TECHNOLOGY DEVELOPMENT FOR TRANSURANIC AND MIXED WASTE APPLICATIONS

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INTRODUCTION

MSE Technology Applications, Inc. (MSE) is under contract to the U.S. Department of Energy (DOE) National Energy Technology Laboratory (NETL) to provide technology test and development services to the DOE Transuranic and Mixed Waste Focus Area (TMFA) for promising mixed waste treatment technologies and methodologies. This work is being conducted through DOE NETL at the Western Environmental Technology Office (WETO) under DOE Contract DE-AC22-96EW9605.

MSE has executed test projects for TMFA or its predecessor groups for the past 10 years. The DOE complex has many complex mixed waste treatment problems that range from offgas emissions compliance to treating or repackaging waste to comply with shipping and storage requirements of the Waste Isolation Pilot Plant (WIPP).

OBJECTIVE/APPROACH

The primary mission of the Thermal Programs division of MSE is to assist its main customer, DOE TMFA, in identifying specific problematic needs of DOE to remediate transuranic mixed waste problems. This is accomplished by working with TMFA to identify promising technologies for test/development at MSE. MSE has been designated by TMFA as its primary center for testing technologies for waste remediation. MSE designs and installs test beds, designs and executes tests, and develops recommendations for and assists in the deployment of successful technologies.

In Fiscal Year (FY) 2001, a high-level oxides of nitrogen (NO_x) thermal treatment unit was tested to treat up to 4% NO_x in typical DOE thermal waste treatment offgas. The unit removed more than 90% of the NO_x (exceeding test goals). The technology is now available for application to thermal waste treatment systems, i.e., joule-heated melters or plasma units, to remove high levels of NO_x that are expected to be emitted. Thermal Programs is actively assisting in deploying this technology for a high-nitrate waste processing facility at the Idaho National Engineering and Environmental Laboratory (INEEL).

Two major projects were initiated by TMFA at MSE this year—Handling and Segregating System for 55-gallon drums (HANDSS-55) and Alternative Technologies to Incineration (ATI).

HANDSS-55 will address a major DOE mixed transuranic waste problem. DOE has thousands of noncompliant [per U.S. Department of Transportation and WIPP waste acceptance criteria

(WAC)] 55-gallon drums containing mixed transuranic waste. Subsystems that were developed by the Savannah River Technology Center and the Robotics Crosscutting program (RBX) at INEEL are being integrated and tested as a full system at MSE. Integration and testing of HANDSS-55 will begin at MSE during FY 2002 and continue through FY 2004 with shipment to the Savannah River Site (SRS) for installation and cold start-up by late FY 2003. The SRS is scheduled to begin hot operations by the end of FY 2004.

The ATI project was also initiated in FY 2001. Due to public pressure, DOE formed a special blue-ribbon committee to investigate the incineration problems and develop recommendations. Based on these recommendations, DOE has ceased operations at all but one of its mixed waste incinerators, which created a need for identifying alternative nonincineration technologies (thermal, nonoxidizing, aqueous based, and chemical separation). Most of these technologies appear to be at a relatively immature stage compared to incineration, and much testing and development will be necessary. MSE has been selected as the center to test many of the candidate technologies. Testing ATI will continue through FY 2006, and deployment of technologies is scheduled to begin in FY 2007.

MSE is also developing three related products for commercialization. Much progress was made in the advancement of these products this year, and the target for commercialization of all three is the end of FY 2004. These products are the mercury removing plasma-enhanced electrostatic precipitator (PEESP); a gas chromatograph (GC)/mass spectrometer (MS) based mercury detector [know as accelerated polychlorinated dibenzo-p-dioxins/dibenzofurans sampling and analysis (APSA)] and a "fast" detector, also GC/MS based, for quickly (compared to baseline technology) analyzing dioxins/furans (highly toxic pollutants emitted primarily from thermal waste treatment systems). Commercialized, these products will detect and remove mercury from coal-fired power plant boilers and provide diagnostic data for minimizing dioxin/furan production in ATI systems.

MSE is committed to providing excellence in technology test/evaluation and subsequent technology commercialization to solve DOE's and private industry's waste cleanup and gas emissions problems.

