CHARACTERIZATION OF DEFENSE NUCLEAR WASTE USING HAZARDOUS WASTE GUIDANCE. APPLICATIONS TO HANFORD SITE ACCELERATED HIGH-LEVEL WASTE TREATMENT AND DISPOSAL MISSION

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ABSTRACT

Federal hazardous waste regulations were developed for management of industrial waste. These same regulations are also applicable for much of the nation's defense nuclear wastes. At the U.S. Department of Energy's (DOE) Hanford Site in southeast Washington State, one of the nation's largest inventories of nuclear waste remains in storage in large underground tanks. The waste's regulatory designation and its composition and form constrain acceptable treatment and disposal options. Obtaining detailed knowledge of the tank waste composition presents a significant portion of the many challenges in meeting the regulatory-driven treatment and disposal requirements for this waste. Key in applying the hazardous waste regulations to defense nuclear wastes is defining the appropriate and achievable quality for waste feed characterization data and the supporting evidence demonstrating that applicable requirements have been met at the time of disposal. Application of a performance-based approach to demonstrating achievable quality standards will be discussed in the context of the accelerated high-level waste treatment and disposal mission at the Hanford Site.

INTRODUCTION

The DOE is required to store, treat, and dispose of high-level waste at its Hanford Site in southeast Washington. Quality data supporting the project's regulatory and engineering needs must be available for demonstrating that the treatment requirements for ultimate disposal have been met. This paper focuses on available agreements regarding *Resource Conservation and Recovery Act* (RCRA) characterization requirements that may be used to facilitate acceleration of Hanford tank waste treatment and disposal.

Over the last few years, DOE has made significant progress in defining and putting into effect characterization requirements for currently stored Hanford radioactive tank wastes to meet data needs for treatment and final disposition. This effort has relied on a teaming approach between DOE, the regulators, and the implementing contractors. An outcome of this effort is the Regulatory Data Quality Objectives (DQO). Through the development and implementation of the Regulatory DQO (1), DOE has laid a solid foundation for determining the quality of data needed for facilitating permitting and compliance activities for treatment and disposal of waste, including both Waste Treatment Plant commissioning and Tank Farm acceleration initiatives. A systematic and technically defensible evaluation of potential, regulated analytes has led to a more limited, prioritized analyte list with associated analytical methods. Validation of these methods for tank waste is being used to develop a credible and sufficient picture of tank waste chemical compositions and a basis for demonstrating that applicable requirements for treatment and disposal are met.

Hanford Tank Waste

Hanford has 53 million gallons of high-level waste, containing 190 million curies of radioactivity, stored in 177 underground tanks. Accumulation of the waste began in 1944 with the inception of the Hanford defense production mission as part of the Manhattan Project. Current operations consist of waste receipts from activities such as deactivation and decommissioning work, analytical and processing laboratories, ongoing tank waste management operations, and early efforts for tank closure demonstrations.

The underground tanks are within ten miles of the Columbia River, the largest river in the Pacific Northwest. Many of the tanks are past their design life, and 67 of the older tanks are known or suspected to have leaked. In addition, the newer tanks are quickly nearing their capacity. The only permanent solution is to treat and immobilize the tank waste into a durable, stable waste form.

RCRA Regulation of Tank Waste

RCRA requirements and their applicability to Hanford waste differ in some important aspects from other DOE sites because of past Hanford-specific practices and its location in Washington State. Under the Washington State RCRA program, the tank waste is designated for multiple RCRA waste codes including those for listed and characteristic wastes. Each of these codes drives a requirement to use particular treatment technologies and/or meet particular numeric performance standards in order to meet the RCRA treatment requirements for disposal. Treatment, storage, and disposal are all permitted activities subject to regulator approval.

The permits will define the detailed characterization requirements for these actions and will define the environmental requirements leading to the data pedigree substantiating that the waste packages are acceptable for disposal. In obtaining these permits, the path to meeting these requirements must be based on requirements tailored to the data needs and what is achievable in analyzing the waste. In addition, tank waste characterization data will be used to support upcoming petitions to the regulators for a new treatment variance and delisting that are needed to further tailor the characterization requirements for vitrifying wastes.

