting, and is not as rugged as the other monitoring equipment.

Ultraviolet/visible spectroscopy is not included because no well-defined target analytes or parameters exist to assess the ability of the technique to meet the necessary functions. Similarly,

particle size distribution is not included because it is difficult to compare precision data from other techniques with the reproducibility of measuring distributions of particles.

Table 3. Measurement Range and Repeatability for Selected At-Tank Analysis Equipment

ANALYSIS	MEASUREMENT RANGE	PRECISION (RELATIVE)
Suspended Solids	0.05 to 8% (path length dependent). Use turbidity if <500 ppm	$\pm 1\%$
Bulk Density (liquid + solid)	from < 1.0 to > 5.0	$\pm 0.1\%$
Refractive Index (estimate of specific gravity)	1.3 to 1.53 standard. Can be modified/extended.	$\pm 0.1\%$
Total Gamma Radiation	selectable	$\sim 2\%$ (estimated)
Near-Infrared Spectroscopy	0.1 to 100%	1 - 5% (estimated)
Raman	0.1 to 1% up to 100% (estimated)	$\sim 5\%$ (estimated)
Temperature	wide range	better than 1%

A summary of data for the first 10 tanks to be transferred to the waste processing facility is given in Table 4. Data was not readily available for suspended solids and chemical forms.

Table 4 summarizes the following: 1) general waste description (i.e., liquid/supernatant, saltcake/slurry, sludge) and their estimated volumes, 2) temperature range of the waste, 3) bulk density and specific gravity ranges (reported as estimated tank average and values of individual samples from different locations in the tank), 4) cesium activity, and 5) water content.

Table 4. Hanford Tank Waste Summary Data for the First 10 Tanks to be Processed* (2005-2015).

LAW STAGING ORDER (subject to change)	TANK (subject to change)	VOLUME kL (kgal)			TEMP. °C (°F)	BULK DENSITY AND SPECIFIC GRAVITY 1. EST. TANK AVERAGE g/mL; 2. SLURRY RANGE g/mL; 3. LIQUID RANGE (SpG)	Cs ¹³⁷ (μCi/ mL)	WATER (%)
		LIQUID	SALTCAKE/ SLURRY	SLUDGE				
1	241-AN-105	2,562 green/ opaque	~ 1,708	Core 153, Seg 22 lower 4" black slurry	19.2- 46.2 (66.6- 116)	1.56 g/mL 1.52 to 1.66 g/mL 1.35 to 1.44 (SpG)	470	46.6
2	241-AN-104	2,273 (600.5)	21 (5.5)	1,700 (449)	21.7- 51.2 (71.1- 126.2)	1.45 g/mL 1.52 to 1.76 g/mL 1.34 to 1.49 (SpG)	470	48.4
3	241-AW-101	3,937 (1,040)	318 (84)	?	25-42.2 (77- 108)	1.56 g/mL --- ---	520	43.6
4	241-AN-103	2,063 (545)	1,552 (410)	0	28.9- 47.2 (84- 117)	1.54 g/mL 1.59 to 1.93 g/mL 1.34 to 1.54 (SpG)	638	48
5	241-AP-101	4,224 (1,116)	0	0	12-23 (53-74)	--- --- 1.26 to 1.37 (SpG)	~200	~55-60
	241-AW-104	3,150 (833)	1,100	?	31 (87)	1.44 g/mL --- 0.988 (SpG);	~5	supernatant 97.8
6	241-AY-101	3,229 (853)	0	314 (83)	liquid: 18-24 (64-76) sludge: 27-40.6 (81- 105)	1.30 g/mL --- 1.08 (SpG)	~85	sludge: 56 supernatant: 84
7	241-AN-107	3,500 (924)		507 (134)	29-39 (85- 103)	1.45 g/mL --- 1.38 (SpG)	~250	liquid: 49.9 solid: 45.5
8	241-AN-102	3,755 (992)		337 (89)	25-39.4 (77- 103)	--- 1.47 to 1.49 g/mL 1.41 (SpG)	350	49.7
9	241-AN-106	1,520 (401)		64 (17)	14-47 (58- 116)	--- 1.17 to 1.22 g/mL ---		76.6

*Data from Tank Characterization Reports obtained June 15, 1998 (for comparative purposes only).

From inspection of Table 4, it is apparent that the combined data for Cesium¹³⁷, density, and specific gravity are distinctly different for each tank to enable unique identification. Furthermore, the ranges listed for slurries (density) and liquids (specific gravity) indicate that these phases are different enough within a single tank to enable discrimination of different tank phases or strata. Many other components have suitable differences in concentration among tanks including water (see the last column of Table 4) and molecular anions such as aluminate ($\text{Al}(\text{OH}_4^-)$) and nitrate (not listed).

Although near infrared (NIR) and Raman spectroscopy are powerful, information-rich techniques that can be used to monitor major tank components such as water and molecular anions, they are also more complicated. This is particularly true when they are compared with physical parameter monitors such as bulk density, refractive index, and suspended solids. Also, NIR and Raman spectrophotometers are more costly and difficult to set-up, operate, and troubleshoot. Most importantly, these techniques provide little added value to an at-tank analysis system designed to meet the previously stated functions.

It should be noted that many chemical species in tank waste exist in various forms (e.g., ionized, as neutral ion pairs, or as complexes). While relative measurements of individual chemical species are possible using optical spectroscopy techniques such as NIR and Raman, it would be exceedingly difficult to *quantify* individual chemical species. To achieve quantification, extensive knowledge of the waste composition and form must be available or calibration or internal standards must be used. In addition, relative measurements could only be compared within a single batch (tank) of waste. If new waste is added, the distribution of chemical forms is likely to change.

