

A STRATEGY FOR THE DEVELOPMENT AND DEPLOYMENT OF ALTERNATIVE MIXED WASTE TECHNOLOGIES IN RESPONSE TO THE PROPOSED SHUTDOWN OF DOE INCINERATORS

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ABSTRACT

The Department of Energy (DOE) has successfully incinerated a variety of the organic-based mixed wastes that were generated from its past and present waste remediation, nuclear energy, and weapons missions. However, recent stakeholder and public concern over incinerator emissions and the increasingly stringent mandates of the Environmental Protection Agency (EPA) to monitor and treat these emissions has caused the DOE to consider closure of all mixed waste incinerators complex wide. Regardless, some of the more challenging mixed waste existing in DOE storage contain sufficient quantities of transuranics, mercury compounds, explosives, and/or reactives, such that they are not amenable to efficient incineration and therefore technically require alternative methods for organic destruction. Consequently, the DOE's Office of Science and Technology (OST) has established a new strategy to develop, demonstrate, and deploy the cost effective and timely alternative technologies needed to replace the role of incineration as well as to address these more challenging waste streams.

General descriptions of the emerging alternative incineration technologies to be advanced through the strategy are provided, and these methods are classified in the three general categories of either thermal, aqueous based chemical oxidation (including dehalogenation), or separations. The strategy presented to develop these methods (and therefore to effectively compensate for any recent and pending DOE incineration closures) requires a broad range of efforts at various development stages, including those involving any basic science research and full-scale integrated demonstrations. To be successful, the specific development and deployment strategy (to be initiated by DOE's and OST's Transuranic and Mixed Waste Focus Area (TMWF)) must also include a regulatory and stakeholder approach, in addition to the traditional technical component.

INTRODUCTION

The U S Department of Energy (DOE) has successfully and safely incinerated various organic based mixed waste streams over the past ten years. However, cost inefficiencies, an increase in public resistance to incineration emissions (e.g., dioxin/furans), and the promulgation of more stringent and potentially expensive off-gas treatment and monitoring requirements has resulted in the closure of two of the three DOE incinerators operating across the weapons complex (1). As a consequence, new and low-emission alternative methods are sought for the compliant treatment of those legacy and future mixed wastes streams that were to be addressed via incineration. Nonetheless,

alternatives were already being sought and developed for those classes of mixed waste (e.g., transuranics, mercury containing, and explosives) that were not amenable to incineration, independent of incineration's closure status.

BACKGROUND

A complex-wide review of those mixed waste streams that may be orphaned as a result of DOE incineration closure was conducted (1). The review's assumption that the treatments offered by the private sector as alternatives to incineration will accommodate this presently identified legacy inventory is only valid if they have sufficient capacity to meet site specific treatment milestones. An analysis, done in part by the DOE's Transuranic and Mixed Waste Focus Area (TMFA), shows that this potential capacity shortfall may indeed exist. In addition, the DOE estimates that the unknown volumes and compositions of future mixed wastes to be generated through remediation and DOE site closure activities will be of sufficient magnitude to justify a comprehensive alternative technology development and deployment program. To ensure success, the program must consist of integrated efforts to equally address issues associated with the technical, regulatory, and stakeholder aspects. Additionally, the program must include a complete portfolio of efforts across the various stages of technology development, including basic science and full-scale deployment.

TECHNICAL STRATEGY SUMMARY

Through DOE's Office of Science and Technology (OST) sponsorship of the Transuranic and Mixed Waste Focus Area (TMFA), the key technical issues will be addressed through a development effort involving side-by-side comparison of emerging alternative incineration methods. Starting in FY 2001, the TMFA will prepare the required facilities for housing the tests and issue the appropriate competitive calls to initiate the full comparison testing program in FY 2002. Under a comparison-testing scenario, specific data will be collected for similar test conditions involving both surrogate and actual waste feed compositions. This will allow direct and equal evaluation of each technology in terms of their performance (e.g., feed rate, residence time, and pre- and post- treatment requirements) as well as their robustness to various waste types. During the testing, essential scale-up, design, and permitting data will be collected.

