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SURROGATE WASTE STREAMS FOR USE IN MWFA FUNDED RESEARCH AND DEVELOPMENT

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ABSTRACT

Researchers developing technologies for treatment of mixed (both hazardous and radioactive) wastes are strongly encouraged to test using materials representative of the wastes targeted by their processes. Using actual wastes is essential for treatability studies and demonstrations prior to implementation, but is excessively costly and impractical during development. Thus, it is a responsibility of the focus area to provide researchers with surrogate recipes for use in development. Data from tests with standardized recipes will also facilitate comparison of results for competing technologies by potential end users and industry. Due to the wide range of waste materials in the DOE inventory and the scope of technology covered by the focus area, no one surrogate will accurately represent all wastes in all applications. The surrogates described are based on generic base compositions representative of that class of wastes, with variable constituents to be added over a recommended test range. Not all of the additives must be tested for each technology; focus should be directed to the constituents and physical forms present in the waste streams targeted by the developer. Excluding some parameters, or reducing the parametric testing rather than using the full range of concentration recommended simply limits the scope of potential application when the data is considered by a potential user. Surrogates are described for debris, sludges, and caustic scrub solution. Soils are recognized as a fourth class, and are considered too complex to represent with a surrogate. Descriptive text is also included to explain how the recipes were developed, and why each test additive is prescribed.

INTRODUCTION

The Mixed Waste Focus Area (MWFA) directs the national research and development effort for treatment of mixed (both radioactive and hazardous) wastes for the Department of Energy (DOE). The MWFA strategy typically includes funding more than one concept for any given technology need for at least two reasons. First, unique requirements at different sites may make one concept more applicable than another. Second, not all technologies will be successfully developed, and multiple options ensure that some treatment will be available for all wastes. To support this strategy, it is imperative that comparable data is developed by the parallel research efforts such that users in the field can select the most appropriate technology, and the MWFA can allocate funding where it can be of greatest benefit. To this end, the MWFA has issued Test Plan Guidance, and will review proposed plans to maintain some commonality.

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Testing on consistent waste formulations is key to establishing comparability in test data. Unfortunately, there is no one typical or nominal waste stream that adequately represents the DOE inventory, or even a broad class of wastes, e.g. debris or sludges. We are dealing with the waste byproducts from 50 years of nuclear processing and R&D. Not only are physical matrices significantly variable, but the compositions within a class of waste cover a broad range. These ranges can be roughly bounded, however, and that is the intent of the matrices described below. A basic mixture is provided, and the range of compositional parameters that testing should cover is suggested. Please note that this covers only the range of compositions of interest. In addition, researchers must design tests to determine the range of operating parameters intrinsic to their technologies and specifically targeted applications.

PURPOSE AND LIMITATIONS OF SURROGATES

Surrogates are used to minimize the problems inherent in obtaining and working with radioactive materials and actual wastes. Frequently, actual wastes are uncharacterized, and funding for site operations are not sufficient to support special handling to support R&D efforts, even for important tests. In addition, characterization of some matrices, particularly debris, cannot be readily extrapolated to other waste streams. By making up a surrogate, exact and complete characterization is possible such that test conditions are well known and reproducible. This is essential for technology development and comparison between competing concepts. Careful experimental design can also minimize generation of hazardous, radioactive, and mixed wastes. Tests using uncontrolled, industrially available materials can be used to define operating limits for most technologies at minimum cost. The relatively low concentration of most hazardous constituents and virtually all radionuclides do not impact the performance of most technologies, and generally they need not be added unless the purpose of the tests includes monitoring their behavior. Waste matrices and experimental plans should be designed to obtain performance data to support design, trade studies, cost analyses, and ultimately marketing plans. Generation of controlled byproducts should be minimized to the greatest extent possible while still developing the required data.

Ideally, a surrogate would be completely representative of the target material as it could be expected to behave in the planned testing. Unfortunately, testing supported by the MWFA includes development of NDE/NDA, melters, chemical oxidation, stabilization, and materials handling technologies, as well as R&D to characterize specific phenomena such as radionuclide partitioning or waste form durability. Waste streams range from large quantities of sludges, soils and debris, to small but problematic streams such as tritiated oils and uranium chips. Thus the permutations exceed the resources available to devise a simple list of standards. Therefore, surrogates are designed to represent as broad a group of wastes as possible to maximize the value of data, and to minimize the number of tests required. Clearly, this requires some sacrifice in how closely any one waste stream is represented. The surrogates described below do not represent any particular waste, but should yield critical data on the ramifications of unique characteristics of specific wastes. For example, the generic sludge recipe is only generally representative of the products of hydroxide scavenging of inorganic contaminants in wastewater. However, when tested with the addition of calcium carbonate at the high end of the variable constituent range, the matrix becomes fairly representative of the West End Treatment Facility sludges generated at Oak Ridge. The surrogate is still not an exact match, but the impacts of the calcium carbonate on melter technology characteristics, such as melt viscosity, corrosivity, foaming, and product durability could be fairly well characterized using this surrogate.

