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TECHNICAL RESOURCE DOCUMENT FOR ASSURED THERMAL PROCESSING OF WASTES

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ABSTRACT

This document is a concise compendium of resource material covering assured thermal processing of wastes (ATPW), an area in which Sandia aims to develop a large program. The contents identify important issues and show where Sandia capabilities enable making significant advances. The report will be valuable to Sandians involved in further ATPW program development.

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1.0 INTRODUCTION

1.1 Background and Intent

Assured Thermal Processing of Waste (ATPW) is a Sandia activity that originated in Sandia/CA site planning conducted during the summer of 1992. During that period several Sandians asked questions like "Isn't confronting how to deal with society's many wastes an area in which Sandia can have major national impact and live up to its strategic intent?" and "Aren't required waste processing activities broad enough that Sandia can build a large, coherent program in the area?" Enthusiastically positive answers to questions like these led to the incorporation of ATPW into the Sandia/CA site's strategic plan with Bill McLean (8300) the sponsor and Don Hardesty (8361) the owner. All three Sandia sectors have supported ATPW program development, which is appropriately viewed as a Sandia-wide initiative led from the CA site.

During the summer of 1993 over two dozen Sandians and several staff of Energy and Environmental Research Corporation, an organization with broad experience in thermal processing, formed a team with the goal of developing the foundations for a Sandia ATPW program that could grow rapidly in funding to a level of tens of millions of dollars per year. The team expressed its goal and defined ATPW in the following statement excerpted from the August 1993 status report.

The ultimate goal of this program is to address and solve the critical issues related to Assured Thermal Processing of Waste for the safe and publicly acceptable destruction or conversion of hazardous chemical and mixed wastes from industry and the defense complex, as well as from municipalities.

Two separate parts of the ATPW team focused on: 1) issues related to conceiving a strong technical program, the technical team, and on 2) those issues related to obtaining financial support for it, the marketing team. Each group developed extensive documentation. This report presents technical material developed by team 1, the technical evaluation team, that the team believes will be valuable to Sandians involved in further ATPW program development. Its contents identify important issues and show where Sandia capabilities enable making significant advances. The report is intended to be a concise compendium of resource material that describes technology issues and Sandia's ability to address them, not a textbook that can serve as a general introduction to ATPW, nor a directed marketing tool. The names of individuals who contributed material and who can be consulted for more extensive discussions appear at appropriate places throughout the report. The team made an effort to learn of all Sandia capabilities and activities related to ATPW, but its coverage is imperfect and emphasizes the California site. The editor, George Fisk (8355), will appreciate receiving material enabling revisions that strengthen the document.

1.2 Organization

This report comprises nine chapters, of which Chapters 3-7 discuss specific major elements of ATPW. Each of these chapters describes the element covered, discusses issues associated with its further development and/or utilization, presents Sandia capabilities that address these issues, and indicates important connections to other ATPW elements. The division of the field into elements was driven by the team's desire to emphasize areas where Sandia's capabilities can lead to major advances and is therefore somewhat unconventional. There is, for example, no discussion of characterizing input waste streams because the team concluded that Sandia capabilities enable approaches that minimize the need for extensive characterization beyond what is done today. Similarly, discussion of air pollution control devices is relegated to a section of the appendix because the area is relatively mature and the industry supporting its needs is well developed.

Chapters 1-8 were prepared by team members who drew on the expertise of fellow Sandians as necessary. The same is true of each section of the Appendix, Chapter 9. Following this introductory chapter, by George Fisk (Org. 8355), Chapter 2, by Jim Ringland (Org. 8112) and Charles Hartwig (Org. 8366), presents a distillation of the team's most important findings. Chapters 3 and 4, by Bob Hurt (Org. 8361), treat, respectively, a variety of both conventional and emerging thermal processes, and opportunities for applying advanced process control to ATPW. Roger Farrow (Org. 8351) discusses in Chapter 5 the roles of sensors in ATPW and specific Sandia capabilities that can be the basis for the next generation of instrumentation. Chapter 6, by Bill Swansiger (Org. 8712), focuses on a powerful new approach to assuring that emissions are always maintained at acceptable levels, even during inevitable periods of off-normal operation. In Chapter 7 Jim Ringland (Org. 8112) identifies important needs for systems analysis and integration and indicates Sandia's role in filling them. Charles Hartwig (Org. 8366) covers in Chapter 8 several issues that connect purely technical areas with those of public policy and perception.

Chapter 9 is an appendix comprising nine sections. Section 9.1 presents instructive material relevant mainly to Chapter 4. Section 9.2 covers air pollution control devices and is related most closely to Chapter 6. Sections 9.3 and 9.4 describe Sandia capabilities that enable a strong ATPW program. Sections 9.5, 9.6, and 9.7 list the many projects presently conducted at Sandia/CA that are strongly related to ATPW. Section 9.8 lists less closely related Sandia projects. Finally Section 9.9 defines the acronyms and initialisms used in the report.

2.0. CONCLUSIONS AND SUMMARY

2.1. ATPW Team Conclusions

Our nation faces a growing waste disposal problem. A wide gamut of waste, ranging from municipal trash to hazardous toxic materials, require safe, economical, and environmentally conscious disposal. Many see thermal processes, including but not limited to incineration, as effective and economical methods for reclaiming value from wastes and ensuring their disposal. Others now question their value, citing concerns that existing thermal processes may generate harmful by-products, may not completely destroy waste, or may lose reclaimable products. Sandia National Laboratories has the capabilities to reduce greatly these concerns about thermal processing of wastes.

The Assured Thermal Processing of Waste program at Sandia is examining a wide variety of waste streams and thermal processes. Waste streams under consideration include municipal, chemical, medical, and mixed wastes. Thermal processes under consideration range from various incineration technologies (rotary kilns, industrial boilers, etc.) to non-incineration processes such as supercritical water oxidation or molten metal technologies.

Below we outline our vision of assured thermal processing of waste and briefly summarize specific contributions Sandia can make in six key areas. The presentation is organized around the ATPW team's five top-level conclusions, followed by brief discussions of each. This chapter concludes with somewhat lengthier summaries of the key topic areas.

The critical central feature in the Assured Thermal Processing of Waste is the concept of assurance.

By assurance we mean all the elements necessary to guarantee to the satisfaction all interested parties—the public, government regulators, and plant operators—that all effluents will be continuously maintained within levels acceptable to all. This has three facets: *ensuring* by proper plant design and operation that thermal processes will meet emissions goals, *demonstrating* that these goals are, in fact, always met, and *defining* acceptable levels to meet in the first place. Assurance entails a spectrum of issues and concerns, ranging from technology (device performance, system integration and control, information management) to economics (cost/benefit of various means of waste management) to sociology and politics (public perception of waste management risks, lack of trust in officials and organizations responsible for waste management). This Sandia initiative acknowledges each of these technical and nontechnical aspects as critical.

Assurance, today, is achieved indirectly. Plant control is based on operating parameters such as temperature, flow rates, and a limited number of emissions measurements. Emissions are evaluated in trials with special measuring equipment. There is, for example, no ongoing monitoring of problematic pollutants such as metals or dioxins. Based on this testing and rudimentary plant control, plant operators and regulators infer that emissions will be acceptable. Such an inference does not provide the assurance a direct measurement could.

The combination of advanced sensing and intelligent control has the potential to add a crucial element of operational assurance that major thermal processing technologies lack — both in ensuring processes meet their goals, and in unambiguously demonstrating that fact to others.

Continuous emissions monitors, which operate in real or near-real time, can meet the goal of demonstrating conformance to emissions requirements more directly than is done today. Process sensors allow a better understanding of what is happening within the kiln, boiler, or other system. Using intelligent control systems, a plant operator (or control system) can compensate for conditions that could potentially lead to an upset before it occurs, thus better ensuring the plant meets its goals. If an upset occurs, the control system we propose may divert and store the effluent for the duration of the upset. When normal operation resumes the stored effluent can be recycled through the processing system. Ultimately, this combination of monitoring and intelligent control can lead to optimizing plant efficiency.

There is considerable promise in novel and emerging thermal technologies that might avoid many emissions assurance issues in the first place.

Some, such as supercritical water oxidation or molten metal technologies, are fundamentally different from incineration. The problems of ensuring and, especially, demonstrating acceptable emissions may be easier for these. Many of these are tied to specific or difficult to handle waste streams.

While Sandia may not always work on all aspects of ATPW for a given application, it is important to always work toward a system-level approach to waste processing that integrates advanced technical features and acknowledges nontechnical considerations.

Thermal processing of waste is ultimately a systems integration task. In addition to the basic thermal process, its control, and its monitoring, many other technical elements must be successfully integrated to ensure that plants meet emissions goals. Provision must be made for upset processing, dealing with temporary off-normal situations that might lead to excess emissions. The feed stream must be managed appropriately. A major portion of a thermal process is the air pollution control system, dedicated to the downstream elimination of unwanted emissions. Solid and liquid wastes and residues after the thermal process must be characterized and disposed of or reclaimed carefully. Of these, Sandia is most likely to make major contributions only in the area of upset processing, but Sandia must understand how all integrate into a functioning system.

Beyond these purely technical considerations, the concept of assurance also incorporates the broader perspective of risk management. This includes risk assessment, cost/benefit analysis, life cycle concepts for resources, and the structuring of less quantitative factors that enter into defining emissions goals. Sandia can work with the public, regulators, and industry on these efforts as appropriate, but will not presume to resolve fundamental issues of rational waste management and public policy through the application of technology alone.

An overall balance is needed in best assembling elements of an ATPW system. Choices should be measured by the benefits gained, risks managed, and cost incurred. By understanding these technical and nontechnical issues, we can best structure our program to anticipate needs of potential sponsors.

Sandia should emphasize activities in six areas: thermal processing, process control, sensors, upset processing, systems analysis and integration (including risk management), and independent assurance.

Thermal processes—The major high volume incineration processes are fairly mature. Here, Sandia should focus on advanced sensing and intelligent control. In some cases, a more fundamental understanding of the ability to model the process would noticeably enhance operational capability. For emerging technologies, Sandia can play a leadership role in fields such as supercritical water oxidation and pulse combustion and can collaborate on specific problems in a variety of others. Cutting across all is the need for better understanding the combustion chemistry of halogenated materials and the chemistry and transport of toxic metals in thermal waste systems.

Process control—Technical challenges vary widely from process to process, with opportunities in hierarchical feedback control, fast feedforward control, and control of overall plant operations. Sandia brings tools in numerical process modeling, adaptive control, pattern recognition, and neural networks. A particularly exciting opportunity is the use of interstage sensing and fast feedforward control to mitigate "puffing" (transient fuel rich conditions that can lead to high releases of carbon monoxide, hydrocarbons, and products of incomplete combustion).

Sensors—Sandia is in a prime position to provide fast indication sensors for upset processing, fast and quantitative sensors for intelligent process control, reduction of the required margin of operation, and continuous emissions monitors that directly demonstrate acceptable emissions. We should take the lead in driving the significant advances in existing sensor technology that ATPW requires: greater speed and sensitivity in sensors that are rugged and simple in operation for use in the field. Many of these challenges can be met through optical diagnostic techniques that Sandia's combustion programs are now developing or using. The class of coherent, nonlinear techniques is especially suitable for ATPW, owing to capabilities for spatially and temporally precise measurements in harsh, high-temperature environments. Sandia also has expertise with other powerful laser and non-laser based techniques used in its research and development laboratories. We can also draw on experience with developing instrumentation for weapons testing and sensors for several environmental, commercial, and industrial customers.

Upset processing—Upsets, off-normal operations that can lead to higher than normal emissions, can be managed by sensing the upset and diverting the effluent stream to a storage tank for reprocessing. With advances in continuous emissions monitoring and fast process switching, we believe such divert-store-recycle systems could be implemented in the future. Sandia should play a role in developing these systems. Sandia brings understandings of basic thermal processes, real-time diagnostics, intelligent process control through process modeling, and system integration.