PROJECT DESCRIPTIONS/RESULTS/BENEFITS/FUTURE ACTIVITIES

Offgas Test Bed Readiness/Maintenance Task

The present offgas treatment test bed is being maintained to accommodate possible ATI thermal waste treatment technologies. This work will include clean out of offgas piping; replacement of the corroded pipe section; clean out of the wet scrubber, baghouse, and ceramic filters; long-term lay-up of the continuous emissions monitoring system; and facility housekeeping items. Figure 1 shows a process schematic of the test bed.

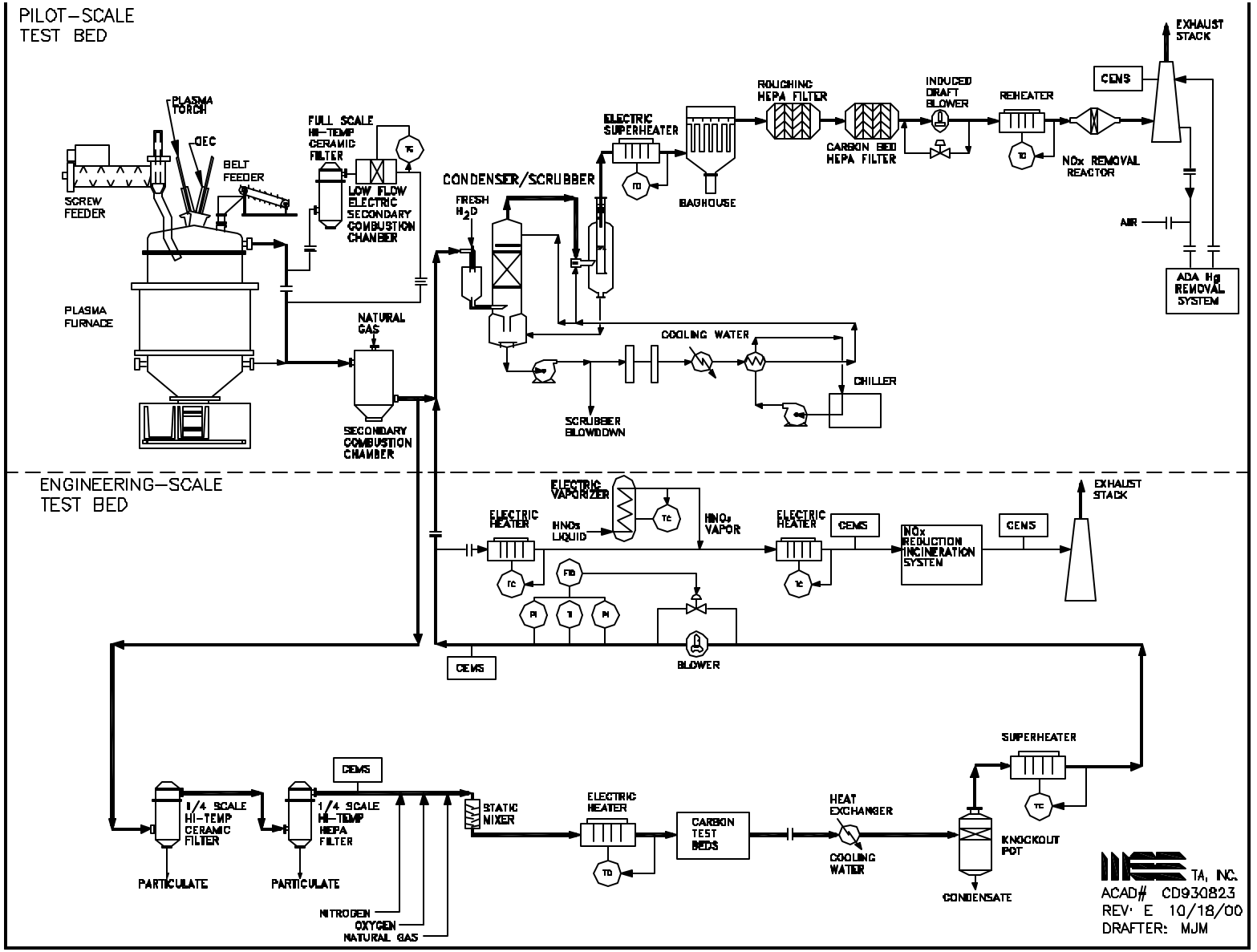

Figure 1. M S E test bed.