Thus, a technology developer as well as the potential end user should understand that the surrogates are not meant to be literal substitutes for testing with actual wastes. The benefits of treatability testing with actual materials cannot be overstated. The presence of even trace amounts of frequently overlooked materials such as chelants, coagulants, or foaming agents, unforeseen chemical speciation, physical form, aging, and even packaging of the actual waste may significantly impact results. Testing with surrogates is meant only to provide some commonality amongst test programs to assist in comparison, and to provide developers with some insight into the type of materials in the DOE inventory. Selection of the proper surrogate should be based on the data needed to provide insight into a specific hypothesis. Simply testing with a surrogate to "see what happens" is a waste of limited resources. In general, all successful development programs should result in data to support clearly defined limits of an effective operational envelope, acceptable waste matrix and contamination tolerances, reliability, availability, and maintainability (RAM) information, and cost. If experimental data cannot be shown to support one of these areas, the need for the test should be questioned. Results should be reported with a full description of the test conditions and the foreseeable limitations of the measurments.

CONTAMINANT OF CONCERN

When necessary, spiked testing should include the RCRA toxic metals commonly found in mixed wastes (Cd, Cr, Pb, Hg, Ag) at concentrations of about 1000 mg/kg, as well as any other regulated metals such as Ni, unless the target application obviates their use. Regulated organic contaminants are to include trichloroethylene, benzene, hexachlorobenzene, and a PCB such as Arochlor 1254 also at concentrations of about 1000 mg/kg. These additives are not meant to be a comprehensive list, merely an abbreviated menu of target analytes representative of the contaminants of concern found in the DOE waste inventory. Metals should be added as hydroxides or oxides whichever is most convenient and representative of the intended surrogate matrix. Sludges will most typically include metals as hydroxides or some other hydrated salt, while debris wastes are most commonly contaminated with oxides or dried salts. The effects of nitrates and chlorides are covered by the variable constituent additives to the test matrices. Practicality may require some compromise, and use of hematite

(Fe_2O_3) is acceptable as a more readily available (and easily handled) material than specially produced $Fe(OH)_3$ sludge. This is an example of how the surrogates deviate from reality and final testing may require use of more accurately designed matrices to characterize materials handling limitations such as pretreatment and feeding equipment.

Selection of any additive should be made based on what the test data is designed to measure, within the constraints of the known characterization data. For example, concerns over dioxin formation might lead an experimenter to spike a surrogate with a known dioxin precursor that may not be present in the targeted waste streams. The data may be expensive to get and only of academic interest. Instead, the limited resources would be better spent selecting constituents most likely to challenge the technology and believed to exist in the waste.

Radionuclide (or surrogate) additives are to be tailored to represent the target waste streams, and may include common nuclides and surrogates such as cesium, strontium, cobalt, uranium, plutonium and cerium. In general, radionuclides are present at very low levels and do not impact chemical of physical aspects of treatment, but nuclides or surrogates must be added in some tests to characterize product durability, offgas system design, and containment capabilities. Unless specifically required by the goals of the testing, nonradioactive isotopes of these elements should be used, particularly as a substitute for fission products. In the case of transuranic elements, cerium may be used. To assist in measurement at very low concentrations, radionuclides may be used, but should be added at levels only great enough to make the required measurements possible without causing unnecessary handling and exposure complications. Physical form must also be considered, e.g. inter-phase partitioning of finely divided plutonium particles (Savannah River debris) cannot be simulated by spiking with a cerium nitrate solution, a particulate form of cerium oxide of comparable diameter is required.

Additional testing may still be necessary for unique matrices such as those containing concentrated contaminants such as PCBs, mercury, selenium, or TRU elements. Maximum use of the special considerations provided by regulatory authorities for treatability testing should be made, but special attention must be given to all requirements such as notifications, materials handling, time and mass limitations, and final material disposition. Test plans requiring significant expenditure of resources for limited, but essential data should always be reviewed with funding authorities and the potential end user to ensure that the testing is necessary and the data to be recorded is sufficient to address the goals of the plan.