Possible alternatives suitable for the comparison study may be thermal (e.g., steam reforming), consist of chemical and aqueous based methods (e.g., direct chemical oxidation), and/or involve organic separation steps (e.g., thermal desorption) (2). Further details for each class are provided below.

Thermal Methods

Thermal methods are relatively high temperature, non-incineration, alternatives (i.e., greater than 800° C) that involve oxidation, reduction, and/or pyrolysis environments to destroy the organic component of the waste matrix, but generate significantly less off-gas than incineration. For example, the plasma generated in

a Direct Current (DC) Arc waste treatment unit results in local temperatures at a magnitude of 10,000 ° C and transfers heat to the waste in primarily a radiation mode. As a consequence, organic components in the waste are pyrolyzed in the oxygen-starved atmosphere of the unit and are essentially converted to their basic elements for later gas-phase oxidation or reduction down stream. Unlike incineration, large volumes of air are not required for oxidation, therefore greatly reducing the net off-gas volumes. However, vitrified waste forms and sufficient slag volumes may be generated, potentially requiring additional stabilization prior to land disposal under the Resource Conservation and Recovery Act (RCRA).

Other specific examples of non-incineration thermal alternatives include steam reforming, molten metal melting, vitrification, molten salt oxidation, and super critical water oxidation. Steam reforming and molten metal melting involve essentially reduction type processes whereby steam, hydrogen, or a reducing metal (e.g., aluminum, or iron) becomes oxidized in the event of converting the organic waste species to char and hydrogen gas. Halogens are retained as salts and residue organic gas phase products may require gas phase oxidation in the primary off-gas treatment train. Unlike incineration, which generates heat as a result of its' exothermic combustion-type reactions, most reductive methods are endothermic and require a constant energy supply, which in turn may increase operating costs.

Molten salt oxidation (MSO) and supercritical water oxidation (SCWO) may be fundamentally considered as controlled oxidation methods. With these methods, the oxidizer, in the form of oxygen or an alternative such a hydrogen peroxide, is delivered to the organic waste species-of-concern via a non-gas media, and therefore emissions are reduced. For the case of MSO this media is usually a molten bed of sodium carbonate, and for SCWO the media is water at pressures and temperatures above its critical point. Water at super critical conditions is highly soluble of organics and insoluble to inorganics. Additionally, supercritical water has the density of a liquid with the flow properties of a gas; thereby making it an ideal media for effectively mixing and contacting with the organic species-of-concern within the mixed waste matrix. The salt media of MSO has the added advantage of being a primary off-gas scrubber, thereby eliminating the generation of any acid gases. However relative to incineration, MSO and SCWO have the disadvantages of requiring longer residence times, excessive waste feed pre-sizing, special materials to resist their corrosive environments, and considerable residue stabilization.

Aqueous Based Chemical Oxidation Methods

Also referred to as chemical redox methods, aqueous based processes use strong chemical oxidizers in acid bath type reactors and are usually operated in the batch or semi-continuous mode. Under these conditions the strong oxidizer is reduced in the course of converting the organic waste component to carbon dioxide, water, and mineral acids. On a more microscopic level, the oxidizer usually creates

hydroxyl radicals in the acidic environment, which in turn remove hydrogens from the carbons in the organic waste specie. The net effect is that the organic becomes more soluble, where conditions for eventual oxidation to carbon dioxide become increasingly more favorable. Cost effectiveness is achieved by recovering and recycling the valuable reduced oxidant with a regenerate step usually involving electrochemistry