Handling and Segregating System for 55-Gallon Drums Project (Ref. 1)

Many facilities within DOE are generating and/or storing radionuclide contaminated hazardous waste (mixed waste) that is classified as Land Disposal Restricted under the Resource Conservation and Recovery Act (RCRA). The Federal Facilities Compliance Act of 1992 (FFCA) requires each facility, at which DOE generates or stores mixed waste, to develop plans for treatment, or for cases where no treatment technology exists, generate plans for developing such a technology. The FFCA provides incentive for accelerating efforts to develop, design, and construct facilities that will render DOE mixed waste into a form that can be disposed of legally and inexpensively. The disposal of mixed transuranic waste must meet the approval of both the U.S. Environmental Protection Agency (EPA) and the Nuclear Regulatory Commission.

The SRS has thousands of drums of mixed transuranic waste that is being stored awaiting certification and transfer to WIPP. The waste comes under the auspices of both the RCRA and the Atomic Energy Act. These drums must meet WIPP WAC before being transferred to WIPP. The SRS committed to the state of South Carolina, through their FFCA, to submit a plan outlining the schedules and activities required to prepare mixed transuranic waste for shipment from SRS to WIPP by January 1999.

A system was developed by RBX and TMFA to repackage drummed, mixed transuranic waste to meet WIPP WAC. This system, HANDSS-55, will economically and remotely open, sort, and segregate noncompliant components of the waste inside the drums and repackage the compliant components in a new drum now suitable for shipment to and acceptance by WIPP. Examples of WIPP WAC prohibited waste items include free liquids, pressurized containers, and heavy/unpadded items that could shift during movement and damage the package interior.

The waste conditioning needs of DOE sites require that new technologies be developed to fill the various needs for remote, automated equipment to protect human health and the environment. Due to the hazardous and radiological components found in transuranic and mixed transuranic waste, many problems are difficult and time consuming to solve or even impossible to complete safely without automated technologies. Currently, if the needs of a waste handling organization require waste conditioning, a person must suit up in personal protective equipment to guard against contamination. There may be additional costs associated with damage to the environment or high dose rates to workers. HANDSS-55 provides this automated, modular waste conditioning function to solve the difficult waste handling issues. Present drum repackaging is done at approximately two barrels per 10-hour day, while HANDSS-55 will process four barrels per 10-hour day, decreasing the time it takes to qualify barrels to be shipped to WIPP, while even more importantly, greatly minimizing the risk of radioactive exposure to workers.

HANDSS-55 provides a robotically operated technology to process transuranic and mixed transuranic waste for shipment to WIPP in New Mexico. The technology incorporated in HANDSS-55 is both automated and modular to allow individual modules to be used with a multitude of other applications. The separate HANDSS-55 modules provide a unique ability to satisfy special needs at any of the many waste generator sites. Specifically for this work, the

system will be used to address the need of SRS to repackage its noncompliant drums for shipment to WIPP.

The four primary modules of HANDSS-55 are the Waste Sorting Module; the Transuranic Waste Repackaging Module; the Process Waste Reduction Module; and the Systems Integration and Control Module. These modules may be used individually or as an integrated system. Each module will be self-functioning and demonstrated separately during development. Following separate demonstration tests, control and hardware integration will be completed to make the modules function as a single integrated system (see Figure 2).