Tank Waste Treatment

During tank waste treatment, the dangerous waste and radioactive constituents in Hanford's high-level tank waste will be separated, if necessary, into lower and higher activity fractions followed by final treatment to make disposable waste forms. The higher activity fraction will be immobilized into durable glass waste forms. The lower activity fraction will likewise be vitrified or, if applicable requirements are met, solidified by supplemental waste treatment technologies.

A significant treatment and disposal challenge presented by tank waste is the overall uncertainty in the detailed characterization knowledge for trace, regulated constituents. In lieu of certain characterization knowledge, bounding or other conservative estimates are being used where needed for permitting and design activities for the Waste Treatment [glassification] Plant currently under construction. In addition, the Waste Treatment Plant based their permitting approach for the required waste analysis plan on the Regulatory DQO. In these cases, the Regulatory DQO provided a foundation on which the regulators and DOE had previously agreed. This established foundation shortened the path forward, a much-needed schedule relief. Results from the implementation of the Regulatory DQO will be used to confirm bounding assumptions for commissioning and future Waste Treatment Plant operations.

Development of Supplemental Treatment Technologies

One of the primary technical implementation strategies for mission acceleration is the development of supplemental treatment technologies for the low activity fraction of the tank farm waste. Effective technology evaluation and selection relies in part on the understanding of, and confidence in, the tank waste characterization data. The formal DOE and regulator agreement to the technical requirements established through the Regulatory DQO can provide a foundation on which to build regulator acceptance and support for establishing regulatory-driven data needs important to permitting and design of supplementary treatment facilities similar to that used for permitting the Waste Treatment Plant.

EVOLUTION OF THE REGULATORY DQO

In the beginning, DOE designated the waste under RCRA and in response Ecology determined that all waste must be characterized during storage and before it is treated. Together DOE and Ecology developed a plan, known as the Regulatory DQO, to define the characterization data needs for waste generated by the DOE and its predecessor, and stored in underground tanks at the Hanford Site. At the time of the DQO conception, the tank waste treatment technology selection was not finalized. Therefore, instead of focusing on waste treatment technology driven needs, the DQO was written for fundamental characterization needs for generators. In essence,

the DQO assumed the treatment process was a "black box" without bias to a specific treatment technology. This approach provides opportunities for applying the DQO to a wide range of Hanford Site clean-up activities.

In development of the DQO, DOE and Ecology achieved a technically defensible basis for establishing characterization data needs using potentially applicable requirements. The outcome of the Regulatory DQO was a prioritized list of 173 compounds for analysis that was selected from an initial list of nearly 1000 regulated compounds. Technical analyses and negotiation leading to this outcome took over a year to achieve. The selection process involved a systematic review of each compound by a team of tank waste chemistry experts, including representatives from DOE and Ecology. The overall evaluation focused on the plausibility of the regulated compounds' existence in the tank waste matrix and a prioritization based on relative toxicity (Fig. 1). Ultimately, EPA and ASTM methods were identified for characterizing each of these prioritized analytes. The detailed, analyte prioritization logic consists of over thirty steps reflecting jointly agreed-to inputs, filters and decision points. A simplified version of the prioritization logic is presented in Fig. 1. A summary of each of the logic steps is provided below.

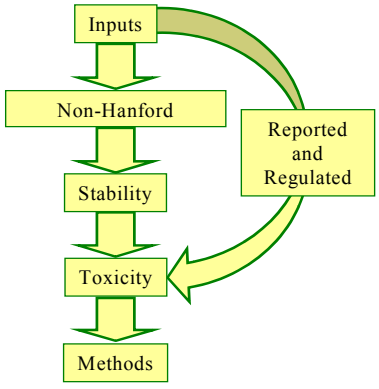

Fig. 1. Logic diagram for analyte selection and prioritization process used in the Regulatory DQO

Inputs – An input list was created from analytes identified in regulations agreed to be applicable by Ecology and DOE, and in previous waste analyses. The regulated analyte inputs are the Toxic Air Pollutant (TAP) lists Classes A (WAC 173-460-150) and B (WAC 173-460-160); Underlying Hazardous Constituents (UHC) list; Universal Treatment Standards (UTS); Double-Shell Tank RCRA Part A permit application, except waste code F039; and Double-Shell Tank Waste Stream Sheet constituents.