Systems analysis and integration (including risk management) and life cycle analysis—Interdisciplinary systems analyses can guide ATPW technology development. These include simple technology screening and selection studies, more complex process modeling and simulation, and risk management activities. Tools for screening and selection studies are drawn from the areas of operations research, decision analysis, and risk assessment. Process modeling and simulation can support the integration of thermal processes, sensors, and process control. Risk management combines quantitative risk analysis and cost/benefit analysis with a variety of qualitative social and organizational factors into a rational decision framework to define the overall goals of assurance. Sandia brings extensive experience in all these areas. We have, in particular, had a lead role in risk analysis in nuclear reactor and defense areas.

Independent assurance—Beyond the technical and process aspects defined above, assurance can be seen as an issue of transfer and translation of technical information. Sandia, as a government laboratory, is well positioned to serve as an impartial yet technically knowledgeable reviewer and arbiter in this process. Sandia must continue to actively explore what the criteria for public acceptance of thermal processing will be, and we should seek to anticipate some of the technical information that will be involved. Sandia can also contribute to the technology of risk communication.

It is worth emphasizing that while Sandia should concentrate on these areas, Sandia should monitor and contribute in specialized ways in several others. In sensors, process control, and some emerging thermal processes, we can take a lead role. Conversely, development of high volume incineration processes is quite mature and what contributions we make will be incremental. Sandia probably does not have a major role in the development of air pollution control equipment, or the control and characterization of solid and liquid residue, and probably a lesser role, but not inconsequential, in feed stream monitoring. Finally, while Sandia can play a significant role in risk management activities through risk assessment, cost/benefit studies, and decision structuring, it is not appropriate for Sandia to take an advocacy position in public environmental policy debates.

2.2 Summary of Sandia ATPW topic areas

The following sections summarize in somewhat more detail the issues and Sandia's capabilities in the areas that Sandia should emphasize: thermal processes, process control, sensors, upset processing, systems analysis and integration (including risk management), and independent assurance. These summarize the Chapters 3-8 in this report, respectively.

2.2.1 Thermal Processes

There are many variations on the design of major incineration technologies, and there are a bewildering variety of emerging technologies for special applications. Chapter 3 concentrates on a subset of known thermal waste technologies that are likely to have significant commercial potential and involve R&D issues closely related to Sandia core competencies. The chapter contains brief discussions of each of the following major incinerator types: rotary kilns, cement kilns, fume incinerators, liquid injection incinerators, industrial boilers, and controlled air incinerators. The chapter also considers a number of promising emerging technologies with important Sandia connections: molten salt oxidation, pulse combustion, supercritical water oxidation, molten metal processing, plasma technologies, co-firing with fossil fuels, and steam reforming.

In general, the major, high-volume incineration processes are all mature technologies. While the design of these systems can certainly be improved, the improvements are likely to be incremental in nature and insufficient to change the public perception of these processes. A more fertile area for Sandia involvement is the development of assurance systems for the major incinerator types. This approach recognizes that these mature processes generally operate properly, as designed, but that the technology does not exist to guarantee, or *assure*, this proper operation on a real-time basis. The ATPW team believes that the combination of advanced sensing and intelligent control has the potential to add a critical element of operational assurance to the major incineration technologies. Advanced control schemes are best applied to fully developed technologies, where the process configurations are fixed and the process dynamics can be characterized using historical data or through measurements on the full scale. Sandia also brings the ability to fundamentally understand and model the process, which helps to more fully enable the control system.

The picture is quite different for many emerging technologies, where basic development work or waste-specific trials are needed. Sandia's contribution to emerging technologies should consist of: 1) playing a leadership role in the basic development of those processes for which Sandia already has a significant stake/foothold, i.e. supercritical water oxidation and pulse combustion; 2) collaborating to address specific problems arising in molten metal processing, steam reforming, plasma processes and the other technologies discussed.

Finally, cutting across all processes is the need for a better understanding of the combustion chemistry of halogenated materials and the chemistry and transport of toxic metals in thermal waste systems. Sandia has unique capabilities in both of these areas.

2.2.2 Process Control

Process control is believed to be an integral part of any assurance system for thermal waste processes, and must be closely coupled to advanced sensing and communication technologies. The complex, multiphase nature of many processes makes the design of optimal control strategies to deal with operational transients a challenging problem. In addition, wastes streams are often heterogeneous and their properties (concentration, volatility, heating value) may vary greatly and unexpectedly in time. Also, poor performance of the thermal system can lead not just to poor efficiency or poor economics (as is the case with many industrial processes) but to a hazardous condition for the employees and the public. Much more is at stake in the control of waste destruction processes than in the control of many manufacturing processes, and the control systems must reflect this basic difference.

Sandia opportunities in process control for thermal waste systems fall under three headings: (1) hierarchical feedback control, (2) fast feedforward control, and (3) control of overall plant operations. Regarding hierarchical control, there is an immediate need for intelligent systems that monitor and control the feed rates of waste, supplemental fuels, and combustion air to assure proper operating temperatures, oxygen levels, residence times, and system pressures. Such a system would optimally steer a process to maintain the operating conditions established during the test burn. There is an exciting future alternative to this current control practice that is based on real-time sensing of hazardous emissions.

The combination of advanced continuous emissions monitors and intelligent controls offers the possibility of real-time emission monitoring and direct control of the processes to minimize these emissions in an economic manner.

For many incinerators burning solid wastes or containers of liquid wastes, a particularly important issue is the so-called "puffing" problem. Highly volatile waste batches can lead to an excess of gaseous fuel in the combustion zone, which in turn may cause system overpressures, the consumption of all available combustion air, and the ultimate release of high levels of carbon monoxide, hydrocarbons, and other products of incomplete combustion. A particularly exciting opportunity in the control of thermal waste processes is the use of interstage sensing and fast feedforward control to mitigate puffing excursions for staged processes. The control concept comprises: (1) fast sensors for detecting fuel rich conditions in or near the primary combustion chamber, (2) fast data analysis and control algorithms, and (3) means of rapid adjustment of the combustion flows in the secondary chamber to consume the fuel rich puff. The basic system can be augmented by incorporating an adaptive control algorithm, in which the basic inner control loop effects fast feedforward control to destroy puffs in the secondary chamber, while the outer loop monitors the success of the inner loop (using existing stack sensing equipment) and adjusts the control parameters of the inner loop.

A variety of advanced tools at Sandia can be brought to bear on this problem, including numerical process modeling, adaptive control, pattern recognition, and neural networks. Sandia's activities and capabilities in process modeling, model-based control, and process control science and technology are briefly summarized in the section.

2.2.3 Sensing

Sensors play a central role in the Sandia ATPW program, both in monitoring process operating parameters and for monitoring emissions. These overlap since emissions monitors can be used as part of a process or upset control system. Process monitors tend to be the simpler of the two, sensing conditions such as temperature and major species concentrations such as oxygen or carbon monoxide. In contrast, emissions monitors are often used to measure concentrations of trace species. These generally involve more complex operating principles. Critical areas of sensor performance are response time and sensitivity. Recently developed *in situ* optical techniques are particularly interesting in these regards. Over the past two decades there have been major advances across a broad range of optical technologies, and many have seen considerable use in laboratory environments. Sandia's Combustion Research Facility has been at the leading edge in both the fundamentals and applications of such laser diagnostics. In addition, other analytic tools, such as mass spectroscopy and Fourier-transform infrared spectroscopy, have become commonplace in the research laboratory but have not seen significant application in waste processing. Summarized below are some of the major sensing needs, applicable capabilities, and development opportunities that we have identified as key to ATPW.

Process control, including mitigating upset conditions such as the "puffing" problem (see Sections 2.2.2 and 2.2.4), requires sensors that monitor such quantities as temperature, total hydrocarbons, carbon monoxide, or oxygen. For gas temperature sensing, we see a current lack of *in situ*, diagnostics that are rugged and sufficiently simple for operation by unskilled personnel in the field. The coherent anti-Stokes Raman spectroscopy technique with which Sandia has considerable experience, provides point-

resolved temperature measurements with potentially fast response. However, currently available instruments are too expensive, bulky and complex. With future advances in laser price/performance ratio, the instrument could become feasible for widespread application in ATPW. For total hydrocarbons or carbon monoxide detection, an infrared multichannel detector could be used to analyze optical emission from gases exiting the primary combustion chamber. This scheme offers simplicity, relatively low cost, and rapid response time. For oxygen, laser-induced fluorescence approaches appear promising.

The development of faster and more sensitive *continuous emission monitors* is receiving much attention from industry, spurred by ever stricter emissions regulations. However, in many cases ATPW demands capabilities not yet commercially available, especially with regard to response speed (required for upset processing) and sensitivity (for monitoring species with extremely low allowable emissions). Sandia sees a variety of approaches worthy of development in this area. Some of these are introduced below; more are discussed in Chapter 5. A key message to draw from this list is that different monitoring needs may have different sensor solutions. Sandia's breadth in this area is an important asset.

Among the many monitoring technologies, resonance-enhanced multiphoton ionization (REMPI) spectroscopy, with which Sandia has considerable expertise, is one of the most sensitive of the optical techniques for monitoring a wide variety of trace species, including chlorinated hydrocarbons and aromatics. For monitoring of metal emissions with sensitivity comparable to existing EPA extraction methods, optical techniques such as laser-induced fluorescence, REMPI, and optogalvanic spectroscopy are promising. For analyzing the metal content of aerosols and particles, the laser spark spectroscopy technique has been shown to detect metals at levels compatible with Clean Air Act standards. Tunable diode-laser (TDL) spectroscopy is a promising approach for monitoring NO_x, SO_x, and hydrocarbons. Sandia is already developing TDL monitoring technology for engineering applications in industrial process control and environmental sensing. For monitoring metal compounds, miniature lasers using infrared or uv wavelengths could provide site-wide maps. Moreover, lidars based on laser induced fluorescence offer exceptional sensitivity for such species as NO, SO₂, and NO₂. Sandia currently has ongoing lidar development programs at the California and New Mexico sites for climate research and environmental monitoring.

2.2.4 Upset Processing

Upset processing is defined here to be the means to prevent any excessive emissions that exit the air pollution control system during periods of off-normal operation from being released to the environment. This can be accomplished by sensing the upset, diverting the effluent stream to a storage tank for the duration of the upset, and recycling the stored effluent into the ATPW system after normal operation is restored. We refer to this as Divert, Store, and Recycle (DSR). The ability to assure the public and the regulatory agencies that emissions from any given incinerator are *always* within established guidelines could be very helpful in getting new incinerators permitted and allowing old incinerators to continue operating. This is especially true for incinerators that burn hazardous wastes.

Besides increased assurance, there are economic incentives for developing DSR and the elements of intelligent process control. Presently, safe and efficient operation of an

incinerator depends, to a large extent, on knowing the composition of the waste feed. It is very expensive to sort and characterize wastes. Having the means to handle upsets would allow the incinerator operator to greatly reduce his waste characterization costs and to operate near design capacity a much greater fraction of the time. For processes and waste streams requiring the assurance offered by DSR, intelligent process control offers the potential to reduce the frequency and duration of upsets, thus reducing the size and cost of the DSR system.

There are relatively few technical obstacles to implementation of a DSR-based upset processing system. The most important enabling technology is development of appropriate upset indicators to trigger diversion of the puff to the storage tank. The storage tanks themselves are proven technology, as are the blowers and diversion valves. The biggest uncertainty in estimating the cost of the DSR system is in deciding how big to make the effluent storage tank. Based on estimates by Energy and Environmental Research Corporation that most upsets last less than a minute, we assumed that a five minute holding capacity would be realistic. Using industry figures for near-atmospheric pressure gas holding tanks operating at 6.5 to 7 inches water column, a tank with the capacity to hold five minutes worth of effluent from a 100 ton per day municipal-solid-waste incinerator would cost about \$780,000 or about 6% of the total cost of plant. The cost of auxiliary equipment, such as valves and pumps, is small compared to the uncertainty in whether to size the tanks to collect one minute or ten minutes worth of effluent. For certain applications, an alternative to a larger storage tank might be to recycle the contents of the storage tank *during* an upset by adding oxygen to the effluent to bring it to combustion air standards and using it *in place* of combustion air. This would greatly reduce the amount of gas to be stored and would thus increase the duration of the largest upset that could be accommodated for a given tank volume.