SURROGATE RECIPES

As stated above, the surrogates are designed as generically representative, and should be chosen based on the goals of the testing to gain insight into a particular hypothesis or phenomenon. Recipes are provided using a base matrix which can be modified by adding variable amounts of specific additives to challenge the system as it would be for specific waste streams. Though each additive is listed for the reasoning described below, the permutations possible by combining all additives is neither required nor completely desirable. Ideally, to completely evaluate a technology, scoping studies would include testing to determine gross effects with the base matrix including the maximum loading of each of these constituents taken individually, and only limited parametric studies to evaluate interactions between these materials. The actual test program should be designed using a reasonable test plan covering the constituents in targeted waste streams. **Initially, testing should be limited to scoping studies to determine which of the variable constituents have significant impacts at their maximum loadings.** If no impact is observed for a particular additive, or the targeted waste streams do not include certain additives, further testing should not be done.

Sludges

Most sludges in the inventory result from process residuals that could not be cost-effectively treated at the time of production, or wastewater treatment solids. The most variable parameters result from the parent process design and include materials such as: filter aid (SiO_2), calcium carbonate, activated carbon, oil, ion-exchange resins, and salt (Table I). The base matrix solids, resulting from corrosion products and dissolved solids from process water, can be used alone to form a test surrogate for inorganic wastewater treatment sludges. These materials should be used in consistent ratios to make up the balance of the test matrix.

Testing at variable SiO_2 levels will demonstrate capability to handle chemically inert, highly refractory materials. Addition of calcium carbonate should be representative of Oak Ridge waste water treatment sludges. This additive can be expected to produce significant foaming in acidic or high temperature conditions, and to consume acid in aqueous solutions. Activated carbon is a high surface area, difficult to oxidize material common in several waste streams, and expected is to be produced in many future operations to absorb organic constituents and mercury. Oil and styrene resins are also commonly found and can be combined with the activated carbon and TCE at the maximum levels to create a 70% organic sludge. Though the grease found in some waste streams is not included, this high-organic mixture should serve as a satisfactory "worst case" for oxidant demand to challenge any treatment process targeted at materials such as the organic sludges produced at the Rocky Flats site. Sodium chloride or sodium nitrate can be added to test high salt levels in melting and stabilization technologies. Calcium sulfate is also commonly found in precipitated sludges such as those produced at Rocky Flats. The sulfate is of particular concern in melting technologies due to foaming and offgas treatment, and grout-based stabilization concepts due to the effects on curing.

Table I. Sludge Surrogate Test Matrix

Variable Constituents	Test Range (wt%)
Filter Aid or Sand (SiO_2)	0 – 70
Calcium Carbonate	0 – 60
Granulated Activated Carbon	0 – 10
Oil (ISO 100)	0 – 30
Styrene cation resin	0 – 20
NaCl	0 – 10
Trichloroethylene	0 – 10
$CaSO_4$	0 - 5
NaNO3	0 – 60
Base Constituent Blend (Balance)	**Wt% of blend used as balance**
Fe_2O_3	15
$Al(OH)_3$	10
Na_3PO_4	5
$Mg(OH)_2$	10
Micro Cel E*	20
Portland Cement	5
Water	35

* Micro Cel E is a trade name for a synthetic calcium silicate adsorbent made by World Minerals, Inc.

Debris

Debris wastes include construction rubble, laboratory and office trash, used equipment, refractory materials such as alumina and graphite, plastics, wood, and a variety of unique test materials. Containers are almost as variable including boxes, drums, and cartons made of carbon and stainless steels, wood, cardboard, plastics, and fiberglass. The base matrix (Table II) includes generic materials found at almost all sites, and the variable constituents represent particular classes of materials that may be problematic for some processes. Though vermiculite does not meet the 60 mm debris definition recognized by the EPA, it is included in the base matrix because it is commonly found in this class of waste streams. Graphite pieces represent graphite molds from Rocky Flats, and can be expected to be very slowly oxidized under all foreseeable conditions. Firebrick (and other types of insulation) is commonly found and will act as an inert or extremely refractory material depending on the conditions. Lead brick and lead solids are pervasive, not readily reactive, volatile at elevated temperatures, and are inherently hazardous under RCRA. Wood and paper are also very common from pallets, blotter materials and packaging, slow to oxidize, and contain significant noncombustible ash. Stainless steel and nonferrous alloys are not separable magnetically, have variable melting points, are not readily oxidized, and may yield RCRA hazardous constituents. The Personal protective equipment (PPE) mixture is to include 50wt% PVC items and 50wt% made up of a variety of non-chlorinated rubbers and plastics such as neoprene and Tyvek. Various forms of PPE and other "job-control" wastes can be found at all sites, particularly a large waste stream contaminated with finely divided (submicron) Pu^{238} at the Savannah River Site. This polymer mixture can be expected to oxidize over a broad range of rates and conditions, and to melt and pyrolize at elevated temperatures.

