WASTE CHARACTERIZATION PROGRAM DEVELOPMENT FOR HANFORD GROUT DISPOSAL

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ABSTRACT

Disposal of the low-level fraction of liquid double-shell tank waste in a cementitious grout matrix requires detailed characterization of the candidate waste streams to allow development of grout formulations and to support the preparation of environmental documentation. The Hanford Grout Disposal Program plan for meeting these requirements is described. This discussion includes the methodology for plan development, the identification of waste species requiring analysis and the corresponding lower limits of detection, and the bases for determining these limits. The use of predictor analysis for determining information required for evaluating the environmental impact of the disposal action is also discussed.

THE HANFORD GROUT DISPOSAL PROGRAM

In fiscal year 1990, the Hanford Site is scheduled to begin final disposal of the low-level fraction of double-shell tank (DST) wastes. The disposal process involves mixing radioactive liquid waste with cementitious materials to form a grout slurry which is then pumped to near-surface concrete vaults for solidification. Each vault is sized to consume 5,500 m^3 of waste.

Grouting selected DST waste is a key part of the overall defense waste disposal strategy developed for the Hanford Site. The disposal of the low-level fraction of DST waste in cementitious grout will make valuable DST storage space available for new wastes, reduce the need for construction of additional tanks, and most importantly, dispose of waste in an environmentally safe manner.

The detailed characterization of the candidiate waste streams is vital to the successful disposal of these wastes.

GROUT WASTE ANALYSIS PROGRAM DEVELOPMENT

The initial challenges in developing a waste characterization plan were to determine the areas of the Grout Disposal Progam that required waste analysis and identify the specific characterization needs for each area. Waste characterization data will be required for three major activities: grout formulation development, preparation of long term performance assessment, and process operations.

The waste characterization requirements for formulation development are driven by the need to prepare an accurate simulation of the candidate waste stream for use in testing of candidate cementitious material blends. Any simulated waste must include all of the major constituents of the actual waste and the appropriate levels of key trace constituents used in formulation acceptance testing. The criteria for formulation acceptance include specifications of maximum leach rates for ^{137}Cs, ^{90}Sr, ^{99}Tc, ^{129}I, and the eight priority pollutant metals (Ag, As, Ba, Cd, Cr, Hg, Pb, and Se), as well as specifications for waste-form physical and rheological properties. The formulations developed using the simulated waste mixture are subsequently verified using the actual waste. The waste analysis data for formulation development must ensure that the formulations developed using the simulated waste mixtures will be applicable to the actual wastes.

The preparation of environmental documentation requires detailed information on the organic, inorganic, and radiochemical constituents of the waste. These data are used to estimate the maximum potential impact of the disposal action on the environment. The potential environmental impact is evaluated based on the calculated concentrations of chemicals and radionuclides in the aquifer beneath the disposal site.

The samples analyzed for process operations are used to verify that the waste staged for processing is within the boundaries of the formulation to be used and within the boundaries of the environmental documentation that has been prepared. These samples will be taken immediately prior to processing and their timely analysis is required to avoid impacting production schedules.

The definition of waste analysis requirements includes the determination of the analytes and specification of the corresponding lower-limit of detection (LLD) required. The definition of the required LLD is based on a defensible evaluation of the requirements and the incorporation of an appropriate degree of safety to ensure data quality and avoid unnecessary sample reanalysis. The approach used in the development of the waste analysis plan was to define a Maximum Permissible Lower Limit of Detection (MPLLD). The MPLLD is the link between the waste analysis requirements and the detection limits used in the laboratory.

The MPLLD is determined based on the impact of reporting a detection limit value. For example, the MPLLD for analytes used to determine the hazardous waste classification is the minimum regulated concentration. Setting the MPLLD equal to the minimum regulated concentration will ensure that any regulated concentration of material will be detected. It also ensures that if a regulated concentration of material is not present, it would not be assumed present due to a high detection limit.