It is worth considering whether a small DSR system could be mated with an existing burner, perhaps one at the Sandia Combustion Research Facility, to test the utility of the concept. Studies of upset conditions, surrogates, etc. could then be conducted without fear of releasing pollutants to the atmosphere. Also, the effluent collected in the storage tank could be analyzed using EPA methods and correlated with real-time process diagnostics. This could be the basis for a subsequent partnership in which Sandia would install diagnostics and intelligent process control along with a DSR system on an industrial incinerator.

We believe that a Divert, Store, and Recycle system is feasible with today's technology for certain thermal processes and waste streams. Even with relatively primitive upset sensors, a first generation DSR system would provide a level of assurance not presently attainable by any other means. Advances in continuous emissions monitoring will make such systems more generally applicable in the near future, and more stringent regulations may ultimately make them necessary.

2.2.5 Systems Analysis and Integration (including Risk Management) and Life Cycle Analysis

A variety of interdisciplinary studies will be needed support the technology activities introduced in the previous four sections and to best match these technologies with the issues, both technical and nontechnical, that they seek to address.

Several of the ATPW areas raise technology selection and integration issues that may be addressed by a range of process simulation and analytic models. At the simplest level, relatively short analyses, using fairly simple tools drawn from the areas of operations research, decision analysis, and risk assessment, may be useful to translate a general problem statement into terms relevant to making focused technological decisions. Data collection from disparate sources and integration into a form useful to all parties is generally the primary task here. At a more complex level, process simulation models, perhaps combined with economic analyses, may be useful to address technology choices that rest on detailed performance trade-offs. Management of a two- or multi-stage thermal processes can involve some combination of feed stream management, control of each of the thermal processes involved, and upset processing. Design for each of these needs to be balanced in a way that recognizes that a change in one may greatly affect another. Some design choices and trades are among various hardware configurations; others are between technological and operational or procedural approaches. One specific example might be the choice between designing a system to divert exhaust during upset conditions for subsequent processing, sizing on-line pollution control systems to deal with all upsets, or some mix of the two.

Beyond this direct support of system design, risk management studies will be needed to support the overall definition and description of assurance goals. Risk management combines quantitative risk analysis, cost/benefit analysis, and a variety of qualitative social and organizational factors into a rational decision framework. Sandia can play in several ways here. Detailed quantitative tools have primarily been applied to the risk analysis part of the problem, and Sandia has considerable experience here. We can also apply our background in cost/benefit analyses and problem structuring to work with the community in the broader risk management activities. While we recognize that public policy cannot be reduced to a series of formulas, the need exists for a structured decision process that includes costs, benefits, and nonquantitative factors.

2.2.6 Independent Assurance

The focus of Sandia's activities will be on the more technological aspects of assurance such as process development and continuous emissions monitoring. However, assurance can be viewed more broadly as an issue of the transfer and translation of technical information. This information is needed both by the regulatory community and by the public at large. Moreover, Sandia, as a government laboratory, can act as an impartial yet technically knowledgeable reviewer and arbiter in this process.

Sandia can work with regulatory bodies in two ways. First, we can assist in defining what needs to be technically demonstrated to show that all laws and regulations are being complied with. Support here may include selecting instrumentation, ascertaining the reasonableness of surrogate molecules, providing information about key processes, selecting key measurables, facilitating working with diverse groups, and providing risk assessments. Sandia can effectively do this job because we have the necessary technical background and we have the proven impartiality of a nonprofit government laboratory. Second, and more directly, Sandia can provide the means to get the necessary technical data itself. Development of continuous emission monitors is a clear example of this.

It is less clear what needs to be demonstrated in order to assure the public that a thermal process is operating in a safe and environmentally conscious manner. Many issues

are not technical. Three aspects of this issue need to be explored. The first step is to understand what the criteria for public acceptance of thermal processes will be. One useful forum to date has been the Western Governor's Association. It may also be worthwhile to pursue facilitated meetings with various other organizations and representatives of various viewpoints. Second and concurrently, we should try to anticipate the technical features that each thermal process has that could be important for assurance and work towards key measurements and means to interpret them that will be available when needed. Finally, we should anticipate the technical means of communicating this information to the appropriate public representatives. Through its computer and design departments Sandia is heavily involved in nation-wide information transfer, including its participation in the National Information Infrastructure Testbed, and is well qualified to help build the appropriate electronic data transfer network.

3.0 THERMAL PROCESSES

3.1 Introduction

This chapter deals with the heart of thermal waste treatment processes: the high- and moderate-temperature devices in which primary destruction of the hazardous material occurs. These high temperature devices are referred to here as simply "thermal processes," and may consist of a single high-temperature chamber, or a combination of primary and secondary chambers. This chapter contains brief discussions of each of the following major incinerator types: rotary kilns, cement kilns, fume incinerators, liquid injection incinerators, industrial boilers, and controlled air incinerators. The chapter also considers a number of promising emerging technologies with important Sandia connections: molten salt oxidation, pulse combustion, supercritical water oxidation, molten metal processing, plasma technologies, co-firing with fossil fuels, and steam reforming. The goal of these sections is to identify R&D needs, to match them to Sandia capabilities, and to make a assessment of the potential for Sandia involvement (or increased Sandia involvement is some cases). These discussions rely heavily on certain key individuals at Sandia and EER who have personal experience with the technology in question, and no systematic attempt has been made to gather information from multiple sources.

A further caveat should be mentioned at the outset: the information provided in this chapter does not constitute a complete treatment of the topic. There are many variations on incinerator design and there is a bewildering variety of emerging waste treatment technologies. Crossing this vector of processes with a vector of waste types results in a vast matrix of potential processes, each with unique advantages, disadvantages, and R&D needs. This chapter concentrates therefore on a subset of known technologies that are likely to have significant commercial potential, and involve R&D issues closely related to Sandia core competencies.

The following section presents a brief separate discussion of each of the major and emerging technologies, focusing on research and development needs and related Sandia capabilities. For many of the more mature processes, the most critical R&D needs relate to sensing and control in which case the discussion is brief and references are made to the appropriate sections of the report. At the end of the process-by-process discussions, a brief summary is given of two overarching themes/ideas that are relevant to many of the individual processes, and for which there is no separate section elsewhere in the report: chemistry of thermal processes, and engineering materials.

3.2 Sandia Contacts

For further information on thermal processes, please contact the following ATPW team members or other appropriate Sandians.

Robert Hurt	(510) 294-3707	Major Incineration Technologies
Steve Rice	(510) 294-1353	Supercritical Water Oxidation Molten Salt Oxidation
Jay Keller	(510) 294-3316	Pulse Combustion
Dale Blankenship	(505) 844-9694	Molten Metal Technology Plasma Technologies Steam Reforming
Jack Swearingen	(510) 294-3022	Co-Firing Military Wastes with Fossil Fuels
Frank Tully	(510) 294-2316	Chemistry of Thermal Processes
John Smugeresky	(510) 294-2910	Engineering Materials

3.3 Major Incineration Technologies

3.3.1 Rotary Kilns

Description

Rotary kiln systems used for waste treatment typically consist of two incineration chambers: the rotary kiln itself, a rotating, cylindrical, refractory-lined vessel; and an afterburner. The kiln itself is a cylindrical refractory-lined steel shell with a diameter less than 20 ft and a length-to-diameter ratio of 2-10. Kilns accept solid and liquid wastes fed on a continuous or semi-continuous basis. Liquid wastes may also be injected with steam or air-assisted atomizing nozzles. Solids residence time in the kiln is typically 1-1.5 hours, while gas residence time is typically about two seconds. Afterburners are typically operated at 2000°F with a residence time of one to two seconds to ensure complete combustion of the remaining volatile components in the flue gas. An auxiliary fuel, and sometimes pumpable liquid hazardous wastes, are used for temperature control.

Design modifications to the basic rotary kiln include a "fast" kiln (which rotates at a rate greater than 20 rpm to enhance mixing), starved air varieties, oxygen-assisted kilns (to reduce flue gas volume and auxiliary fuel requirements), and slagging kilns.

Research and development needs

R&D needs are summarized in the following prioritized list :

1. Assurance/control systems. Kilns are subject to puffs caused by feeding highly volatile or explosive solid wastes. Optical access to the rotating refractory-lined primary chamber may be difficult, but kilns are traditionally fitted with an afterburner, providing the possibility for interstage sensing and feedforward control. Puffing sensors are discussed in detail in the control section.
2. Improved understanding of dioxin/furan formation pathways. This is an important issue for most of the existing high-volume incineration technologies and is closely tied to the issue of assurance and safety. Polychlorinated dioxins and furans may form in the combustion chamber or at lower temperatures downstream in the air pollution control system.
3. Improved understanding of metals behavior. The high temperatures and mechanical agitation in kilns lead to high dust loadings and carry-over of toxic metals. Kilns and APC systems are designed to handle this loading for most wastes.
4. Measurement device for gas and flame temperatures. Furnace temperature is a primary control variable for incinerators, but its measurement is complicated by the presence of hot walls (making pyrometric techniques difficult) and particulate matter (making fine-wire thermocouples impractical).

Sandia capabilities that can address the needs

The development of assurance systems comprising advanced sensing and control is a promising area for Sandia—this is discussed in detail in the control sections. Such a system could be specially tailored to mitigate the puffing problem characteristic of rotary kilns. Sandia's applied sensing capabilities could also be brought to bear on the problem of temperature measurement in kilns. Sandia is also well poised to conduct fundamental studies of dioxin formation and toxic metal transformations. Both of these activities could be directed at major incineration types as a class, rather than rotary kilns in particular. The lack of any laboratory or pilot-scale combustion equipment capable of handling heterogeneous bulk solids may be a significant gap in Sandia's capabilities. This need might be met through industrial partners.

Evaluation

Rotary kilns are an important thermal waste technology that deserves Sandia's attention. Sandia's role would not necessarily involve the construction of bench or pilot-scale kilns, but could focus on sensing, and model-based control in a collaborative effort with kiln manufacturers and users. This has been the approach taken in the steel sensor development project in 8361, where all experiments

involving molten steel are performed at the facilities of the industrial partner, Bethlehem Steel.

3.3.2 Cement Kilns

Description

Cement kilns are inclined, rotating, refractory-lined cylinders, which are fired with fossil fuels to calcinate a blend of raw materials such as limestone, clay, shale, and iron ore. Raw materials are fed into the upper "cold" end, while fuels are typically fed into the lower "hot" end, so that the flow of exhaust is countercurrent to that of the feed materials. Solids residence time is on the order of two hours.

Liquid wastes are input directly into the kiln burner flame. The countercurrent flow of gas and solid in kilns make it quite difficult to feed solids in a manner that ensures adequate residence time for the solids *and* the volatile matter derived from them. There are three primary methods of feeding solid wastes: a) they can be introduced through a hatch at a point part-way down the kiln, b) they can be injected at the hot end of the kiln at a high velocity so that they land at a point far enough up the kiln to allow sufficient solids residence time, c) they can be burned in a separate kiln or combustor with the flue gas ducted into the hot end of the kiln.