Reported and Regulated Compounds – Compounds previously detected in the waste and tank waste vapor phases were identified based on information available on the Tank Waste Information Network System (TWINS) and 242A Evaporator Condensate data. Detected compounds also listed on the regulatory analyte input list were then evaluated for relative toxicity. Regulated compounds not previously reported as being detected in the Hanford tank waste ("non-detected" compounds) were further evaluated for possible applications at the Hanford Site and stability in the tank waste environment.

Non-Hanford – Non-detected, regulated analytes were evaluated for potential exclusions based on uses in industrial applications not associated with Hanford (2). An example of a compound excluded based on its industrial application is Epichlorohydrin (CAS# 106-89-8, Chloro-1,2-propylene oxide) which is a chemical intermediate in the production of epoxy resins. During this step of the DQO process, DOE and Ecology agreed that polycyclic aromatic hydrocarbons (PAHs), chlorinated pesticides and herbicides likely to be used at Hanford (3), polychlorinated biphenyls (PCBs), and compounds identified in specific compilations of, historical chemical use would be retained for further evaluation.

Stability – Non-detected, regulated analytes which could not be excluded based on industrial application, were reviewed for stability in the highly alkaline (pH >9.0), nitrate/nitrite rich (oxidizing), elevated temperature, and radioactive waste environment (4). The compounds were screened on a compound-by-compound basis and the susceptibility of the functional group to reaction mechanisms such as addition (condensation and radical coupling), elimination (dehyrohalogenation), hydrolysis, oxidation, radical reductive dehalogenation, substitution (nucleophilic displacement by hydroxide ion) and possible degradation were considered.

Toxicity – Detected, regulated compounds and the down-selected list of non-detected, regulated compounds were screened for relative toxicity and carcinogenicity (1, Appendix C). The toxicity and carcinogenicity rankings were based on information obtained through the UHCs, Class B TAPs, and slope factors from the EPA Integrated Risk Information System (IRIS) and the Health Effects Assessment Summary Table (HEAST) databases. Regulated analytes with relatively higher rankings remained on the prioritized analyte list. Regulated compounds with lower or unknown toxicity and carcinogenicity ranking(s) were removed from further consideration if they were non-detected and were retained for a methods assessment if they were previously reported as detected.

Methods – The EPA guidance document, SW-846, was used as a basis for identifying analytical methods applicable to the down-selected compounds (5). Methods were selected based on those providing the most reliable identification and methods allowing the greatest number of analytes per method. Potentially adaptable methods or methods with minor modifications were identified for down-selected compounds not included in SW-846.

A timeline for the development and initial implementation of the DQO is shown in Fig. 2. The DQO was issued by DOE in December 1998 and approved by Ecology in January 1999. Work planning immediately commenced and Step 1 implementation was initiated under the Waste Treatment Plant contract in May 2000. The Waste Treatment Plant RCRA permit, waste analysis plan, and Delisting and Land Disposal Restrictions (LDR) strategies followed over the next couple of years. The limited and regulator-approved analyte list from the Regulatory DQO provided a foundation for initiating these activities.