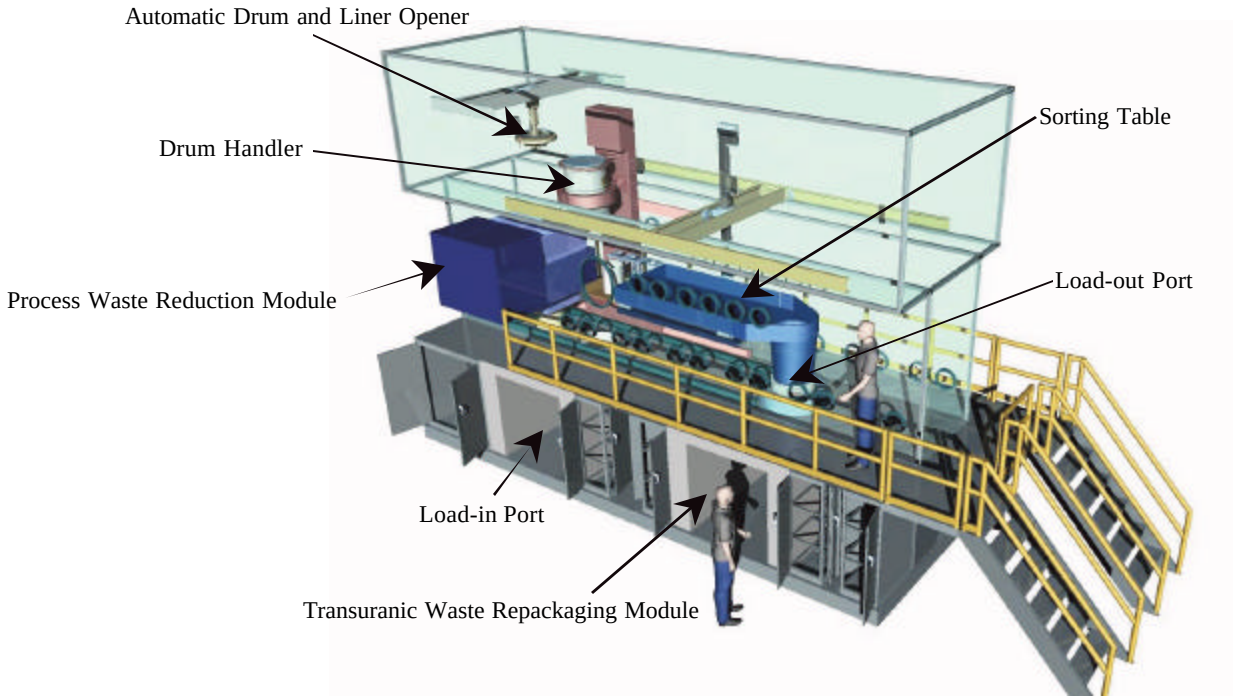

Figure 2. HANDSS-55.

Waste Sorting Module

The Waste Sorting Module is comprised of two components: 1) the remote drum and liner opener; and 2) the waste sorting station.

Remote Drum and Liner Opener: This component is automated and functions remotely to open 55-gallon metal drums and their accompanying polyethylene liners that contain waste. Personnel are removed from the hazardous environment of accessing waste inside the drums. The remote drum and liner opener was tested (in a noncontaminated environment) and is operational.

Waste Sorting Station: This station receives waste from the opened 55-gallon drums and visually identifies each item. Each item will be classified as acceptable or not acceptable for a specific wastestream. Those items that are identified as not acceptable are removed from the wastestream using remote automation. The noncompliant items that are removed from the

wastestream are then tracked in a database and are set aside for final disposition. The remaining waste is classified and weighed for disposal records.

Transuranic Waste Repackaging Module

This bagless transfer port offers a capability that does not exist today. The bagless transfer allows waste to be moved from a contaminated environment to a standard waste box or other WIPP acceptable shipping container. Radioactive materials may be bagged or placed directly into the container. Automating the loading process reduces labor requirements and cost. The system has low cost on a per container basis and is adaptable for a remote-handled environment.

Process Waste Reduction Module

This module will size reduce the cut open 55-gallon drums and liners for volume efficient waste disposal. The process reduces shipping and storage costs through decreased volume. The processed drums and liners will be added to the shipping container for final disposal.

Systems Integration and Control Module

The modular design of HANDSS-55 provides a versatile control system that allows operation from either a central control system or an individual module control. The touch screen menu-based control system provides a user friendly environment that is simple and powerful for the operator. Voice recognition will be standard with the Waste Sorting Module and is available as an option for the other modules. The control system format allows the user to operate the equipment at high- or low-level automation to allow for fully automated or manual control.