Research and development needs

R&D needs for cement kilns are similar to those for rotary kilns and are summarized in the following prioritized list:

1. Assurance/control systems. Control of cement kilns is difficult due to the dual purpose (waste destruction and cement manufacture). This may be an argument for pursuing advanced control systems. Optical access to the rotating refractory-lined primary chamber may be difficult, but other sensor locations are possible.
2. Dioxin formation. As in rotary kilns, but organics in cement raw materials may also contribute.
3. Behavior of organics in kilns. Destruction and removal efficiencies are an issue due to the countercurrent flow of solids and gases, as is the role of organics in cement raw materials. These organics can interfere with the measurement of hydrocarbon emissions from unreacted waste materials or can interact with chlorine in the waste to potentially form dioxins/furans.
4. Temperature measurement and flame detection sensors. Measurement of gas temperature is complicated by the presence of hot walls (making pyrometric techniques difficult) and particulate matter (making fine-wire thermocouples impractical). Flame temperature sensors or flame monitors would be useful, but the "hot spot" in kilns is not stationary.
5. Metals behavior at the high kiln temperatures.

Sandia capabilities that can address the needs

Again, the development of assurance systems comprising advanced sensing and control is a promising area, which is discussed in detail in the control sections. Sandia is also well poised to conduct fundamental studies of dioxin formation under conditions relevant to cement kilns. Both of these activities could be directed at major incineration types as a class, rather than cement kilns in particular.

Also, the need for temperature measurement in the hot refractory-lined chamber is a challenging problem in applied sensing that Sandia is well equipped to tackle. Thermographic techniques (Organizations 8361, 8746) could be applied to avoid problems with the moving flame front in kilns. Spectroscopic techniques should also be explored to measure gas temperature (see the sensing section) in the presence of hot walls (a difficult problem for pyrometric or thermographic techniques).

Evaluation

Cement kilns are an important thermal waste technology that deserves Sandia's attention.

Sandia's role would not necessarily involve the construction of bench or pilot-scale kilns, but would focus on chemistry, sensing, and model-based control.

3.3.3 Industrial Boilers

Description

Industrial boilers and furnaces (BIFs) are enclosed, pressurized devices constructed to produce steam for on-site process needs. Boilers have the advantage over other technologies that they recover the valuable heat content of combustible wastes. Boilers are classified either by the method of heat transfer (watertube, firetube, and cast iron) or by the fuel-firing system. The majority of industrial boilers are fired with oil or gas, in which hazardous liquids, typically waste oils and solvents can also be destroyed. Some boilers use coal or wood as the primary fuel and these may be used to process municipal wastes, refuse-derived fuel, and hazardous solid wastes. For solid fuels both stoker and suspension firing systems are in operation.

Liquid wastes and sludge's are destroyed by injection as sprays comprising small droplets of 40 mm or less. Atomization is usually accomplished either mechanically using rotary cup or pressure atomization systems, or using gas fluid nozzles with high-pressure air or steam. Solid particles are typically removed prior to injection by gravity or filtration.

Research and development needs

Problems with BIFs are the same as those for fume and liquid injection incinerators with the addition of acid gas corrosion and fouling and slagging due to the presence of heat transfer surfaces. Destruction and removal efficiencies (DRE) for the principal hazardous constituents becomes an issue in BIFs because they are not

primarily designed to burn hazardous waste. They have limited residence times and incorporate active cooling for heat recovery. The R&D issues are:

1. Assurance/control systems;
2. incomplete combustion (due to heat extraction and limited residence times);
3. dioxin formation;
4. acid gas corrosion of boiler tubes, fouling, slagging, flame impingement (as in combustion systems burning ash-containing fuels).

Sandia capabilities that can address the needs

Relevant Sandia capabilities are listed in the discussions on cement kilns, rotary kilns, and liquid injection incinerators. Additional relevant Sandia capabilities are in the area of corrosion, fouling and slagging. The Multifuel Combustor (Org. 8361) is equipped for deposition and slagging studies during suspension firing of liquid or pulverized solid fuels, such as coal or biomass. While fouling and slagging are important problems affecting the economics of BIF operation, the problems are somewhat less compelling because they do not relate directly to the ATPW teams concept of assurance. The problem of acid gas corrosion could be effectively addressed by the combination of materials and combustion expertise at Sandia (see materials section).

Evaluation

Boilers and industrial furnaces are important waste treatment processes which lie primarily in the domain of industry. Regulations are changing to make waste destruction in BIFs more difficult. Again, work on assurance systems and combustion chemistry can be targeted toward all major incinerator types, including BIFs. A parallel effort is underway at Sandia (Org. 8362) to develop a program for the combustion of refinery fuel gases to aid industry (primarily oil refiners and petrochemical manufacturers) to meet impending regulations on air toxics from BIFs.

3.3.4 Liquid-Injection Incinerators

Description

Liquid injection incinerators are very common devices for destroying liquid hazardous wastes in industry. The heart of the system is the waste atomization nozzle (burner) which atomizes the waste and mixes it with air to produce a suspension (i.e., a mist or fog) which ignites and burns as it proceeds through a combustion chamber. Typical combustion chamber residence times and temperatures range from 0.5-2 sec. and 1,300-3,000°F, respectively. The furnace can be as simple in design as a refractory-lined cylinder, or it can be relatively complex, utilizing combustion air preheat and firing multi-fuel streams. Flame impingement on a furnace wall is undesirable because it can lead to refractory corrosion and a loss of energy. Technology innovations include vortex burners and submerged quench reactors.

Research and development needs

Liquid injection incinerators have many R&D needs in common with other incineration technologies discussed above, including control/assurance systems, incomplete combustion/PICs, and sensors for high temperature measurement. Issues specific to liquid injection systems are nozzle wear and clogging, flame impingement, fouling and slagging for wastes containing inorganics.

Sandia capabilities that can address the needs

For the general incineration issues, see the discussions in the sections above. Regarding the issues specific to liquid injection incinerators, in particular flame impingement, atomization, Sandia's expertise (8362) in spray combustion is quite relevant. The BERL facility in particular could be used to optimize burner design to achieve desirable flame characteristics when burning various liquid wastes.

Evaluation

This is the most commonly used incinerator for hazardous waste disposal, and as such deserves the attention of the ATPW team. Also, Sandia is well equipped to attack the combustion design aspects of this problem in the short term with existing bench and pilot-scale facilities at the CRF. This is not the case for bulk solids incineration systems, where Sandia would need to focus on sensing, team with other organizations, or develop new facilities.

3.3.5 Fume Incinerators

Description

Fume incinerators treat gaseous streams to destroy hazardous compounds, or to control odor and visible emissions. There are three general types of fume incinerators: flares, direct flame incinerators, and catalytic incinerators. Flares are used primarily in chemical plants and petroleum refineries, typically for the control of volatile hydrocarbons. They are used when the waste gas contains combustible constituents above the explosive limit or just below the lower explosive limit. A flare is basically a stack with a pilot flame at the end, a source of steam and supplemental fuel, and an exit nozzle. Flaring is typically used when the heating value of the gas stream cannot be recovered because of the uncertain or intermittent flow, due to, say, process upsets or emergencies. In direct flame incinerators, waste gas is passed through a flame in a vertical or horizontal refractory-lined chamber. A supplemental fuel is usually required to maintain combustion. Because of the absence of particulate matter, heat is typically recovered downstream. Catalytic incinerators are normally used to destroy gaseous waste at low concentrations, typically less than 25% of the lower explosive limit. The gas is preheated and passed over a catalyst bed. As with direct flame incinerators, a recuperative heat exchanger is usually used for the gas preheat.

R&D needs and Sandia capabilities

The most important issues in fume incinerators are those shared with most other major incinerator types and include control systems and combustion chemistry (DRE, PICs). The single-phase processes (flares and direct flame incinerators) are simpler to reproduce/simulate in the laboratory, and are quite amenable to fundamental modeling of fluid dynamics and chemistry. As this is also an important class of processes, it would be a logical choice for testing and demonstrating sensing/control/assurance systems at Sandia. Catalytic combustors are more complex and rely on heterogeneous chemistry. The match to Sandia capabilities is not as good in this area, but we do have significant experimental (Org. 8300) and modeling capabilities (Surface CHEMKIN, Org. 8745) related to surfaces. Technological issues here include catalyst poisoning by heteroatoms.

3.3.6 Controlled Air Incinerators

Description

Also known as stationary hearths, these incinerators comprise both a primary and a secondary chamber. Waste is charged into the primary chamber and a controlled flow of combustion air is introduced, usually up through the hearth on which the waste sits. The primary chamber is operated sub-stoichiometrically, causing pyrolysis and partial combustion of the waste. Flue gas from the primary reactor contains volatiles which are burned out in the secondary chamber, or afterburner. Here 140-200% excess air is provided, as well as sufficient residence time for complete burnout. Liquid wastes may be injected either in the primary or secondary chamber. Supplementary fuel may be provided in both chambers for the maintenance of temperature.

R&D needs and Sandia capabilities

The needs for controlled air incinerators are essentially the same as those listed for rotary kilns—both are high-temperature, two-stage combustion systems. The particulate problem is not as severe for controlled-air units as the gas flows are slow in the primary chamber. There are, however, increased problems with solids burnout, due to the partially reducing conditions in the primary chamber.

3.4 Emerging Technologies

3.4.1 Supercritical Water Oxidation

Description

SCWO is an emerging technology for the treatment of hazardous wastes that are a) in the aqueous phase or b) best handled in water for safety considerations or to facilitate handling and transportation. In SCWO, aqueous wastes are oxidized in the supercritical state at process temperatures 375-600°C and pressures of >220 bar. The process is related to commercial wet air oxidation (WAO) processes but operates at higher temperatures, where reactions proceed to completion over a time scale of minutes.

There has been a very significant investment in this technology directed at the treatment of Hanford tank waste and low level mixed waste, propellant demilitarization (demil), munitions demil, chemical warfare agent demil, and energy recovery from low grade fuels . There are at least three private companies actively marketing this technology. Two of these companies have equipment available to customers, although this equipment is still considered developmental. The technology is ready for the commercial market for a very restricted and well defined subset of the potentially broad selection of wastes that may be processed in the future.

Research and development needs

There are major obstacles to be overcome before these complicated waste streams (listed above) can be treated in full-scale operations. These are, in order of importance:

1. System fouling from build-up of inorganic salts, either present in the waste feed or produced *in situ* from oxidation of heteroatoms in the organic waste feed;
2. corrosion of the reactor related to acids and salts (equipment life);
3. effectiveness of polishing the final effluent for ultimate disposal;
4. amount of CO in gaseous effluent;
5. energy use and costs vs. recovery;
6. fundamental oxidation chemistry.

The first two are critical for the success of SCWO as a general waste-treatment method. The other four are technology improvements that have important implications.

Sandia capabilities that can address these needs

The flow in a SCWO reactor is very complicated. The amount and location of heat released by the reaction influences the multiphase flow which in turn influences salt deposition and reactor corrosion. The design and optimization of this system is a complex problem in chemical reactor engineering. Although Sandia does not have a large staff of chemical process engineers, Sandia's strength in materials science, mechanical engineering, and chemistry can be exploited to form effective teams for solving chemical engineering problems. As a result, we currently have an active and successful program that addresses fundamental issues in SCWO. We also have an active applied program developing a pilot scale processor for a specific customer in the DoD. Sandia has modeling capabilities and materials scientists, especially metallurgists, which could also contribute to this technology. There is an opportunity to make multicomponent parts for reactor construction that provide chemical resistance and strength. Sandia is weak in facilities and infrastructure that can handle the chemical storage, handling, and disposal demands that many of the applied technology development program opportunities would require.

Evaluation

Can Sandia make a critical impact?—Yes, and already has. Although programs at other laboratories are as large or larger, SNL is well positioned for providing critical experimental results that impact technology development on our applied projects, on other federally funded projects, and in the private sector. It will be important to continue to identify key aspects of the needs of this emerging technology to preserve and expand our role. Our role should emphasize our strength in materials (chemical resistance) and fundamental reactivity. We can also successfully act as a project manager for the development of actual processing equipment when properly partnered with an A&E firm. Sandia's contribution should be forward looking and not bound by fractional improvements on existing SCWO methodology.