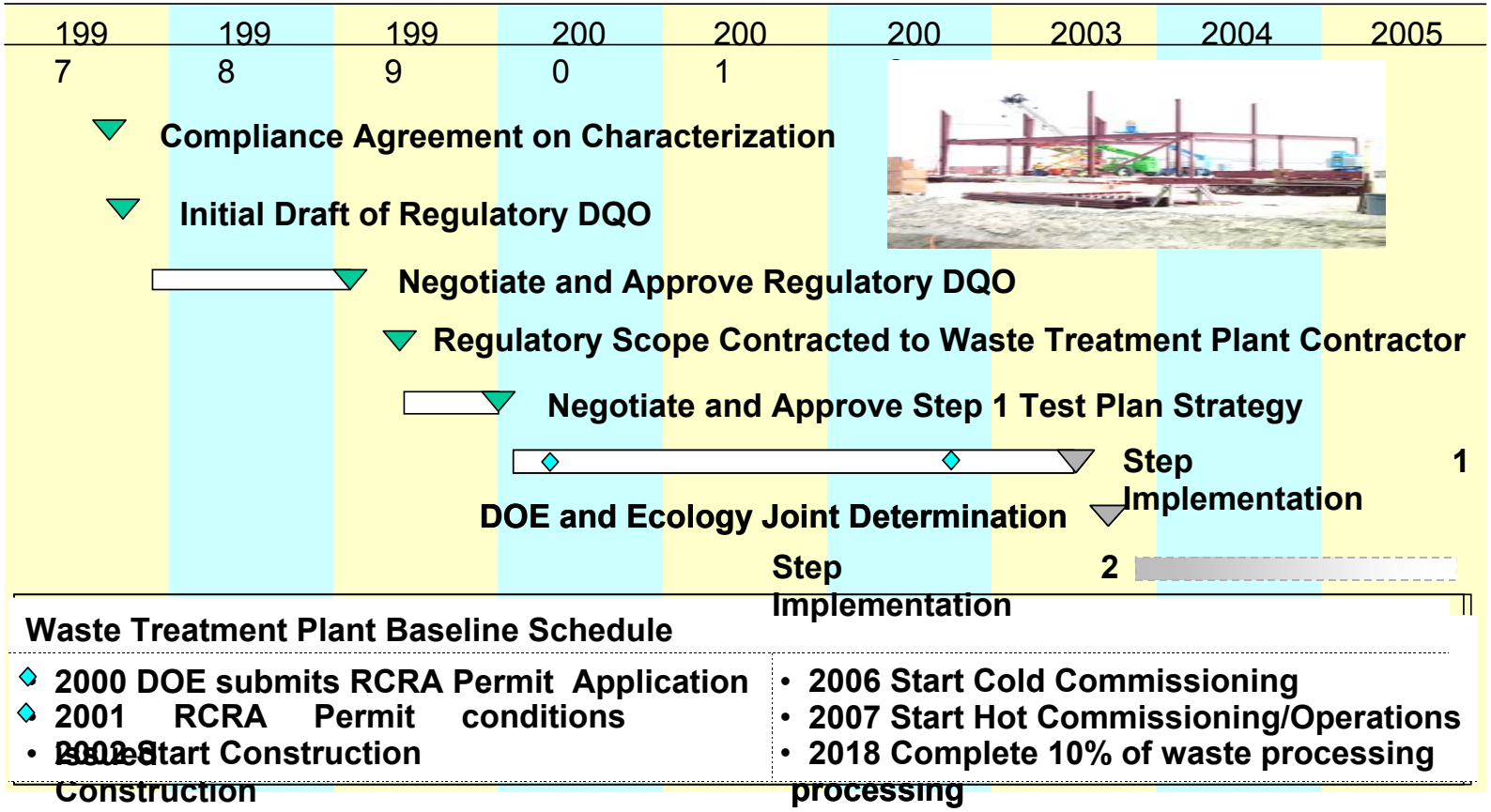

Fig. 2. Timeline for Regulatory DQO development and initial implementation

The DQO execution plan is comprised of two major steps; validation and implementation (Fig. 3). As a part of Step 1 (validation), spiked standard solids and liquid samples are being tested for all 173 prioritized analytes. The analytes are divided into twelve groups, consistent with the selected analytical methods. In addition to pH, the analyte groups are volatiles, semivolatiles, PCBs/pesticides, polar volatiles, organic acids, anions, ammonia, cyanide, mercury, metals by ICP-AES and metals by ICP-MS. If a method is shown to meet performance criteria with the standard matrices, analyses proceed with application to two actual tank waste matrices, representing a solid phase and a liquid phase. DOE and Ecology agreed that the waste samples were to be supernate [liquid] tank waste with a high concentration of organic constituents relative to other tank waste and a solid phase tagged as a high-level waste feed. Tank waste from 241-AN-102 and 241-AY-102 was selected for the liquid and solid waste matrices, respectively. This structured approach was specifically designed to provide a clear, defensible basis for tailoring data-gathering efforts for permitting and compliance to what is achievable through analysis of tank waste.