Table II. Debris Surrogate Test Matrix

Variable Constituents	Test Range (wt%)
Graphite (nominal 3" pieces)	0 – 30
Alumina Firebrick (nominal 3" pieces)	0 – 30
Lead Brick (nominal 3" pieces)	0 – 10
Wood (nominal 3" pieces)	0 – 30
Stainless Steel (nominal 3" pieces)	0 – 20
Non-ferrous metals (copper, aluminum)	0 – 5
Paper	0 – 25
PPE (50% PVC/50% non-PVC)*	0 – 20
Base Matrix (Balance)	**Wt% of blend used as balance**
Carbon Steel (nominal 3" pieces)	20
PVC (nominal 3" pieces)	5
Wood (nominal 3" pieces)	10
HDPE (nominal 3" pieces)	15
Sand	15
Portland Cement	15
Vermiculite	10
Water	10

Soils

Surrogates should not be used. Due to aging effects and nuances in the natural soil matrix, representative soil samples should be used whenever possible. Organic contaminants can be added if necessary, but any testing with spiked inorganic contaminants must be qualified, or verified using actual contaminated soil samples.

Scrubber Blowdown

The caustic scrub used in a wet offgas treatment system is nominally controlled at a pH of 8 and blown down (bleed stream) based on specific gravity to control the level of suspended and dissolved solids. Primary constituents are NaCl (the caustic reacts with HCl captured from the offgas), corrosion products, and metals condensed or captured as flyash, Table III. This surrogate is only about 14 wt%.

solids, and can be made up in a more concentrated form using less water (representing an evaporator product) to demonstrate higher waste loadings. Water should not be included in calculating waste loading.

No particular chemical variables need be investigated. Instead the emphasis is primarily on maximizing the waste loading, i.e. minimizing the fraction of non-hazardous additives required to convert the solution to a stable waste form passing TCLP and ASTM C-39 (compressive strength). Preventing leaching of the anions is not a requirement, but is a desirable attribute in that it maintains the structural integrity of the waste form.

Table III. Caustic Scrub Surrogate

Solution matrix	Concentration (wt%)
NaCl	10
SiO2 (insoluble)	1.5
Fe_2O_3 (Insoluble)	1.0
$CaSO_4$ (Insoluble)	0.5
Contaminants (spiked as oxides)	mg/kg as metal
Lead	4000
Cadmium	1000
Chromium	1000
Mercury	2000
Silver	2000
Nickel	2000

CONCLUSIONS AND RECOMMENDATIONS

Developers and vendors are strongly encouraged to base test plans on the surrogates described above. Tests should be conducted to establish the range of effective application for a technology. By definition, this includes testing beyond the expected range of operation to ascertain the failure mode for the technology and to determine the limiting parameters. Not all constituents or operating parameters must be tested, only those applicable to the waste streams to which the technologies are to be evaluated for application. Consideration should be given to not only the chemistry of the surrogate, but the physical form of the matrix as well, and how these variables may affect the test results. Screening tests, measuring the impacts on technology performance at maximum additive concentration should help to focus additional testing on only those parameters limiting the scope of operation.

If there are questions on the applicability of some surrogates or test variables, answers should be sought through the focus area or operations personnel, but it should be expected that characterization data is limited, and in many cases is based solely on process knowledge. Test plans should be developed to maximize the utility of data from each test, and to minimize the generation of regulated residuals.

Operations personnel are encouraged to review the surrogate formulations and comment on limitations to allow the focus area an opportunity to adjust the recipes to provide more useful performance information.

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SURROGATE WASTE STREAMS FOR USE IN MWFA FUNDED RESEARCH AND DEVELOPMENT

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- **Strategy includes funding competing technologies**
  - Not all concepts are successful
  - Waste stream characteristics may be unique
  - Autonomous sites with differing requirements

- **Comparative performance data is critical**
  - Allows user to write RFP and evaluate bids
  - MWFA Test Plan Guidance

Why use Surrogates?