Commercial importance—Limited at this time as this is a new technology.

Potential future importance—This technology could have a significant impact on chemical munitions demilitarization and could have broad applicability to much of the chemical industry and municipal hazardous waste. SCWO competes with incineration on many fronts, but may be less susceptible to political forces and may be a better method for some wastes.

Significance of research needs—Applications of supercritical fluids are increasing steadily, and an improved fundamental understanding of density dependencies of reactivity and phase behavior is an important area of research from both an engineering and scientific view. Hydrothermal processing is a wide open field for the production of new specialty materials.

Sandia's ability to meet the research needs—This is primarily chemical processing at high temperatures and pressures. Our facilities are limited. Sandia has the right mix of experimental and computational talent to address specific questions whose answers can provide breakthrough improvements in reactor design. SNL does not have the facilities, experience, or talent to build SCW reactors beyond equipment needed to test underlying fundamental chemical, metallurgical and fluid handling/processing principles.

3.4.2 Pulse Combustion

Description

Pulse combustors oxidize waste at high-temperatures in premixed, acoustically-coupled (pulsating) flames. Pulse combustors can be used as small stand-alone units, or in connection with catalytic combustors as post processors. Sandia has also explored their use as auxiliary burners to enhance the performance of larger furnaces through enhancement of internal transport processes. The technique is especially suited to well-defined gaseous streams, such as those contaminated by small concentrations of volatile organics. The technology is commercially available for heating applications, but the waste treatment applications are in the early stages of laboratory development. Advantages of the process over nonpulsating combustion include enhanced energy and mass transport (which can lead to high

DRE for small reactor volumes or to high heat transfer coefficients in energy-recovery applications), and self-aspiration.

Research and development needs

Pulse combustion is a specialty process that can only compete for well-defined gaseous waste streams. Nevertheless, a sufficient number of waste streams fall into this category, and so little work has been done in the waste sector that Sandia should certainly pursue its further development. The fundamentals of pulse combustion are reasonably well understood. More fundamental work is necessary if the technology is to be extended to heterogeneous streams (sprays, aerosols). For single-phase, gaseous waste streams, the remaining work is primarily in engineering development (scale-up) and in the application to specific waste streams. A database is needed of pulse combustor performance, with respect to DRE, PIC formation, etc., on various waste streams of interest to sponsors. Engineering work is also needed to design workable thermal treatment *systems*, incorporating pulse combustors as one unit operation. An example is work in progress at Sandia (8361) for treatment of VOC-laden streams at the Savannah River site. Part of this engineering systems work could be the development of sensors and control systems.

Sandia capabilities

Sandia is in a unique position to take the lead on the further development of pulse combustion-based waste treatment technologies. The CRF has a dedicated laboratory, and has had an active program sponsored by DOE involving both experimentation and modeling, including several patents on control of the process and its application to waste treatment.

3.4.3 Molten Salt Oxidation

Description

There is an excellent white paper describing this technology and its application to hazardous waste treatment by R.L. Gay of Rockwell International. Much of the information below is based on this and on discussions that took place at a workshop at LANL in March 1992. Note that additional current information should be available in October 1993 after an upcoming conference on *Emerging Technologies in Haz. Waste Treatment V*, which will be attended by at least one of the ATPW team member (S. Rice).

Molten salt oxidation (MSO) is a process developed primarily by Rockwell International in the 1970's for treating waste with an emphasis on mixed waste. It was developed through pilot scale and demonstrated the ability to destroy a large variety of wastes. As with many waste treatment technologies, complete destruction of organic waste under ideal conditions is achieved. Waste oxidation is at the 99.9999% level. No acid gases are produced since they are absorbed by the sodium carbonate pool. Consequently, no gas scrubbing system is needed. It appears to be excellent for trapping heavy metals, making it attractive for treating mixed waste and particularly contaminated solid carbon based/plastic materials such

as wipes, gloves, and boots from plutonium processing work areas. The process is targeted for material not amenable to incineration (waste containing high explosives, liquid on vermiculite, leaded gloves, nitrate rags, tritium containing waste).

Status summary

1. Application of this technology is restricted to the destruction of combustible wastes.
2. Operation is difficult with wastes of high inert solid content.
3. There are safety concerns with wet or aqueous feeds.
4. There is insufficient data on the cost of construction and operation for commercial units.
5. There are issues involving spent salt recovery and recycling, disposal of ash, and halide salts. Does the process make more waste than it destroys?
6. There are problems with chemical interactions between halogens and heavy metals, which can form unusually volatile metal halides.
7. Possible bypassing of wastes in the reactor.
8. Limited equipment life; material erosion and corrosion.
9. Uncertainties surrounding PICs.

Research and development needs

There is a program in the DOE at LLNL, Rockwell, and DOE Grand Junction run by T.J. Carlson. In 1992, at a workshop he was holding at LANL, he expressed interest in more basic research. Fundamental questions are: what is the chemistry of PIC formation in molten salts? What are the transport properties of a frothing 900°C salt eutectic? How does the average and time-varying residence time vary with salt bed configuration? What are the phase diagrams? What are the actual reaction rates and catalytic effects of the salt? Applied problems include: development of diagnostics on the effluent gas and salt bed (e.g., NaCl content of salt bed, on-line viscosity monitor, and *HCl off gas monitor*), and the development of ceramic lined metal vessels.

Evaluation

Can Sandia make a critical impact?—Maybe. LLNL is heavily involved in this DOE project for mixed waste and has their own project applying MSO to explosive demilitarization. Our impact could be in: 1) gas effluent monitoring, PICs and metals 2) fluid dynamics of the reacting mixture, 3) vessel design incorporating special materials, and 4) salt bed diagnostics and chemistry.

Commercial importance—Limited at this time. The process may have value for low level medical rad waste (wipes, gloves, vials, samples, etc.). LANL still intends to incinerate most mixed wastes such as wipes and other sites plan to as well. DOE hasn't fully decided whether it needed this technology or not.

Potential future importance—Significant and growing, as incineration of solid low level mixed waste looks less likely. The process may someday be very important for medical waste. It can be made fairly compact for small units at hospitals, etc. The process must be shown to be distinct from incineration and free of the same risks, especially PICs.

Significance of the research needs—This is a relatively mature technology. The biggest problems are:

1. Salt separation and recycling schemes. Work in this area has no significance beyond direct application to this technology.
2. Quality of effluent and on-line monitoring/control of salt bed composition. There is an opportunity for clever high temperature/composition monitoring devices.
3. Molten fluid behavior and behavior of the reacting medium.

Sandia's ability to meet the research needs—Like SCWO, this is essentially a chemical process operating at high temperature. We don't want to be the primary champions of MSO, but we may want to solve selected problems associated with it. Aside from off gas and salt monitoring development which could be done small scale, and fluid dynamics modeling, which would be mostly theoretical/computational, we would have a hard time breaking in without a significant initial commitment. LLNL is clearly heavily involved. It would be best to approach the source of the project, DOE Grand Junction, or Rockwell to get a more crystallized view of research needs and opportunities.

3.4.4 Molten Metal Technology

Description

Catalytic extraction processing (CEP) is a developmental waste destruction process owned by a small U.S. company, Molten Metal Technology (MMT). Similar technology is being developed by Ashland Oil for processing of their own refinery waste streams. Conventional basic oxygen steelmaking equipment is used, in somewhat modified form, to process waste through direct contact with a molten bath of iron at 2700°F. The waste—both organic and inorganic components—is destroyed (broken down into elemental form) by dissolution in the iron. Carbon from organic components of the waste can combine with oxygen in the metal phase to give CO. Any CO or H₂ produced bubbles up through the molten metal phase and exhausts out the top. The partitioning of metals between the molten and slag phases can be controlled by manipulating the redox chemistry. The slag and melt phases can then be tapped off separately to selectively recover materials for reuse. Advantages of the technology include its high thermal mass (preventing “flame-out”

or unsteady combustion), vitrification of inorganic oxides, versatility (the acceptance of waste in various physical forms, recycle/recovery of valuable materials. Because of the material recovery and recycle options, CEP has a good chance of avoiding the "incineration" label.

R&D needs and Sandia capabilities

Further development and scale-up work is needed for this new process, as well as pilot-scale or full-scale data on specific waste streams of interest. There are development/optimization opportunities in a number of areas, including: (1) design for injection of bulk solids; (2) process modeling, (3) engineering materials, and (4) on-line instrumentation and sensing. On-line sensing is challenging, as it is in steelmaking, due to the optical access problems and the hostile environment.

Sandia is well-positioned to help with these problems since the solutions require expertise in materials handling, modeling, and process chemistry. Much of the work in 8361 on sensors and control for basic oxygen steelmaking may be directly applicable, since the processing equipment and conditions are similar. Molten Metal Technology is strong financially, with significant capital. Sandia (1833, 8361) and MMT are currently collaborating to apply the technology to DOE weapons components. This is an enormous opportunity for Sandia, *and the CRF should continue to aggressively pursue this program, most likely in the areas of sensing and control.*

3.4.5 Plasma Technologies

Description

Waste materials are pyrolyzed or partially oxidized in the presence of an arc-induced plasma. The off-gases are typically combusted in a separate chamber. In this way the process operates like a controlled-air (staged) incinerator with the plasma enhancing breakdown of the principal organic hazardous constituent. Both liquids and solids can be handled, including large solid metal objects. The products are the same as in conventional incineration, except salts and metals are typically melted and recovered as slags or melts, not as powdered or sintered oxides.

Advantages of plasma processing include: inherently staged configuration, rapid start-up, and high-temperatures (which ensure complete pyrolysis), vitrification of inorganics, and reduced gas volumes for post treatment. Disadvantages of the processes include inorganic vaporization at the high temperatures, electrical energy input, and the need for complex equipment and operation.

The PEAT process

Plasma Energy Applied Technology (PEAT) Inc. has a plasma torch process that is being evaluated for the destruction of DOE weapon components at Sandia (contact: Dale Blankenship, Org. 6623). The process is attractive for organic wastes as well as waste feeds containing organics mixed with metal. As in the case of MMT, this technology does not use an oxidizer and is focused on recycling of organics into carbon monoxide and hydrogen, coupled with recovery of valuable metals. A 250-

kW plasma torch creates a high temperature zone in which metals melt and collect at the reactor bottom, while a slag phase forms on top. At the 1000 to 1500°C temperatures in the reactor, the organic components of the waste volatilize and react with the steam in the headspace above the molten layers. The bottom phase of molten metal can be tapped off to give a Cu-Ni-based ingot enriched in heavy metals. The slag phase can also be tapped off and sold as material for roof shingles or abrasives. The advantage to this technology is that both organics and inorganics can be taken care of in one step. PEAT Inc. is a subsidiary of a larger firm, so it has access to a substantial amount of supporting capital.

R&D needs and Sandia capabilities

Sandia (Org. 6623) is currently evaluating the PEAT technology for destruction of weapon components. There appear to be opportunities for Sandia to support this development in the area of sensing. On-line measurements of gas phase composition would be very useful for process control.

In addition, there are other plasma processes of interest to the DOE. In general these are air-fired incineration processes, which have the added advantage of producing a vitreous, non-hazardous product.

3.4.6 Co-Firing Military Wastes with Fossil Fuels

Description

This section focuses on the destruction of two classes of difficult-to-incinerate materials, energetic wastes and fine waste powders, by co-firing with coal or oil in existing facilities. The demilitarization of rocket motors and missiles, in accordance with disarmament treaties, has led to large amounts of waste propellants (energetic materials) that must be destroyed. This potential fuel is varied in composition, but each type is very well characterized and known. The Army and Navy are currently examining the use of waste propellants as supplemental fuels for oil burners and Sandia (Org. 8113) has recently proposed an integrated program on cogeneration of energetic material in collaboration with LLNL, the U.S. Army Environmental Center, GenCorp Aerojet, EER, and others.