The use of oxidizers considerably stronger than oxygen results in thermodynamic conditions that allows for organic destruction at temperatures (e.g., 150 to 450 °C) an order of magnitude lower than that of incineration or other thermal based alternatives. Consequently, little or no off gas is produced, outside of that generated by water vapor or from the presence of any volatile organics, tritium, and/or mercury. To their disadvantage, aqueous based chemical alternatives will require sizing/shredding of the in-coming waste feed (i.e., ¼ inch in size or smaller) and will generate copious quantities of aqueous and sludge residues requiring further stabilization if RCRA land disposal requirements are to be met. Residence times for the digestion of a particular organic-based mixed waste stream may be on the order of hours or days compared to the seconds and minutes achievable with incineration. Mixing will be critical and some waste streams may be too recalcitrant for the process, and therefore the alternative may be uneconomical as a result of the high frequency of oxidant bath change out. In addition, the aqueous based alternative may not achieve the required level of organic destruction as required by RCRA's Universal Treatment Standards (UTS) or the level of organic destruction that would be achieved with a traditional thermal method. However such alternatives may be appropriate for transuranic (TRU) waste since they are usually exempt from the RCRA UTS requirements.

Examples of aqueous based chemical alternatives in advanced development and/or near deployment stages include direct chemical oxidation, acid digestion, mediated electrochemical oxidation, and acid catalyzed oxidation. Other aqueous-based processes, such as the commercially available solvated electron technique, are only applicable to halogenated organics, but have been successfully demonstrated on mixed wastes containing polychlorinated biphenyls (PCBs).

Separation Methods

Alternative incineration methods involving separation processes are simply those that remove the organic contaminants of concern from the bulk of the waste matrix. They are essentially pre-treatment steps since the separated and removed organic requires destruction via any of the other methods, including incineration. The distinct advantage of this class of alternatives is that they can significantly reduce the volume and complexity of the waste to be treated, but the additional steps involved may increase waste handling and costs. Separation processes utilizing solvent extraction requires the tailoring of specific solvents for specific organic contaminants and they usually require solvent recovery and recycle methods to be cost effective. Commercial solvent extractive methods involving

mixed waste have been applied to PCB contaminated soils and numerous methods are under development for specific contaminants in waste water and sludges (e.g., trichloroethylene). However, the removal of organics from mixed waste debris streams may present challenging contacting schemes and waste pretreatment steps to ensure efficient contaminant removal.

Thermal desorption is another effective separation technique and is usually independent of the organic component in the waste. Like simple drying, thermal desorption involves the application of heat, either direct or indirect, to volatilize the organic(s) from the waste matrix. Removed organics are then recovered for additional destruction via condensation. Commercially available vacuum systems lower the required volatilization temperature of the organics, but some recalcitrant organic complexes may be inseparable from the bulk of the waste matrix. Like solvent extraction, advanced delivery and pre-treatment of the waste may be required for sludge, paste, and debris-type mixed wastes to allow for uniform heat transfer. Some thermal desorption systems may also effectively destroy the volatilized organic under high temperature and oxygen starved (e.g., pyrolysis) environments.

Where applicable, existing DOE owned or contracted test facilities will be used, in part, to leverage previous efforts conducted in alternatives development and house planned efforts in comparison testing. Examples include the Army's chemical warfare destruction test units at Aberdeen, Maryland; the Hemispheric Center for Environmental Technologies (HCET) at Florida International University (FIU) in Miami; and DOE's Western Environmental Treatment Office (WETO) in Butte, Montana. Current TMFA planning indicates that the mediated electrochemical oxidation process is best suited for comparison testing at the Army's Aberdeen facility and a solvent extraction separation method under development at HCET should also be leveraged. WETO will be home to the bulk of the comparison testing and may house up to a half dozen other incineration alternatives.

To ensure a successful program involving tests to equally compare alternatives, the above-identified facilities will have to be pre-equipped with the necessary data collection, monitoring, and diagnostic equipment. Specifically, equipment to equally measure and compare the destructive removal efficiency (DREs) of various organic contaminants in the waste and to determine the presence of gaseous pollutants, such as dioxins/furans will be essential.

In addition to comparative testing, the TMFA will recommend that support be provided to a basic science program. The basic science program will address key areas of research (e.g., material science, off-gas chemistry, pollutant formation mechanisms), long-term stewardship, and/or identify emerging alternative methods not yet recognized. On the other hand, the TMFA may directly sponsor the full-scale demonstration and/or subsequent deployment of a selected technology at a respective DOE site. More than likely, the deployment will be for the primary purpose of addressing a specific site need in regard to a difficult mixed waste stream that requires an alternative to incineration.