Alternative Technologies to Incineration Project

The ATI project was initiated in response to a DOE blue-ribbon committee appointed to respond to the problem of public nonacceptance of hazardous waste incineration as an environmentally safe option. Only one of four DOE thermal waste treatment systems remains in operation and it may be shut down within 2 years. The blue-ribbon committee identified several ATI as a starting point for consideration. The DOE appointed blue-ribbon committee issued recommendations for waste treatment alternatives in December 2000.

MSE was selected by TMFA as the main test center for obtaining data for evaluating ATI. Initial work is focusing on INEEL's 3,100-cubic-meter project. The 3,100 cubic meters of waste must be shipped to WIPP by the end of 2002. INEEL's most immediate need is to treat thousands of cubic yards of sludge, contained in barrels, to rid them of hydrogen and hydrogenated organics to qualify the waste for shipment to WIPP.

The ATI testing will range from bench- to pilot-scale demonstrations. Technologies considered may be from five classes of incineration alternatives: thermal without incineration (carbon arc, steam reforming, and plasma), aqueous-based chemical oxidation, dehalogenation, separation (soil washing, solvent extraction, and thermal desorption), and biological treatment. Side-by-side comparison testing at WETO is expected to be initiated in FY 2002 and completed by the

end of FY 2006. It is expected that data will be collected, summarized, and issued for evaluation by others. This data would be used for performance evaluation, design/scaleup, and permitting of selected ATI.

The ATI project is testing various sorbents for their ability to immobilize free aqueous liquids in INEEL waste drums (see Figure 3). Drums containing free liquids do not meet WIPP WAC. A test bed is also being designed and installed to test the concept of thermally desorbing surrogate sludge drums laden with hydrogen and hydrogenated organics (see Figure 4). Drums with certain levels of hydrogen are also not allowed to be shipped to WIPP.

Figure 3. Fourteen-day sorbent test at 70°F.

Other ATI will be selected for testing by issuing a request for proposal and awarding subcontracts. For each tested technology, a test bed will be designed and installed, a test plan developed and issued, testing performed, and a report issued. The technologies may vary from thermal nonoxidizing systems to nonthermal aqueous-based systems and separation systems.

The overall benefit of the HANDSS-55 project is SRS and other DOE sites with mixed transuranic waste drums that are suspected of not meeting WIPP WAC will have a technology to open and repack the drums so they can be shipped and buried at WIPP.