It is potentially attractive to use large coal-fired boilers in industry and utilities to destroy certain types of hazardous waste, blended with coal in small quantities. Combustion of the primary fuel, coal, would determine the combustion zone characteristics (temperatures, oxygen levels, residence times), and assure a stable environment for destroying waste. The large throughput of coal-fired systems would allow significant quantities of waste to be destroyed while maintaining very low waste mass fractions and not altering the process chemistry significantly. Most coal furnaces are, however, suspension-fired devices that use coal in fine powdered form (mass mean particle diameter: 50 μm) and cannot handle bulk, coarsely divided, or shredded waste. Certain wastes are already in fine powder form, however, such as military dyes and smokes, and these materials are also known to be difficult to incinerate. Incineration in grate systems or in fluidized or fixed beds is impractical as the fine powders are too easily entrained into the gas phase. During suspension firing in incinerators they often do not burn to completion, as

slow heterogeneous reactions are necessary to consume the solid carbonaceous matter. Many military smokes and dyes suffer the additional problem of high sodium and sulfur contents, leading to deposition and corrosion problems. Blending of these fine powders, as a minority component in pulverized coal fired burners is possibly an attractive option.

Research and development needs

There are several issues at stake with respect to energetic materials and powdered smokes and dyes: (1) The energetic materials must be treated in some way before they can be safely transported to sites of co-firing, (2) The fuel must safely be introduced into the burner—e.g., as an oil/solid slurry or powder mixture, or with the waste material first dissolved in a solvent. Redesign of existing nozzles may be necessary. There may be a way to feed the fuel that minimizes modifications to existing burners. Low NO_x burners may present special considerations. (3) Burning characteristics of these fuels will have to be determined—e.g., burning rates of droplets, solid particles; flame shapes; emissions characteristics; corrosion problems; fate of inorganic components. For coal, concerns with fuel feeding and ash softening, slagging, and fouling would also have to be addressed. In all of these co-firing studies, sensors for the detection of heavy metals and other toxic species would be most useful.

Sandia capabilities

The overall combustion, modeling, and diagnostic expertise of Sandia's Combustion Research Facility—including its expertise in coal combustion and in the pyrolysis of energetic materials—gives Sandia very strong credentials for working in this new area.

3.4.7 Gasification and Pyrolysis Processes: Steam Reforming

Description

Gasification and pyrolysis are terms that refer to a large and diverse class of processes in the energy or waste technology sectors. The general features of such processes and their advantages and disadvantages are discussed briefly in this section. The ATPW team did not find strong ties between Sandia and any specific gasification/pyrolysis process, with the exception of Synthetica's steam reforming process, discussed below.

In general, gasification systems treat waste thermally with a less than stoichiometric air supply to produce combustible gas (primarily CO and H₂) which is often used as a fuel or chemical feedstock. The gas is compatible with many existing combustion technologies, such as gas turbines allowing gasification systems to generate electricity very efficiently in combined cycles. Gasification systems have been applied to municipal solid waste, biomass materials (e.g., wood wastes in the NREL process), chemical warfare agent (cogasified with coal), municipal sludge (also cogasified with coal in the Texaco Cool Water Plant), and automotive tires. The technology is commercial for fuels, also for many waste streams, though it is not in widespread practice. There are no operating commercial facilities for MSW

alone in the U.S. (as of August 1992); there is one commercial plant which cofires municipal sludge with coal. General issues associated with gasification/ pyrolysis processes include the effect of heteroatoms (Cl, F, P) on refractory and metal corrosion, and pollutant chemistry (organic and inorganic) under reducing conditions.

Steam reforming

Steam reforming is a variant on gasification/pyrolysis, in which heat is supplied to volatilize the organic portion of the waste through direct contact with high temperature steam. Sandia (Org. 6623) is currently involved with the company Synthetica, to evaluate their steam reforming process for various DOE wastes. Efforts are underway to procure and install a demonstration-unit Synthetica steam reformer at the New Mexico site. The unit will be instrumented for process and performance studies and can also be used to test specific DOE wastes. In Synthetica's process, a waste such as a sludge is subjected to a steam environment at about 400 to 600°C. The organic components of the waste volatilize and go into a reactor that operates at 700 to 1000°C. In this reactor, the water-gas shift reaction occurs, converting volatile hydrocarbons and steam to CO and H₂. These product gases can be catalytically oxidized or used to provide energy for fuel cells. This technology is very good for wastes that are purely organic. Any inorganic components become part of an untreated residue, so it is not a suitable technology for use with wastes high in metal content, which includes explosives feeds.

R&D needs and Sandia capabilities

Important issues in steam reforming include steam/organic chemistry, destruction and removal efficiencies, and materials problems associated with the high temperature (1000°C) and reducing environments. Sandia is well suited for providing the necessary research and development in materials. This is also an excellent opportunity to apply sensors and diagnostics to a demonstration-scale waste destruction process.

3.5 Chemistry of Thermal Processes

In the above review of individual process, numerous questions arise concerning the chemistry of the process, both organic (chlorinated and non-chlorinated) and inorganic. Three main themes are apparent in this very diverse area: 1) rational selection of surrogates for sensing and regulation. Surrogates are species whose presence correlates well with the presence of critical toxic and carcinogenic species, but are found in higher concentrations or are, for other reasons, more easily detected. 2) pathways and mechanisms of dioxin/furan formation, and 3) inorganic chemistry, especially related to toxic metals. A few general (and subjective) comments on these topics are presented below.

For hydrocarbons, enough fundamental work has probably been done to make intelligent choices of surrogates to replace CO and total hydrocarbons. Sandia experts in the chemistry of hydrocarbon pyrolysis and oxidation should collaborate with diagnostics specialists to devise improved sensing schemes for hydrocarbon emissions. For chlorinated compounds, more fundamental work is needed to choose surrogates and to understand the pathways leading to polychlorinated dioxins and furans. Monitoring HCl

might be a good first step, but the correlation between HCl concentration and the chlorinated toxins may well be environment dependent. Both homogeneous reactions and heterogeneous reactions on various surfaces must be considered, as well as reducing and oxidizing conditions. Sandia, and the Combustion Research Facility in particular, is well poised to launch a fundamental effort to improve our understanding of the high-and-intermediate-temperature chemistry of chlorinated hydrocarbons. This effort could be leveraged by incorporating kinetic results into CHEMKIN and Surface CHEMKIN to make engineering predictions of reaction rates under process relevant conditions. A concerted effort would be required, however, to discover process modifications that would improve the thermal process (e.g., additives that could reduce dioxin and furan emissions).

Inorganic chemistry also plays a large role in many thermal processes. The fate of toxic metals is the most important issue, with fouling, slagging, salt melt chemistry and metal melt chemistry being important in certain processes. The importance of these problems has been recognized for some time (EER, for example, has an established metals partitioning model). Sandia has significant capabilities to deal with these problems, and could make important fundamental contributions.

3.6 Engineering Materials for Thermal Processes

Issues related to engineering materials in thermal processes may not capture the attention of the public or of regulatory bodies, but they do have important effects on the economics and operation of most thermal waste systems. For certain technologies, such as supercritical water oxidation, the combination of corrosive wastes, high pressures, and high temperatures make materials issues *critical* to the ultimate success of the technology.

In this section, the materials issues related to Assured Thermal Processing Of Wastes as an integrated approach are summarized. Many of the issues for ATPW are similar to those identified for the fossil fuel power generation industry. Resolution of the common materials issues have high potential to significantly impact a relatively large number of jobs in the construction and engineering marketplace. Note that many of the materials issues for thermal processes discussed here are also applicable to air pollution control and upset processing systems. The intent is to identify differences in materials issues by ATPW sub-systems while attempting to look more globally and identify those issues most likely to affect the overall effectiveness of an ATPW System.

Incineration technologies—processes in which the destruction and stabilization of the organic waste occurs as decomposition reactions via thermal oxidation at temperatures greater than 900°C—represent significant challenges for materials. They must survive severe chemical and physical attack of containment and heat exchanger materials by the waste stream constituents. Chemical attack comes from the highly corrosive organic liquids and gases present at temperatures that can be as high as 1330°C. Acid gas corrosion of metals is one type of chemical attack associated with conventional incinerators. High temperature reducing environments contribute to chemical attack for some of the emerging technologies for thermal processing of wastes. In supercritical water oxidation and molten salt technologies, moderate pressures at high temperatures represent challenges for materials to withstand chemical attack. Adding pressure to the processes add additional demands for materials performance. Physical attack is due to the highly erosive conditions resulting from particulate materials entrained in those gases and liquids as they move into and out of the combustion chambers. It is the simultaneous combination of these three

conditions (temperature, corrosion, and erosion) in incinerators that makes the challenge so significant. The effects of the attacks, referenced above, result in surface coverage of either built up slags (oxidation products) and/or deposited/condensed layers of incomplete-combustion products. Such coverage results in fouling which both reduces material flow and inhibits efficient heat transfer on heat exchanger surfaces. Two major categories for materials research for addressing the above referenced challenge are:

- Development of materials, both bulk materials and coatings, to withstand the severe environment
- Evaluation of the long term behavior of materials to corrosion and erosion and wear at elevated temperatures

This would involve both metallic and ceramic systems. For the long term, improvements in the bulk materials of construction will lead to minimization of maintenance and replacement costs. Development and evaluation of intermetallic and composite oxidation resistant alloys can both provide benefits to the longevity and predicted life expectancies of incinerators. In the near term, development of non-stick coatings, capable of withstanding elevated temperatures and capable of retrofitting *in situ* would be beneficial to existing facilities. Potential candidates might include thin diamond films for certain applications.

Both hot liquids and gases can be fed into the combustion chambers, so materials must be able to survive those conditions. Additional demands also result from thermal cycling, from day to day and from cycle to cycle, where condensation can provide additional challenges for simultaneous severe environmental conditions. Wastes are sometimes fed into the combustion chambers by atomization. Nozzles used for the atomization must be especially resistant to erosion.

The real challenge is to have high performance materials at relatively low cost. Materials must be available in large quantities in forms amenable for construction of the large physical plants. Although good candidate materials are presently under development for advanced aircraft power plants and heating elements, additional development for commercialization to meet the needs for incineration technologies will be needed. In this regard there are ample opportunities for Sandia to utilize our Materials and Applied Mechanics capabilities and the Materials Science and Process Research and Development experiences to address this issue. Sandia's capabilities in this area are summarized in the Appendix.

3.7 Summary

The major, high-volume incineration processes are all mature technologies. While the design of these systems can certainly be improved, the improvements are likely to be incremental in nature and insufficient to change the public perception of these processes. A more fertile area for Sandia involvement is the development of assurance systems for the major incinerator types. This approach recognizes that these mature processes generally operate properly, as designed, but that the technology does not exist to guarantee, or assure, this proper operation on a real-time basis.

The ATPW team believes that the combination of advanced sensing and intelligent control has the potential to add a critical element of operational assurance to major incineration technologies—both in actuality, and as perceived by the public.

This general statement is particularly applicable to the major incinerator types that are responsible for most of the hazardous waste destruction capacity in the U.S. Advanced control schemes are best applied to fully developed technologies, where the process configurations are fixed and the process dynamics can be characterized using historical data or through measurements on the full scale.

The picture is quite different for many emerging technologies, where basic development work or waste-specific trials are needed. For processes in the early stages of development, where baseline performance has not been established, and process configurations are subject to change, the development of tailored intelligent control systems for specific applications is difficult. The development and demonstration of intelligent control systems can, however, be a useful endeavor for those emerging technologies whose baseline operating characteristics are well understood, either on the laboratory or pilot-scale.

In addition to these two areas, the ATPW team should continue to search for novel processes to treat specific waste streams that are of interest to important potential sponsors. When dealing with specific waste streams, the team should not restrict its attention to the processes discussed in this document, but should consider a wide range of possible technologies, including very novel approaches. This document does not treat a large number of specialty processes, as the need for them should be dictated by the specific waste stream of interest.