The detection limits used in the laboratory are defined in relationship to the MPLLD from the intended use for the data and the potential impact of reporting values at the detection limit. For example, the reporting of many radionuclides at their detection limit will not significantly impact formulation development work as the cementitious dry material formulation is independent of these concentrations. Thus, it is acceptable for formulation development work to report the concentrations of *radionuclides* at the MPLLD. Detailed analysis of the uses for the data of each sample type lead to the general rule that the LLD for waste analysis for the purpose of preparing simulated waste mixtures should be the MPLLD and a detection limit of one order of magnitude below the MPLLD for analytes used in the verification of waste form performance or for use in the preparation of environmental documentation. These graduated limits will allow cost effective analyses to be carried out for the preparation of simulated waste mixtures by using the less stringent detection level but, also ensure that data obtained when analyzing samples for the preparation of environmental documentation will be well below the action levels of the applicable environmental standards. The LLD used for methods development is two orders of magnitude below the MPLLD to ensure that analytical methods will retain sufficient accuracy when implemented for routine use. The setting of the LLD for methods development two orders of magnitude below the MPLLD will also ensure that any species measured by this method will be detected well below the action level, the MPLLD.

WASTE ANALYSIS REQUIREMENTS

Required analytes and corresponding MPLLDs were determined for grout formulation, performance assessment, and process operations during the definition stage of the waste analysis plan. Process operations samples have been analyzed for two waste streams: phosphate sulphate waste from N Reactor operations (PSW) and dilute slurry from double shell tanks (DDSS). Table I provides representative chemical compositions for these waste streams. The approach used for determining the species requiring analysis used for the development of this plan resulted in a unified set of analysis requirements for all candidate waste types, except for the operational analyses. Differences in operational analyses result from the need to balance the data requirements with the capabilities and schedule constraints of operational laboratories. This subject is discussed in greater detail below.

WASTE ANALYSIS REQUIREMENTS FOR GROUT FORMULATION DEVELOPMENT

The waste analysis requirements for grout formulation development result from the need to prepare a simulated waste mixture and to verify the suitability of the waste stream for disposal.

The suitability for disposal is determined by comparison with the classification limits of 10 CFR 61.55(1). The resulting waste analysis requirements for formulation development are shown in Tables II and III.

TABLE I

Reference Compositions for Candidate Grout Feed Streams.

Component	Sulfate waste (M)	Phosphate waste (M)	DDSS waste (M)
Na	0.1	1.1	10.8
F	BDL	BDL	0.1
Cl	BDL	BDL	0.2
NO_2	0.0	0.0	2.0
NO_3	0.0003	0.1	2.6
OH	0.02	0.03	5.4
CO_3	0.005	0.03	0.2
PO_4	BDL	0.3	0.02
SO_4	0.03	0.01	BDL

BDL = Below Detectable Limits

TABLE II

Inorganic Species and Corresponding Maximum Permissible Detection Limits for Formulation Development Sample Analysis.

Species	Maximum permissible lower limit of detection (g/m^3)
Ag	5
As	5
Ba	100
Cd	2
Cr	5
Hg	0.2
Pb	5
Se	2
Total Organic Carbon	100
Al, Ca, Cl, CO_3, Cu, F, Fe, K, Mg, Mn, Mo, Na, Ni, NH_3, NO_2, NO_3, OH, PO_4, SO_4, Zn, Zr, U, Rare Earth Elements	500

TABLE III

Radionuclides and Corresponding Maximum Permissible Lower Limit of Detection Values for Formulation Development Sample Analysis.

Radionuclide	Maximum permissible limit of detection (Bq/m^3)
^{3}H	1.5 E+12
^{14}C	3.0 E+11
^{59}Ni	8.1 E+12
^{60}Co	2.6 E+12
^{63}Ni	2.6 E+13
^{90}Sr	1.5 E+09
^{94}Nb	7.4 E+09
^{99}Tc	1.1 E+11
^{129}I	3.0 E+09
^{137}Cs	7.4 E+10
^{241}Pu	2.0 E+11
^{242}Cm	1.1 E+12
Other gamma emitters	7.4 E+08
Total alpha	9.3 E+17
Total beta	1.5 E+09
Total uranium	1.1 E+06
Total plutonium	2.0 E+11