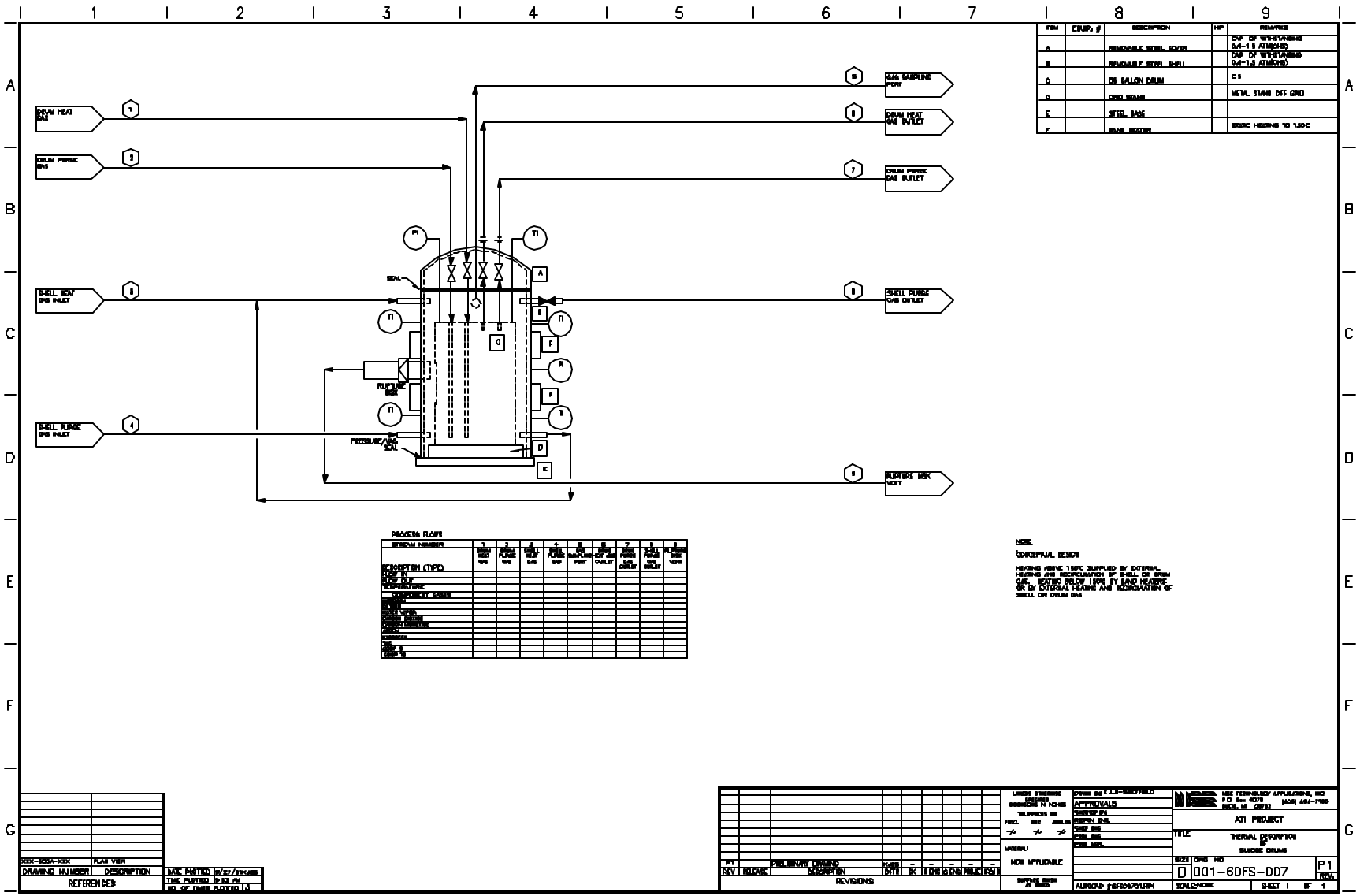

Figure 4. ATI process schematic.

Accelerated Polychlorinated Dibenzo-p-dioxins/Dibenzofurans Sampling and Analysis

"Fast" GC/MS dioxin/furan sampling and analysis (also know as APSA) development will continue in support of the ATI demonstration tests. Because one of the requirements for ATI is to remove organics from the treated wastestreams, there is the possibility that dioxins/furans may form and emissions may be emitted. The APSA method is projected to yield sampling/analysis results in approximately 3 hours versus the EPA Method 23 turnaround time of weeks, making the technology extremely useful as a near on-line diagnostic tool.

This technology combines a novel application of thermal desorption sampling with a standard GC/MS technology to sample and analyze offgas for dioxin/furan content at offgas temperatures up to 1,800 °F without sending the sample to an outside vendor for analysis (see Figures 5 and 6). This could have a very beneficial use as an offgas system diagnostic tool. This diagnostic capability could be very useful in characterizing offgas at various process points in ATI systems and could aid in process optimization to minimize dioxin/furan production within the system. The technique may also be directly applicable to screening soil or other solid waste samples for dioxin/furan or polychlorinated biphenyl.

Figure 5. APSA sampler.

Figure 6. APSA GC/MS.

The primary objective of the FY 2001 APSA activity was to test high-resolution (HR) MS as a means of overcoming background interferences previously observed in offgas samples taken from a DOE pilot-scale incinerator (modified WETO 6-foot plasma arc centrifugal treatment system) and an EPA experimental marine boiler at Research Triangle Park (RTP). To obtain offgas samples at a manageable cost, a secondary objective was to construct a bench reactor capable of generating dioxin containing offgas samples.