Finally, cutting across all processes is the need for a better broad understanding of the combustion chemistry of halogenated materials and the chemistry and transport of toxic metals in thermal waste systems.

4.0 PROCESS CONTROL

4.1 Introduction

This section is dedicated to process control, its application to thermal waste treatment processes, and its role in providing improved assurance that these processes operate in a safe manner. Process control is essential and an integral part of any assurance system for thermal waste processes, and must be closely coupled to advanced sensing and communication technologies. Indeed, many of the benefits of advanced on-line sensors will be realized only if they are properly coupled to intelligent process control systems. In the absence of a control strategy, for example, a process may have to be shut down if continuous emission monitors or temperature sensors indicate an excursion from normal operation. It has been reported that the process shut-down or waste feed cut-off in such a case can cause *higher* emissions than the condition that led to the original process excursion. It is clearly important not only to sense abnormal emissions, but to steer the thermal process in an intelligent and orderly fashion back to stable operation. As stated in the summary section on thermal processes:

The ATPW team believes that the combination of advanced sensing and intelligent control adds essential elements of operational assurance to thermal waste processes—both in actuality, and as perceived by the public.

In addition to increasing the assurance of safe operation, process control can provide benefits in the form of reduced energy and labor costs, higher throughput, continuous operation, and longer equipment lifetimes. Commercially available controllers for various industrial processes have begun to incorporate adaptive and learning ideas and recent products have added rule-based systems as high level monitors of simple feedback and adaptive controllers. As the development of sensor technology permits access to previously unmeasurable variables, intelligent control concepts will be needed to sort through massive amounts of data and to generate timely and satisfactory control decisions. The technical challenges and the benefits of applying intelligent control vary from process to process. Process specific issues are discussed in the section on thermal processes and in a separate document entitled "Assured Thermal Waste Processing: Technology Fact Sheets" compiled by Wyman Clark, Jerry Cole, and Bruce Springsteen at EER and Taz Bramlette and Chuck Hartwig at Sandia.

For further information on process control, please contact:

Richard Wheeler	(510) 294-2443	Advanced Control Systems
Robert Hurt	(510) 294-3707	Process Engineering
Andy Lutz	(510) 294-2761	Process Modeling

4.2 Control of Thermal Processing of Wastes

Control of thermal waste treatment processes poses a number of special problems. The complex, multiphase nature of many processes makes the design of optimal control strategies to deal with operational transients a challenging problem. Wastes streams are often heterogeneous and their properties (concentration, volatility, heating value) may vary greatly and unexpectedly in time. Also, poor performance of the thermal system can lead not just to poor efficiency or poor economics (as is the case with many industrial processes) but to a hazardous condition for the employees and the public. Much more is at stake in the control of waste destruction processes than in the control of many manufacturing processes, and the control systems must reflect this basic difference. Indeed, to change the public perception of these processes, the Sandia ATPW team should strive for new sensing/control schemes that could provide a qualitative advancement in our ability to control emissions to the environment.

A particular control issue for many incinerators burning solid wastes or containers of liquid wastes is the so-called "puffing" problem. Highly volatile waste batches can lead to an excess of gaseous fuel in the combustion zone, which in turn may cause system overpressures, the consumption of all available combustion air, and the ultimate release of high levels of CO, hydrocarbons, and other products of incomplete combustion (PICs). It is not practical to design the primary or secondary combustion chambers to ensure complete consumption of the largest puffs. Further, the air flow cannot always be raised to a level sufficient to consume any puffs that may arise, as the overall lean conditions during normal operation (steady-state) can lead to problems maintaining the furnace gas exit temperature. An ideal system would adjust the combustion conditions in response to the varying volatility of the feed, but this requires *fast sensing and response*. Although existing CEM's provide near real time response (on the order of minutes), it is not fast enough to actively control the combustion process to mitigate emissions from volatile puffs.

4.2.1 Control of Emissions vs. Control of Operational Parameters

There is an immediate need for an intelligent, hierarchical control system that would monitor and control the feedrates of waste, supplemental fuels, and combustion air to assure proper operating temperatures, oxygen levels, residence times, and system pressures. Such a system would optimally steer a process to maintain the operating conditions established during the test burn.

There is an exciting future alternative to this current control practice that is based on real-time sensing of hazardous emissions. The combination of advanced CEMs and intelligent controls offers the possibility of real-time emission monitoring and direct control of the processes to minimize these emissions in an economic manner. Although the current regulatory framework is insufficiently flexible to allow widespread use of this type of control presently, it is a fertile area for future-oriented R&D. The shift toward more rational, risk-based, permitting procedures and operational regulations may make this type of control system possible, and very attractive, at some time in the future.

From the point of view of mathematical control *theory*, thermal waste systems can be treated as members of the generic class of stationary industrial processes. The challenge is to apply state-of-the-art control concepts, in conjunction with sensing and model development, to develop unique control schemes for thermal waste systems.

Sandia opportunities in process control for thermal waste systems include: (1) hierarchical feedback control, (2) fast feedforward control, and (3) control of overall plant operations.

4.2.2 Hierarchical Feedback Control

Simple feedback control is routinely applied to maintain process flows, pressures, and temperatures at their desired setpoints. Improvements in operation can be expected, however, by the development of hierarchical feedback control schemes in which, for example, the output of temperature sensors or continuous emissions monitors is used to intelligently select the individual setpoints and to provide for an optimal (or at least orderly) procession to the new setpoints.

Because the process can be controlled through the adjustment of numerous process variables (flows, pressures, etc.) finding the optimal control strategy is not trivial. Process models are very useful in this endeavor, and can be derived empirically (from full-scale data) or developed from fundamental models of subprocesses such as combustion chemistry, heat transfer, metals behavior etc. Sandia has substantial and unique capabilities in the development of numerical models of high temperature processes and the application of those models to process control, as discussed in the following two sections.

Process modeling—Sandia, as the developer of the CHEMKIN package, has widely recognized capabilities in chemical kinetics modeling for combustion systems. Sandia has taken a systematic modular approach to the development of application-specific numerical models. A variety of machine-transportable, problem-independent codes have been developed at Sandia (Org. 8745), including CHEMKIN, and associated software/databases for thermodynamic and transport properties. These packages can be coupled with problem-specific codes to speed-up the development of numerical process models. Also available and in wide use are a number of fluid-dynamics codes for common flow geometries, such as perfectly stirred reactors (PSRs), stagnation flows onto rotating disks, boundary layer flows, and premixed flames. These reaction-engineering submodels or "building blocks" can be combined to yield models of more complex processes, as has recently been done by Sandian Andy Lutz in the case of turbulent diffusion flames. The use of relatively simple, reaction engineering models to approximate complex process flows is a very attractive approach for studying process *dynamics* and developing control strategies. The reaction engineering approach may not be as useful as comprehensive multi-dimensional computational approaches for attacking detailed problems in thermal processor *design*, but it is a powerful tool for studying *process dynamics* and for developing *control schemes*, as discussed below.

Model-based control—There are a number of ways in which process models can be incorporated in a control scheme. Models can be used to compute control actions in real time on the plant floor, or can be used in the development of hard-wired control algorithms. Sandia (Org. 8745) has developed model-based control schemes for chemical vapor deposition processes through a working collaboration with ISI, a silicon valley based software company that markets process control software. Sandia-developed process models and ISI software are used in combination to design control strategies which can be directly implemented in hardware (in the form of process-specific analog controllers). This approach does not involve digital computations on the plant floor in real-time, and thus

allows the use of more complex models (often incorporating detailed chemical kinetics) in the development of the control scheme.

In summary, Sandia has a variety of modeling tools at its disposal for the simulation of complex thermal processes involving flow, heat transfer, and chemical kinetics. Sandia also has experience in applying these models to the development of advanced, process-specific control schemes, for processes such as chemical vapor deposition and pulse combustion.

Control configurations—There are several possible feedback control configurations for thermal waste processing systems, using either existing CEMs or dedicated process control sensors. These possibilities are discussed below.

1. The output of existing CEMs (for CO, THC), or temperature and flow sensors could serve as input to a hierarchical feedback controller to adjust combustion air flows, liquid fuel flows, solid feed rate, or other variables. Analog controllers could be designed and tuned using numerical process models assembled from existing or modified Sandia software (PSR codes, turbulent diffusion flame codes, etc., coupled to CHEMKIN). Use of existing sensors (immediately before the stack) could be used to correct process upsets in near real time, thus minimizing the emission resulting from, say, a change in feed composition. Puffs of unburned material or PICs could not be completely intercepted by this technique, but the integrated emissions from these excursions could be reduced. Certainly for longer term excursions, related, say, to feed changes or equipment faults, an intelligent hierarchical feedback control system could serve to adjust process parameters in an optimal fashion to reduce integrated emissions.
2. The output of new *in situ* sensors with fast response could be combined with fast control algorithms and hardware (see section below on feedforward control) to handle process excursions on an even shorter time scale. These sensors could be positioned at the stack, or before (upstream of) the air pollution control (APC) system, for faster response. As long as EPA-approved continuous emission monitors are still available at the stack to meet regulations, the new sensors could be located as far upstream as possible. They could also be semiquantitative (with limited accuracy but high speed) and still be useful in process control. *A wide variety of techniques can be considered as candidates for process control sensors, if the sensors are used to supplement, and not to replace, approved CEM's.*

A variety of advanced tools in control theory can be brought to bear on this problem, including adaptive control, pattern recognition, and neural networks. These are discussed in more detail, in general terms, in a later section. Each of these techniques attempts to compensate for our incomplete knowledge and incomplete models of the complex behavior and dynamics of thermal waste processes. Sandia's activities and capabilities in advanced process control science and technology are briefly summarized in the final section of this control chapter.

4.2.3 Feed Forward Control with Interstage Sensing (Puffing Control)

An exciting opportunity in the control of thermal waste processes is the use of interstage sensing and fast feedforward control to mitigate puffing excursions for staged processes. The principle is illustrated in the Figure 1 below.

Figure 1. Principle of Feedforward Control with Interstage Sensing.

The control concept comprises the following elements:

1. Fast sensors for detecting fuel rich conditions, low oxygen levels, or low temperatures within the primary chamber, or at the junction of the primary and secondary chambers.
2. Fast data analysis and control algorithms that can detect abnormal gas phase compositions or temperature.
3. Means of rapid adjustment of the combustion flows (increase in air flow, decrease in auxiliary fuel flow) in the secondary chamber to consume the fuel rich puff. This may require additional equipment such as a compressed air vessel for rapid response.

The basic system can be augmented by incorporating an adaptive control algorithm as seen in Figure 1. The basic inner control loop effects fast feedforward control to destroy puffs in the secondary chamber, while the outer loop monitors the success of the

inner loop (using existing stack sensing equipment) and adjusts the control parameters of the inner loop. In this way, the fast feedforward loop can "learn" the optimal way to respond to puffs, by introducing perturbations in its control philosophy and observing the effect, as detected at a later stage by the CEM system directly before the stack.

The entire process, from signal detection through control valve actuation on the secondary chamber should be accomplished on a time scale of seconds. This places stringent requirements on the sensor and control algorithm. *In situ* sensors are envisioned for this application, in particular tunable diode laser spectroscopy (for CO or other infrared active species; Sec. 5.4.16), infrared absorption/emission with array detection (for CO, C-H containing species, etc.; Sec 5.4.9). These sensors are attractive for their speed, ability to make measurements in particle-laden streams, and relative simplicity. Tunable diode laser spectroscopy requires two opposing points of optical access, while dispersive IR absorption/emission can be accomplished with a single optical access port, if an existing hot surface in the equipment can be used as a broad band absorption source. These sensors and other candidates are discussed in more detail in the section on diagnostics. There is also a need in the industry for interstage oxygen measurements. Low oxygen concentrations can be an even better indicator of volatile puffs than high levels of CO or hydrocarbons. There is presently a technological gap in the area of fast *in situ* oxygen sensing, and an opportunity for Sandia diagnostics experts to do some important scoping work.