The inorganic analytes (Table II) were selected based on the experience of Oak Ridge National Laboratory (ORNL) in developing grout formulations for the Hydrofracture Program, and discussions with cement industry experts to identify materials which could impact grout formulations, i.e., sulfate, fluoride, lead. The list of materials obtained from these experts was then supplemented with materials known to be in use at Hanford such as ammonia and the rare earths. The resulting augmented list is the inorganic analytical requirement for formulation development samples. The MPLLD for the majority of these analytes was set at 500 g/m^3. This ensures identification of materials which would impact the formulation and allows preparation of an accurate simulation of the waste for formulation testing. The MPLLD for the eight priority pollutant metals was reduced to the respective minimum limits for designation as a dangerous waste to make certain that the concentrations used were representative when candidate grout formulations are tested for the Extraction Procedure (EP)-Toxicity characteristic.

The radionuclides requiring determination are shown in Table III. Analyses of these radionuclides are required to determine waste classification and to allow testing of candidate formulations for their leach index, in accordance with American Nuclear Society (ANS) 16.1 protocol(2). The MPLLDs for the radionuclides are the limits for class A, B, and C low-level waste stated in 10 CFR 61.55. These MPLLDs will ensure that the concentrations of ^{137}Cs, ^{90}Sr, and ^{99}Tc used for simulated waste mixture preparation are representative of the actual waste concentrations and allow accurate determination of the wastes suitability for disposal.

WASTE ANALYSIS REQUIREMENTS FOR LONG-TERM PERFORMANCE ASSESSMENT

The waste analysis requirements for a Performance Assessment (PA) sample must ensure that all the required information is obtained to develop a complete chemical and radioisotopic source term for modeling long-term performance of the grout system. The PA analysis predicts the maximum groundwater concentrations of the inorganic materials listed in the National Primary(3) and Secondary(4) Drinking Water Standards, as well as the certain long-lived radionuclides which have been shown to be significant contributors to the total long term environmental dose.(5)

The groundwater concentration standards and MPLLD for each component requiring determination are listed in Tables IV and V. The inorganic elements tabulated include all those listed in the National Primary and Secondary Drinking Water Standards and those for which the U.S. Environmental Protection Agency (EPA) has proposed recommended maximum concentration limits. The organic materials which are included on these lists are not shown, as they have not been used in the waste generating processes, and therefore cannot be present in the waste from these processes. The absence of these materials has been verified by all analyses performed on candidate waste streams to date. The radionuclides listed are significant contributors to the total long-term environmental dose. The detection limit required for these analyses is one order of magnitude below the MPLLD shown, because the analytical results are used for the preparation of environmental documentation.

TABLE IV

Inorganic Chemical Concentration Standards and Corresponding Maximum Permissible Lower Limits of Detection for Performance Assessment.

Analyte	Drinking Water Standard (g/m^3)	MPLLD (g/m^3)
Ag	1.00 E+00	4.09 E+01
As	5.00 E-02	2.05 E+00
Ba	2.50 E+00	6.14 E+01
Cd	5.00 E-03	2.05 E-01
Cl	2.50 E+02	1.02 E+04
Cr	1.20 E-01	4.91 E+00
Cu	1.30 E+00	5.32 E+01
F	4.00 E+00	1.64 E+02
Fe	3.00 E-01	1.23 E+01
Hg	3.00 E-03	1.23 E-01
Mn	5.00 E-02	2.05 E+00
NO_2	1.00 E+00	4.09 E+01
NO_3	1.00 E+01	4.09 E+02
Pb	2.00 E-02	8.18 E-01
Se	4.50 E-02	1.04 E+00
SO_4	2.50 E+02	1.02 E+04
Zn	5.00 E+00	2.05 E+02

The MPLLD for each analyte required for PA was derived from the appropriate performance standard using Eq. (1).

$$\text{MPLLD} = \left(\frac{A}{S}\right)\left(\frac{Ft}{V}\right)P \tag{1}$$

where

A = the release apportionment factor
F = the groundwater flowrate under each disposal vault (m^3/yr)
t = the release time (yr)
V = the volume of waste disposed per disposal vault (m^3)
S = the engineered safety factor that ensures the standard is not exceeded
P = the performance standard (Bq/m^3 or g/m^3).