A bench-scale reactor, for the purpose of generating simulated offgas samplers containing elevated levels of dioxins/furans, was fabricated, successfully operated, and dioxin/furan samples were taken. The samples were sampled using the equipment mentioned above and analyzed by GC/HR MS [Montana State University (MSU) subcontract] to isolate the presence of previously observed severe background interferences.

The FY 2001 work demonstrated that HR MS could resolve and quantify dioxins/furans in the presence of background interferences expected in difficult offgas samples containing a complex mix of other organic and inorganic compounds.

The main objective of FY 2002 work will be to improve detection limits and quantify accuracy of the APSA method. The multiyear goal (by the end of FY 2004) of this work is to have a field deployable instrument capable of meeting regulatory detection limits with a sampling and analysis cycle of 3 hours. Even if regulatory detection limits are not achieved, the instrument will still be useful as an industrial process diagnostic tool, i.e., useful for measuring dioxin/furan levels at various points in process offgas that is upstream of the stack.

The FY 2001 HR MS results will be used to identify background interferences in thermal desorption based sampling and analysis of offgases for dioxins/furans. Procedures will be developed to reduce background interferences to a level that low-resolution (LR) MS detectors can be used to identify and quantify the dioxins/furans. The goal is to reduce interferences by modifying thermal desorption procedures or modifying hardware. If procedure or hardware modifications are not successful, other strategies, i.e., in-situ partial solvent extraction, will be investigated. A final report will be written.

MSE's work scope is to continue developing fast methods of dioxin/furan sampling analysis with emphasis on thermal desorption based methods or other methods, such as supercritical fluid extraction, if thermal desorption techniques prove infeasible. Thermal desorption samples will be compared to Method 23 extraction and analysis. Analysis will be primarily by GC/LR MS; but because of the complexity of analyzing for the 210 possible dioxin/furan congeners and the complexity of background interferences, a limited number of samples will also be analyzed by GC/HR MS at MSU and at a commercial, certified laboratory.

The EPA at RTP is conducting research that may have a bearing on the present task to develop a fast method for sampling and analysis for offgas dioxins/furans. A subtask in this project is to coordinate efforts in this project with related research being performed at EPA RTP, the Diagnostic Instrumentation and Analysis Laboratory at Mississippi State University, and SRI, Inc.

The FY 2003 goal will be to complete tests on desorption/extraction procedures with GC/MS and SRI, Inc.'s Jet-REMPI customized thermal desorption hardware. The FY 2004 goal is to commercialize the technology.

Plasma-Enhanced Electrostatic Precipitator

The PEESP technology is being developed by MSE and Croll-Reynolds to address the possible mercury emissions from ATI and also mercury emissions from coal-fired power generation plants. The EPA has set a goal to reduce mercury emissions from coal-fired plants by 90% within the next decade. Presently, it is estimated that U.S. power plants emit 40 tons of mercury per year.

The PEESP technology enhances Croll-Reynolds present electrostatic precipitator by adding a proprietary reagent gas (see Figure 7). The gas is injected through electrically charged electrodes into the target mercury-laden offgas. The injected, now ionized, reagent gas reacts with elemental mercury and mercury compounds to form a mercury compound that is readily dissolved in the precipitator water spray and is removed with other pollutants from the offgas. Initial bench-scale results show that the PEESP removes 90% of mercury in a simulated offgas. Efforts are ongoing to advance the technology from bench scale to pilot scale.