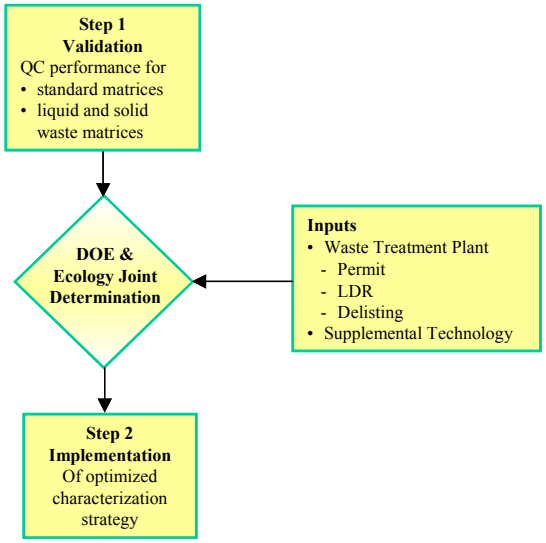

Fig. 3. High-level logic for Regulatory DQO implementation

For analytical method validation, target quality control limits consistent with EPA SW-846 guidance (6) are applied to this work with exceptions needed for radioactive wastes clearly identified up-front. Successes and failures are evaluated on a real-time basis with participation from both DOE and Ecology. Step 1 is ongoing. DOE and the Regulators will use the results of Step 1 in refining selected methods, the analyte list, and additional tank waste to characterize in Step 2. In addition to the information developed through this effort, the maturity and corresponding data needs for the Waste Treatment Plant will be better known and will inform the Step 2 decision process. Data gathered from Step 2 will be used to confirm the Waste Treatment Plant permit assumptions.

This juncture between DQO Steps 1 and 2 also provides an opportunity to support mission acceleration and identify approaches aligned with the budget constraints. At the time the Regulatory DQO was negotiated, the supplemental technologies for tank waste treatment were not specifically identified. Similar to any other permitted waste management activity, supplemental treatment will be permitted. Because of the Regulatory DQO, initial negotiations

for this permitting will be facilitated through using the established agreements and results. Ideally, the anticipated initial reports from the Step 1 work will be issued so the analytical results will also be available for negotiating detailed permit requirements for the supplemental technologies.

CONTEXT FOR CHARACTERIZATION

DOE has undertaken a serious endeavor to accelerate and streamline tank waste treatment and site remediation under a significantly reduced budget scenario. Under the DOE's vision for accelerating cleanup completion at Hanford from 2070 to 2035, accelerating tank waste treatment is essential to achieving this objective. At this point, significant progress has been made in constructing and permitting the Waste Treatment Plant. However, this plant alone will not be able to process all of the tank waste by the mission end date of 2028. DOE is stepping up to this challenge by actively working with their contractors and regulators to find ways to accelerate treatment and site remediation with less money, yet remain overall protective of human health and the environment.

Regardless of the paths to complete treatment and disposal, the basic requirements under RCRA remain essentially the same. For Hanford tank waste now in storage, the major steps include treatment and either immediate disposal or interim storage followed by disposal. At each major processing step along this pathway, an understanding about the waste composition increases due to both process information and ongoing empirical data gathering. When the waste has ultimately been treated to meet applicable requirements, there must also be a corresponding body of data and documentation demonstrating that fact. This increasing definition is depicted in Fig. 4 where the parameter of interest is the evolving detail in the data pedigree of the waste.