Examples include the potential demonstration of a molten metal technology for treating classified materials at the Sandia National Laboratory (SNL); and the partial funding of a Hanford initiated contract for deployment of a plasma-vitrification hybrid process at a fixed commercial facility. Ongoing development efforts (such as testing of the Delphi Detox system, a chemical oxidation process near Oak Ridge, or the demonstration of a method to treat troublesome transuranic Pu-238 containing job control waste at the Savannah River Site) will continue to be managed and may be altered to fit with in the established conditions of the broader comparison testing.

In addition to developing and demonstrating the primary organic treatment step, the TMFA will support necessary technology development efforts in ancillary systems to ensure the deployment of fully integrated system alternatives. In particular, emphasis will be placed on developing and demonstrating waste feed handling/sizing methods, and residue treatment/stabilization processes. These components are necessary since many of the chemical and aqueous based incineration alternatives require considerable waste pre-sizing and generate significant quantities of secondary solid and liquid wastes. Even though the proposed alternatives will likely generate lower volumes of more benign emissions relative to incineration, continued evaluation and demonstration of off-gas treatment and monitoring methods will also be necessary to ensure support for these new technologies. In particular, continued research in the development and testing of a continuous dioxin/furan analyzer will be recommended

REGULATORY STRATEGY SUMMARY

As the research, development, and demonstration of the alternative technologies is initiated and advanced on a technical front, it will be paramount to recognize the key regulatory issues to ensure that the alternatives meet all compliance requirements, and are therefore subsequently permissible for full-scale deployment. Therefore, it will be necessary to collect specific data during early development and demonstration steps to ensure a timely permitting process. These data will consist of, but may not be limited to, information associated with destruction removal efficiencies, dioxin/furan and other pollutant formation, and the dynamics of the alternative systems in response to upset conditions. Identification of these necessary data will be obtained by developing a working relationship with the appropriate State and Federal agencies (e.g., EPA) early in the technology's development life. One such effective relationship already exists and was a result of a Memorandum of Understanding (MOU) established between the DOE and the EPA in the spring of 2000.

STAKEHOLDER STRATEGY SUMMARY

In equal importance to its technical and regulatory components, the TMFA's comprehensive incineration alternatives program will support a critical stakeholder/political aspect to ensure public input and gauge public acceptability. The need for a stakeholder component was exemplified by a recent lawsuit by residents of Jackson Hole, Wyoming. These residents were in resistance to the establishment of a hazardous waste incinerator for mixed transuranic waste at DOE's National Laboratory in

neighboring Idaho. The lawsuit was temporarily withdrawn upon DOE's subsequent establishment of an independent Blue Ribbon Panel of experts to identify alternatives. After a six-month evaluation, the Panel not only identified several appropriate alternatives for the Idaho incinerator, but also endorsed the TMFA's strategy for developing alternatives to DOE mixed waste incineration complex wide. As a result of the Panel's recommendation back to the DOE in December of 2000, the TMFA has begun to receive the additional resources needed to implement the strategy summarized in this document.

Based on the Jackson Hole experience, the TMFA will seek public input for all research, development, demonstration, and deployment efforts involving activities associated with identifying alternatives to mixed waste incineration. The present TMFA stakeholder strategy may involve use of the existing Citizen Advisory Boards (CABs) that have been established at all of the significant DOE sites and National Laboratories.

The TMFA and its sponsored investigators and technical developers, will present periodic status updates and results of their specific efforts and contributions to the CAB. As a consequence of the feedback received in public response to these updates, associated development efforts will be appropriately altered, accelerated, or terminated as allowable under existing budget and schedule constraints. In addition, the TMFA will leverage and potentially benefit from the successful stakeholder program established by the Department of Defense (DoD), as a result of their efforts to identify publicly acceptable alternatives for chemical warfare destruction.

REFERENCES

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