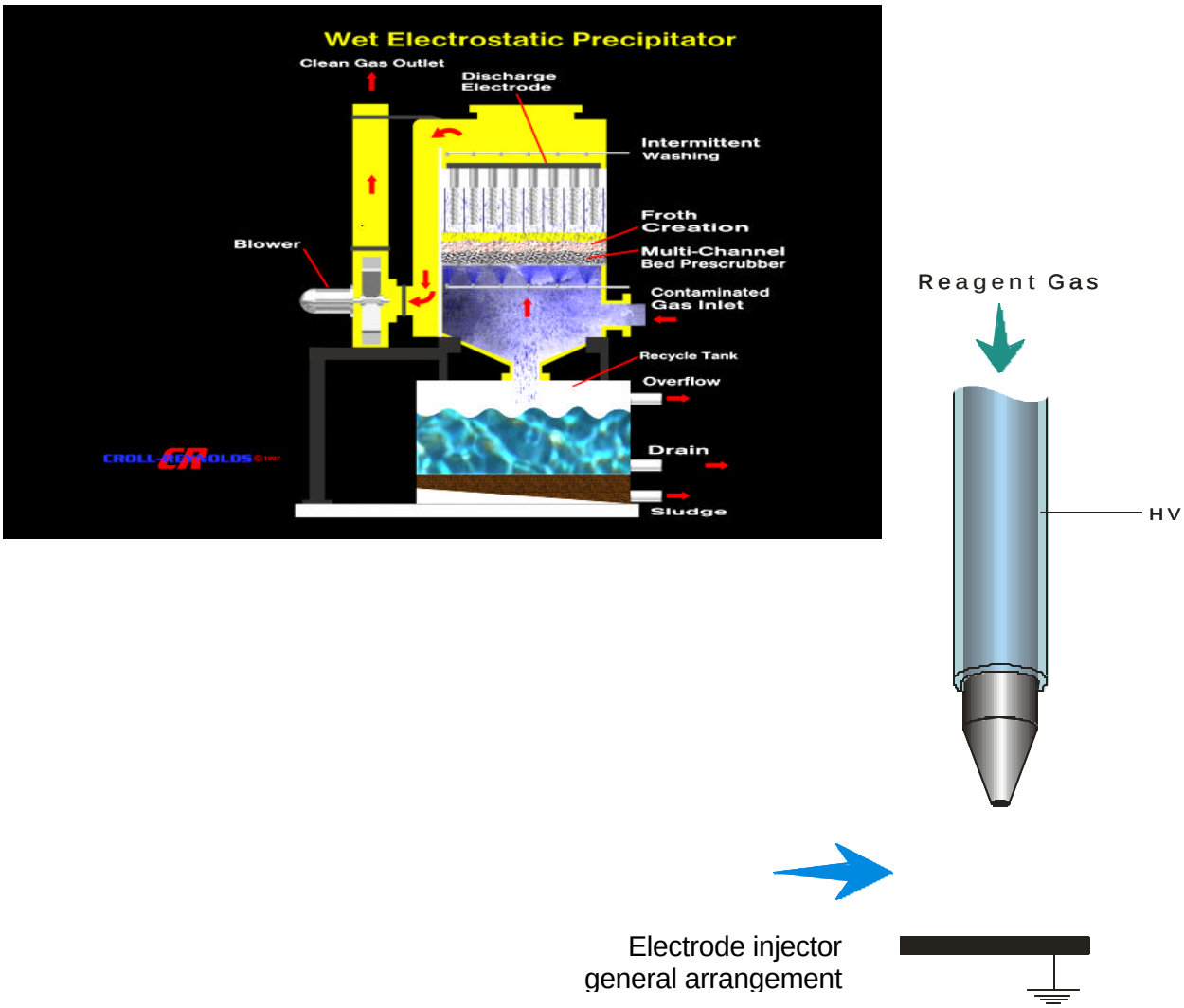

Figure 7. PEESP.

"Fast" GC/MS Based Mercury Monitor

The "fast" GC/MS based mercury monitor technology fulfills a need to be able to identify various mercury species in a mercury containing offgas or soil in a timely manner. This technology is being developed privately by MSE. The present EPA Method 29 and Ontario-Hydro method require that a sample be sent to a certified laboratory, and obtaining results can take weeks. Also, both baseline methods do not identify specific mercury species, especially mercuric chloride and methlymercury. Identifying specific mercury compounds is important in optimizing mercury producing and mercury emitting processes for minimum emissions. This technology could be used as a diagnostic device to characterize coal-fired boiler gases, mercury content in soils, and mercury in ATI processes. To date, proof of concept qualitative data has been obtained. Ongoing work to obtain quantitative data is being executed using an MSE proprietary sampling method.

REFERENCES

1. *Functional and Operational Requirements for the Deployment of HANDSS-55 at the Savannah River Site,* INEEL/EXT-99-00055, January 1999.