Performance standards for inorganic materials are stated in several published reports including 40 CFR 142.3, 40 CFR 143.3, and an Environmental Protection Agency release (6). Performance standards for radionuclides are obtained by dividing the values stated in Table II (7) by 25 to give the concentration in drinking water that would result in a dose of 0.04 Sv/yr. The resulting standards were adjusted by an apportionment factor of 0.2 to allow for the potential contribution of other site disposal actions to the concentrations of modelled materials in the groundwater. The release period for the grout was taken to be 10,000 yr. An engineering safety factor of five was used to ensure that the MPLLDs calculated using Eq. (1) were conservative.

TABLE V

Radionuclide Standards and Corresponding Maximum Permissible Lower Limit of Detection for the Analysis of Performance Assessment Samples.

Isotope	Drinking Water Standard[a] (Bq/m^3)	MPLLD (Bq/m^3)
^{3}H	1.5 E+06	6.1 E+07
^{14}C	4.5 E+04	1.8 E+06
^{60}Co	4.5 E+03	1.8 E+05
^{90}Sr	6.0 E+02	2.4 E+04
^{99}Tc	9.0 E+04	3.6 E+06
^{129}I	4.5 E+03	1.8 E+04
^{137}Cs	1.5 E+03	6.1 E+04
^{226}Ra	1.1 E+02	4.3 E+03
^{237}Np	3.0 E+00	1.2 E+02
^{238}U	4.5 E+02	1.8 E+04
^{239}Pu	1.5 E+02	6.1 E+03
^{241}Am	4.5 E+01	1.8 E+03

[a] derived from reference (6)

The detection limits calculated using Eq. (1), are conservative but reasonable estimates of the detection limit requirements for PA waste analysis. The values are conservative because the assumptions used do not take into account any of the engineered features of the disposal system e.g., vaults, barriers, or any allowance for radioactive decay during the release period.

OPERATIONAL WASTE ANALYSIS REQUIREMENTS

Candidate wastes for disposal are sampled for three reasons: to obtain waste samples for formulation proof testing, to ensure that the waste to be processed is within the bounds of the prepared environmental documentation, and performance assessment analysis and verification. The processes generating candidate waste streams for disposal in grout involve the use of some organic materials. These organic materials must be identified and accounted for. Direct analysis for all organic compounds of concern using EPA approved procedures (8) is not possible because of the high radiation levels associated with some of the candidate wastes. The high radiation levels, 0.5-1 Gy/h per 100-mL sample, make finding alternative methods of analysis for organic materials necessary. The approach chosen was to use predictor analyses for the routine operational confirmation of organic composition of waste staged for processing.

Predictor analyses are analyses which have been shown to provide an accurate estimation of the concentration of a particular group of compounds. For example, the Total Organic Halogens (TOX) analysis, SW-846 method 9020, is a predictor analysis for the total concentration of halogenated organic compounds. If the TOX value is low enough to predict that the concentration of any halogenated organic compounds present would be below levels of concern, this predictor analysis would provide all of the information required to safely manage this waste with respect to halogenated organic compounds. The results of the predictor analysis would have then eliminated the need for detailed characterization for specific halogenated organic compounds. The predictor analysis method used is an extension of this concept to specific predictor tests for classes of organic compounds expected to be present in Hanford Site wastes. Compounds to be determined using this technique include normal paraffin hydrocarbon (NPH), ethylenediaminetetraacetic acid (EDTA), tributyl phosphate (TBP), citric acid, and their degradation products. The use of predictor analyses to provide waste stream composition data will provide the required compositional information for waste management and significantly reduce the radiation exposure of operations and analytical laboratory personnel. The operational characterization of each waste batch will include a complete analysis for the inorganic and radiochemical components shown in Tables II-V, and determination of the organic and radiochemical components and concentrations using predictor analyses.