- Consistency in testing yields comparative and reproducible data
- Can design feeds for specific test objectives
- No one or representative waste for DOE inventory
- Incomplete or incorrect characterization available
- Reduces cost and liability in scoping tests
- Reduces logistics problems

Surrogate Waste Limitations

- No one surrogate is suitable for the broad range of technology types under development
- Recipes representing a class of wastes generally do not represent any one waste perfectly
- Physical form and chemistry are both critical
- Potentially important effects from subtle differences may be lost (chelants, speciation, etc.)
- Age cannot be duplicated

Contaminants of Concern

- COCs are critical to measurements of durability or partitioning, but generally are at concentrations that do not affect the physical or chemical behavior of a system
- Secondary waste issues are critical to dedicate limited R&D resources to testing
- Use of regulated additives should be minimized
- Test should be designed to provide specific data, not to “see what happens”

Contaminants of Concern

- Heavy Metals
  - Common DOE Waste RCRA Toxic Metals: Cd, Cr, Pb, Hg, Ag
  - Also any other regulated metals in target wastes, e.g. Ni
  - Add at 1000 mg/kg in form typical for matrix, e.g. ash/oxides
- Organics
  - TCE, benzene, hexachlorobenzene, and a PCB such as Arochlor 1254
  - Add at 1000 mg/kg
- Radionuclides
  - Fission/activation products added as nonradioactive isotopes
  - Transuranic elements simulated with cerium
  - If radionuclides must be used as tracers they should be limited to values sufficient to support analyses, but less than that causing unwarranted handling or disposal problems

Surrogate Recipes

- **Basic Matrix**
  - Sludge
  - Debris
  - Soil
  - Scrubber Blowdown
- **Variable Constituents**
  - Additives to emulate specific waste streams
  - Not all permutations are necessary or desirable
  - Scoping studies should test individual additives at maximum values
  - Additional testing may be necessary to support specific niches

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Sludge Surrogate

Basic matrix is a water treatment sludge

Constituent	Wt%
Fe_2O_3	15
$Al(OH)_3$	10
Na_3PO_4	5
$Mg(OH)_2$	10
Micro Cel E	20
Portland Cement	5
Water	35

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Sludge Surrogate

Variable additives emulate specific wastes

Additive	Test Range Wt%
Filter Aid or Sand (SiO_2)	0 – 70
Calcium Carbonate	0 – 60
Granulated Activated Carbon	0 – 10
Oil (ISO 100)	0 – 30
Styrene cation resin	0 – 20
NaCl	0 – 10
Trichloroethylene	0 – 10
$CaSO_4$	0 - 5
NaNO3	0 – 60

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Debris Surrogate

Base matrix is typical of construction debris

Constituent	Wt%
Carbon Steel (nominal 3" pieces)	20
PVC (nominal 3" pieces)	5
Wood (nominal 3" pieces)	10
HDPE (nominal 3" pieces)	15
Sand	15
Portland Cement	15
Vermiculite	10
Water	10

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Debris Surrogate

Variable additives emulate specific wastes

Variable Constituents	Test Range (wt%)
Graphite (nominal 3" pieces)	0 – 30
Alumina Firebrick (nominal3" pieces)	0 – 30
Lead Brick (nominal 3" pieces)	0 – 10
Wood (nominal 3" pieces)	0 – 30
Stainless Steel (nominal 3" pieces)	0 – 20
Non-ferrous metals (copper, aluminum)	0 – 5
Paper	0 – 25
PPE (50% PVC/50% non-PVC)	0 – 20

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Soil Surrogate

- Surrogates are NOT recommended for soil testing
  - Soil matrix is too complex
  - Aging and freeze/thaw cycling is not readily simulated
  - Speciation is difficult to predict
- Uncontaminated soils taken from near the site should be used
  - Spiked organic contaminants may be useful
  - Testing with spiked inorganic contamination must be verified using samples of actual waste

Scrubber Blowdown Surrogate

Matrix is based on a caustic scrubber operated to maintain a specific gravity setpoint

Solution matrix	Concentration (wt%)
NaCl	10
SiO2 (insoluble)	1.5
Fe_2O_3 (Insoluble)	1.0
$CaSO_4$ (Insoluble)	0.5

Scrubber Blowdown Surrogate

Additives are typical of solids entrained in offgas

Contaminants (spiked as oxides)	mg/kg as metal
Lead	4000
Cadmium	1000
Chromium	1000
Mercury	2000
Silver	2000
Nickel	2000

Conclusions

- Developers and vendors are strongly encouraged to test using the surrogates
- Screening tests should be designed to focus test plans on constituents limiting operations
- Potential users need data to evaluate bids and compare competing technologies
- Testing should include all targeted waste matrices to validate performance claims
- Chemistry and physical form must be considered