The amount of evidence required to support final disposition varies depending on the waste generated and the path for treatment. Due to its nature and multiple sources, Hanford tank waste has a range of characterization needs to meet waste acceptance criteria. Critical to success in reaching a final disposition decision is that adequate supporting evidence demonstrating that

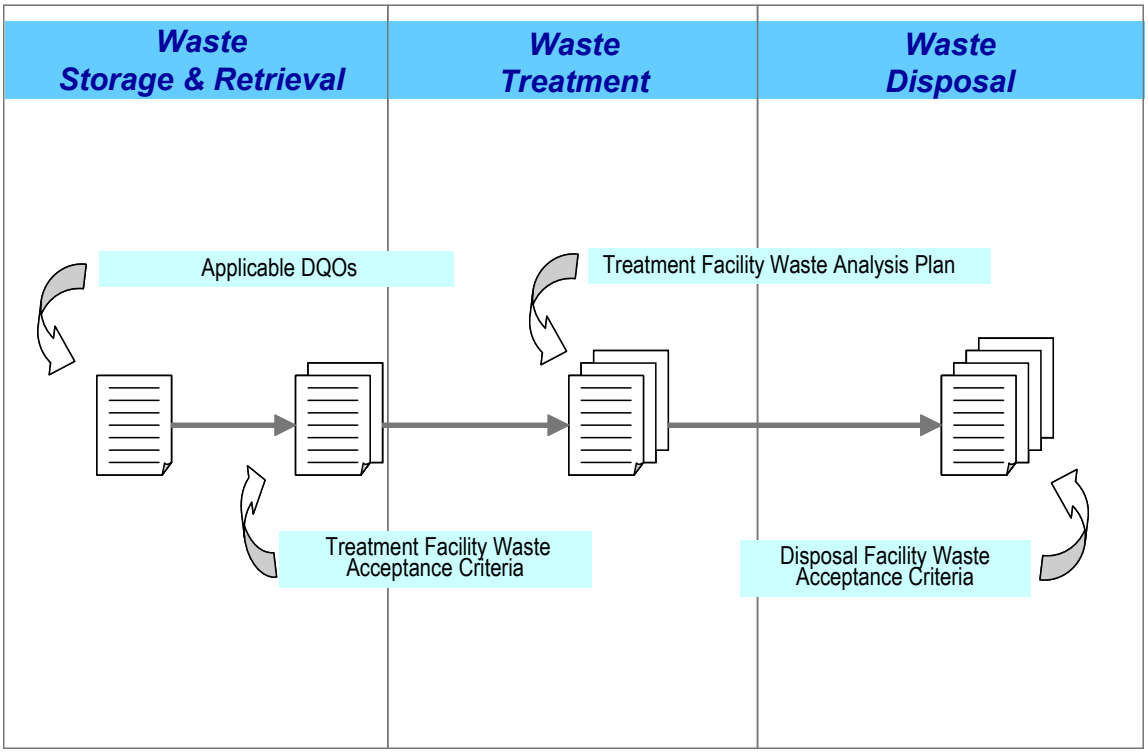

Fig. 4. Development of waste data pedigree

applicable requirements have been met (i.e., the data pedigree) is acceptable at the time of disposal.

Through the Regulatory DQO, fundamental agreements on plausible, regulated constituents for the stored tank waste have been established. In order to bring the Waste Treatment Plant and supplemental treatment technologies on-line, clearly identified needs for treatment processes and the data pedigree for the treated waste products will be required. The Regulatory DQO is key technical input for the Waste Treatment Plant in establishing their RCRA characterization requirements. With this growing foundation, the Regulatory DQO provides the opportunity for a head start on establishing characterization requirements and the necessary data pedigree for the supplemental technologies.

POSITIONED FOR ACCELERATION

As we enter into a new era of acceleration by bringing supplemental tank waste treatment technologies on-line, we are in a better position for establishing detailed characterization requirements (analytes, methods, and quality control) than when the Regulatory DQO was initially conceived.

We now have a technically defensible approach accepted by both DOE and our regulators to evaluate characterization of constituents important to protection of human health and the environment. Because of the groundbreaking work already established, the process of defining characterization requirements has been streamlined. Our dialog begins, for the most part, with the particular technology and an established, shorter list of constituents for evaluation.

In order to accelerate waste treatment under reduced budgets, continued tank waste characterization efforts must be tailored to obtaining effective data. In defining the data needs for treatment, a deliberate cooperative effort among regulators, contractors, and the DOE should focus on collecting data that serve decision-making needs. Progress toward this end will be best supported by an attitude reflected by Nancy Wentworth, director of Quality staff for the EPA Office of Environmental Information (2002), "Get the right data, Get the data right, and Keep the data right."

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