The fact that no specifically regulated compounds have been detected or are expected to be present in any of the candidate waste streams for grout disposal means that the only requirement for organic speciation information is verification that the concentrations of nonlisted organic compounds are within the acceptable range for the grout disposal process. This verification will be two fold in approach: first, each batch of waste will be verified by comparison of the analytical data, including that provided by predictor analyses, with the limits established for the grout formulation during development, and secondly, by proof testing of the formulation in the laboratory using actual samples of the waste batch. This two fold approach will ensure that each batch of grout feed will be acceptable for grout disposal prior to the processing of that batch. The operating waste analyses requirements for organic materials for the first two candidate waste streams for grout disposal, phosphate/sulfate waste and DDSS, are shown in Tables VI and VII.

The limited analyses required for PSW are a direct result of the tight control exercised over the waste generating processes. The phosphate waste is generated by the decontamination of the primary cooling system of the Hanford Site N Reactor using TURCO-4512A, which is subsequently neutralized using sodium hydroxide. The operating conditions, flowsheets, and records of chemicals added during the decontamination process will be used to calculate the concentration of chemicals in the waste stream. The organic chemicals present in the decontamination waste are expected to be citric acid and diethylthiourea; predictor tests have been developed for each of these compounds and are shown in Table VI. The sulfate waste is generated from the regeneration of ion-exchange columns for the 107-N Fuel Storage Facility. The generation of this waste is governed by detailed operating procedures and process flowsheets. Review of these documents has shown that no organic materials are added during processing. The predictor analyses shown in Table VI have been verified by the comparison with actual characterization data on archive samples. Good agreement was found.

The predictor analyses for DDSS cannot be developed from the analysis of process flowsheets due to the complexity of the generation process for DDSS. The dilute components of DDSS are generated at 18 different plant locations on the Hanford Site; the dilute wastes are then mixed and transferred to a central evaporator for concentration to DDSS. The study of plant flowsheets was used to focus the predictor development process on chemicals used in the waste generating process. The predictors for

TABLE VI

Predictor Analyses for Phosphate/Sulfate Wastes.

Predictor analysis	Predicted compounds
Total organic carbon	Total quantity of organic material present
Total organic halides	Verification of the absence of insecticides and polychlorinated biphenyls
Direct injection organics	Verification of the absence of hydrazine
Inorganic/organic sulfur	Estimation of diethylthiourea concentration
Phosphate	Estimation of diethylthiourea construction Estimation of citrate concentration

TABLE VII

Candidate Predictor Compounds Analyses for Double-Shell Slurry Feed.

Predictor test/ analysis	Predicted materials/compounds
Total organic carbon (SW-846 method 9060)	Total quantity of organic material requiring identification
Total organic halides (SW-846 method 9020)	Polychlorinated biphenyls, organohalide pesticides, halogentated volatile organics, acrolein, acrylonitrile, acetonitrile, chlorinated herbicides
EDTA	EDTA, EDTA degradation products
HEDTA	HEDTA, EDTA degradation products
Normal paraffin hydrocarbon	Long chain organics, long chain carboxylic acids
Tributyl phosphate	Tributyl phosphate, monobutyl phosphate, dibutyl phosphate

DDSS are being developed by analyzing representative waste samples for a broad range of chemicals using techniques to identify chelating and complexing agents and their degradation products(9) as well as analyses for extractable components based on SW-846 methods to determine other organic components. The predictor analyses for DDSS, shown in Table VII, are currently in the process of being verified by an extensive waste analysis program. This verification process is expected to be completed in fiscal year 1987.

SUMMARY

The accurate definition of the required waste analysis for each Grout Disposal Program activity has enabled the clear definition of the required tasks for successful completion of all required waste analysis. This definition process resulted in significant cost savings to the grout program by eliminating unnecessary analyses and has also saved time and effort by eliminating incomplete analyses of samples. The testing of analytical methods to determine their suitability for use revealed the need to develop new methods (prediction analyses) for the characterization of organic materials in double-shell slurry. The development of these predictor analyses for organic materials will result in a reduction in operator dose due to improved analysis techniques.

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