Tank Waste Mixing Scenarios: Equipment Selection Considerations

The best types of measurement equipment for use with radioactive waste are ones that do not contact the sample. Gamma monitors and the Coriolis bulk density/mass flow monitor are both non-invasive technologies and are highly appropriate for meeting the functions of the at-tank analysis system. Combining suspended solids measurement with the above two measurements results in an analysis system with very high discriminating power. However, even the combined data of gamma radiation, bulk density, and suspended solids can not always determine if adequate mixing has been achieved when presented with the possibility described below.

One scenario that was presented to the design team was that of waste containing highly dense particulates resembling lead shot. In this scenario, the liquid components of the tank may achieve homogenization, but the solid components would settle out and exist at higher concentrations at greater tank depths. This would indicate a lack of complete mixing if only the suspended solids monitor and bulk density monitor data were used. If the hypothesis is correct that gamma activity is caused by liquid phase components, then gamma monitoring should be capable of determining completion of liquid mixing.

However, a complicating factor exists if the levels of gamma radiation in different liquid phases to be mixed are similar (or not discernable because of the measurement precision limitations).

To address this possible scenario, a refractive index monitor was included in the at-tank analysis system design because of its high precision and ability to measure only liquid phase mixing, independent of suspended particles.

At-Tank Analysis Equipment Selection

Perhaps one of the most valuable at-tank measurements that can be made is suspended solids. Suspended solids can not exceed a level of 2% per the Privatization Contract specification. Similar to other optical spectroscopy techniques, the only wetted parts in the suspended solids monitor are sapphire windows that are sealed to a stainless steel (or Hastaloy) body. A unique feature of one transmission-based suspended solids monitor is the option for window-cleaning jets. Suspended solids are likely to be highly correlated with the degree of tank homogeneity. The electronics and control equipment can be located remotely from the measurement head for these monitors.

The Coriolis effect is exploited in a novel density and mass-flow-measuring device that does not have any intrusive components in its triangular-shaped flow path. This device measures bulk density with exceptional precision (± 0.0002 g/mL or better than 0.1%, relative). Bulk density is the combined liquid and solid density of a solution or slurry. The usefulness of bulk density for determining completion of mixing and the non-invasive nature of the device make this a strong candidate for inclusion in the at-tank analysis system.

Refractive index is a measure of only liquid (not solids) density and can be measured by refractometry with very high precision (± 0.0002 N_D , approximately 0.1%). The rugged, temperature-compensated device uses only a small sapphire prism sealed to a stainless steel body. It is commercially available and is reportedly unaffected by sample color and presence of suspended solids or turbidity. The electronics and control equipment can be located remotely from the measurement head for this device. However, the charge-coupled device (CCD) detector will require remote placement in a shielded housing. A slit-shaped, coherent fiber-optic imaging bundle made from sapphire will be placed in the focal plane where the CCD detector normally resides. This will allow the detector to be placed away from the high radiation environment. In addition, the dynamic range of the monitor will be modified to permit measurement of refractive indexes <1.33 , if acceptable resolution can be maintained.

Based on other-party surveys of tank-waste analysis data, Cs¹³⁷ is thought to exist predominantly in the liquid phase. Therefore, monitoring Cesium (or total gamma radiation, because Cesium will usually be the predominant species) is expected to provide a measure of liquid homogeneity, similar to monitoring refractive index for liquid density. However, the precision of gamma monitoring equipment is significantly poorer than that achievable by refractometry (estimated at $\pm 2\%$). Gamma monitoring is included in the at-tank analysis system because it is a well-developed, non-invasive technology, it has sufficient precision to be a useful indicator of tank homogeneity, and radioactivity is an important safety and process parameter.

Equipment variations may be made in the future as more information is obtained on new products (e.g., the suspended solids monitor may be based on reflectance rather than transmission). The combined information obtained from these measurements should provide nearly unequivocal determination of completion of tank mixing and suspended particle concentration. As process-engineering experience is gained, one or more monitors may be found unnecessary, or as new at-tank analysis system functions are defined, other instrumentation will be reconsidered.

Concept Design of the At-Tank Analysis System

A concept design of how the monitoring equipment described above will be integrated into a system and coupled with the nested, fixed-depth fluidic sampler is shown in Figure 1. The at-tank analysis system will be integrated into a computer-controlled system operable from a remote, non-hazardous location.

A 1-in. internal diameter (i.d.) pipe will be tapped into the 1-in. i.d. sampler pipe upstream of the sampling needle. Two Xomox valves (identical to those used in the AEA system) will be used to direct the waste stream to the sample bottle station or to the analysis system. The monitor measurement heads will be mounted on a pipe that has a vertical incline. This will allow the waste to drain by gravity, thus minimizing sample carryover and standing waste that could contribute to fouling. Periodic flushing using the fluidic sampler flush line will also minimize fouling. In addition, flush solution can be prepared with known properties (e.g., bulk density, specific gravity) and used as a calibration solution. The flush solution would also serve as a zero level (baseline) calibration sample for the suspended solids and gamma monitors.

Heat tracing will be required to maintain the waste at an elevated temperature to avoid precipitation and recrystallization. An instrument enclosure may be used to contain one or more of the monitors to meet explosion-proof requirements and to provide improved temperature control. The enclosure may require air or nitrogen purging. Some instruments may require localized cooling with air or water if high analysis system temperatures must be maintained.

All of the monitors will be placed in the same shielded enclosure that houses the AEA sample bottle station. Electrical connections will be made to the monitor control electronics and data display terminals, which will be located in an environmental enclosure with the sampler control electronics. This enclosure will be placed remote from the monitor measurement heads to allow system operation in a less hazardous environment.

Figure 1. Conceptual Design of the At-Tank Analysis System and Fluidic Sampler Interface.