In this control scheme, a semiquantitative measurement may suffice, thus reducing the amount of time averaging needed. Note that these sensor configurations may not provide the accuracy needed for CEM applications (or to satisfy regulators) but may be very useful for providing a fault diagnosis (with normal/abnormal output) or semiquantitative results adequate for tunable controllers. Note that these same fast sensors also find use in the sense/divert/reprocess schemes discussed elsewhere in this document.

4.2.4 Input Sensing and Feedforward Control

The scheme in Figure 1 can also be carried out with input sensing instead of interstage sensing for certain waste streams. For example, changing compositions of VOC-laden gas streams could be sensed prior to injection in fume incinerators, and the burner flows adjusted to optimally consume the combustible material present. If the sensing can be accomplished upstream of the inlet to the incinerator, much additional time can be made available for feedforward control actions. The opportunities are fewer to apply this technique to solid wastes, which are very difficult to characterize.

4.3 Control of Overall Plant Operations

Another promising area of activity for Sandia is in the application of systems science and engineering to the design, permitting, and operation of thermal waste treatment systems. A thermal waste treatment process is an extremely complex system, involving an interplay of economics, environmental impact (both from volume reduction of waste and from plant emissions), government regulation, and public health and perception. The problem of finding the optimal plant configuration or operating strategy cannot be solved if the optimization "control volume" is restricted to the boundaries of the plant site. Also, there will likely be a shift in the government toward more rational, risk-based permitting procedures. This shift will bring the systems aspects of the problem to the forefront.

Arguments can also be made for rational, risk-based *operational* regulations. In either case, Sandia could play a role in the development of these new regulations.

This section on control does not explore any of these possibilities in detail, but simply points out the important role that systems engineering, risk analysis, and policy may play—all areas in which Sandia has considerable expertise, in organizations such as 6904 and 8112).

4.4 Sandia Activities in Process Control

Sandia is currently applying process control concepts in a number of application areas. These include projects in the intelligent processing of metals (Organizations 8361, 8173, and 1833), robotics (Org. 1600), navigation guidance and control (Org. 9132), and automatic target recognition and unmanned aerial vehicle operation (Org. 8430). This last project includes an effort to implement certain neural network capabilities (developed in Org. 8173) using the new hardware.

As discussed above, Sandia (Org. 8745) is involved in continuing collaborations with ISI, a silicon valley based software company, to develop real-time, on-line controllers for industrial process based on Sandia-developed process models. In addition, Sandia (Org. 8170) has maintained a contract with a group at Yale that is developing adaptive, learning and neural network techniques for the intelligent control of complex systems. Their work has focused on the use of neural networks for the identification and control of nonlinear dynamic systems. The results of their research on analytical problems have been very encouraging. However, they are interested in seeing if the methods they have developed can be adapted and scaled up for use on realistic applications. They have an active group and represent an extension of Sandia resources in the general area of intelligent control.

4.5 Gaps in Sandia's Capabilities

Sandia's effort in control is currently much smaller than its efforts in sensing and modeling. Many of the control-related activities cited above involve collaborations with outside organizations. Classical process control, with an emphasis on advanced techniques and industrial applications, is a fertile area for growth at Sandia as it effectively leverages existing capabilities in sensing and modeling.

5.0 SENSING

5.1 Introduction

Fast and reliable sensors will be a crucial component of any thermal processing system expected to provide strict assurance. Sensors have two main roles in this respect: monitoring the operating parameters of the process and monitoring process emissions. These will be referred to as process and emissions monitors, respectively. Of course, these roles can overlap, as when an emissions monitor is used to control the operation of an air pollution control system, or when a process monitor signals a process condition associated with certain emissions. Examples of process monitors include thermocouples, pyrometers, pressure transducers, flowmeters, level indicators, and hot-wire anemometers. Examples of emissions monitors include Fourier-transform infrared spectrometers (FTIR), gas chromatographs (GC), mass spectrometers (MS), transmissometers, and flame ionization detectors (FID).

Process monitors are typically relatively simple devices that provide a continuous visual or electrical readout which responds rapidly to changing conditions. Such monitors will be termed "continuous" and "real-time," respectively. (In the following discussion, "continuous" will denote an update rate greater than or equal to 10 Hertz, and "real-time" will denote a response time less than or equal to one tenth of a second. "Near" will be used with either term to indicate a response or update lag time not worse than one minute.) In contrast, emissions monitors are often used to measure the concentration of particular species, which generally involves a more complex principle of operation. Existing emissions monitors are thus less likely to provide real-time or continuous operation, especially since many require sample extraction and treatment prior to measurement. The development of continuous emissions monitors CEMs is currently an active research area.

5.2 ATPW Sensing Requirements

The degree of assurance provided in a thermal processing system relies heavily on the performance of sensors used to control the process and to monitor emissions. For example, one method of assurance may be based on emissions sensors which continuously monitor the process effluent and which, in the event of an upset, trigger a corrective action. Alternatively, a process sensor that contributes to the optimum operation of the system is part of the assurance system; both types of sensors play a role in providing assurance.

ATPW will require technical advances in numerous areas of process and emissions monitoring. For process monitoring, these will include not only enhanced sensor performance, but also the identification of process parameters that are sensitive to upset conditions and advances in quantitatively interpreting this information. For example, temperature and flow velocity measurements provided by relatively simple instruments could flag puffs of unburned reactants with sufficient speed to allow corrective actions. An analogous strategy in emissions monitoring involves detecting an indicator or "surrogate" species instead of attempting to directly sense the species or condition of interest. For example, carbon monoxide levels might be monitored as an indication of incomplete combustion of hydrocarbons.

A critical area of sensor performance in ATPW is response time. Advanced process and effluent control schemes will rely on sensors incorporated into control loops, requiring instruments with fast response times and high reliability. Existing emissions monitors typically exhibit a lag time of minutes or longer, which is probably unacceptable for use in control loops or for initiating effluent diversion or reprocessing steps. Such lag times usually result from sample extraction and preparation processes, e.g., drying and filtering. However, recently developed *in situ* optical techniques, capable of working directly in the process stream, could offer a significant speed advantage over extractive methods. Many optical techniques can operate at kilohertz rates, using pulsed lasers. A comparable speed advantage could be realized in process monitoring applications, where optical techniques working directly in the combustion zone could provide measurements earlier in time (relative to the release of effluent) than physical-probe-based methods used further downstream.

Another weakness of many extractive methods results from measurement inaccuracy or loss of information suffered through sample handling and processing. In many of the EPA "manual" analysis methods, gases are suctioned from the process stream, cooled, filtered, and dried before analysis. This can result in significant chemical changes in the sample, including perturbations in major constituents such as CO and CO₂ and large changes in reactive or transient species, including important pollutants. In contrast, *in situ* optical methods can potentially provide superior chemical characterization of the process gases, and, as a result of not requiring insertion of a physical probe, improved temperature and flow velocity measurements. In situations where extractive sampling is acceptable, optical methods can often work with samples that are maintained under conditions nearly identical to the process stream, e.g., samples transported in heated lines and receiving little or no processing prior to analysis.

5.3 Emerging Technologies

Over the past two decades there have been major advances across a broad range of technologies relevant to monitoring, particularly for optical techniques. Commercially available lasers have improved enormously with respect to performance, size, and cost as a result of improved materials, better designs, and newly developed laser media. Newly developed nonlinear crystals and laser dyes have greatly extended the range of available wavelengths. Advances in optical components such as fiber optics and integrated sensors, electro-optic modulators, mode-locks, and Faraday isolators have resulted in new capabilities for technique developers. Tremendous gains in computer power and performance/cost ratio and in electronic instrumentation have boosted capabilities in data acquisition and analysis.

Accompanying these advances in underlying technologies, research and development activities in advanced sensing have significantly increased. In particular, an area of combustion-related sensing research referred to as *combustion diagnostics*, has seen tremendous growth, with the development of laser-based *in situ* methods at the forefront. Laser and other optical methods have received the greatest attention as a result of the need for non-intrusive measurements in potentially harsh environments, where physical probes are impractical or perturbing. Among the first methods investigated for combustion applications were so-called linear techniques such as Raman scattering, laser-induced fluorescence (LIF), Rayleigh scattering, and laser-Doppler anemometry (LDA). These techniques involve directing a laser beam into the region of interest and analyzing the

emitted or scattered light. Determinations of sample temperature, chemical composition, pressure, and flow velocity can be obtained from a small probe volume, sometimes with excellent temporal resolution.

In recent years, a new class of nonlinear techniques has emerged, offering new capabilities such as enhanced immunity to background luminosity and particulates, increased sensitivity, and detection of species for which methods did not previously exist. Examples include coherent anti-Stokes Raman spectroscopy (CARS), degenerate four-wave mixing (DFWM), multi-photon-excited LIF, and resonance-enhanced multiphoton excitation (REMPI). Sandia, e.g., in the Combustion Research Facility, has in the past been known for its leading-edge research in both fundamentals and applications of laser diagnostics. Many of these techniques, particularly the linear methods, are approaching maturity as analytical or diagnostic probes in the research laboratory and are thus attractive candidates for near-term application in process monitoring. Several of the more complex nonlinear techniques, however, are less mature in either experimental technique or theoretical understanding and are further from commercial application.

In addition to laser-based techniques, other analytical tools have become commonplace in the research laboratory but have not seen significant application in waste processing. Examples include mass spectroscopy, Fourier-transform infrared spectroscopy (FTIR), and non-dispersive infrared spectroscopy. Many of these techniques are available from scientific instrument vendors.

Table I summarizes measurement capabilities of various techniques. Table II summarizes costs, response time, and status for selected techniques. In Table II, cost estimates begin with a minimum capability system and extend to a well equipped system. The response times represent minimum values (obtainable under ideal conditions, such as when wavelength scanning is not required) and do not include time for data processing, which may vary widely depending on the application.

Section 5.4 is a compendium of sensing techniques, issues and limitations, together with Sandia capabilities and potential project opportunities. The techniques were selected on the basis of their suitability for ATPW applications, Sandia expertise with the method, and research and development opportunities. Thus, well established or mature devices such as thermocouples, pitot tubes, mass flowmeters, etc., are not included. This is not to imply that such devices will not play important roles in ATPW systems, only that in our judgment significant Sandia development opportunities are unlikely. The following Sandia staff and contractors (other than ATPW technical team members) made valuable contributions to Section 5.4: Michel Bonin, Insitec Measurement Systems; David K. Ottesen, 8713; Eric A. Rohlfing, 8353; Larry R. Thorne, 8102; Joanne V. Volponi, 8353; and James C. F. Wang, 8713.

Table I. Measurement capabilities of various techniques.
(Entries in bold are discussed in this document.)

Method	O ₂	CO ₂	CO	SO ₂	NO _x	HCl	THC	Organics	Partic.	Metals	Temp.
Chemiluminescence					.						
Coherent anti-Stokes Raman spectroscopy	.	.	.			.					.
Degenerate four-wave mix.		.	.	.	.	.	.	.		.	.
Differential absorp. spectroscopy		.		.	.	.		.		.	.
Electrochemical	.	.	.	.	.						
Electro-catalytic	.										
Flame ionization detection							.				
Fourier transform infrared		.	.	.	.	.	.	.			.
Gas chromatography	.	.	.	.	.	.		.			
Imaging and thermography											.
Ion mobility spectrometry						.		.			
Laser-induced fluorescence				.	.			.		.	.
Laser spark spectroscopy										.	
Mass spectrometry	.	.	.	.	.	.		.			
Multiplex infrared emission/absorption		.	.	.	.	.	.	.	.		.
Non-dispersive infrared		.	.	.	.	.	.	.			
Non-dispersive ultraviolet				.	.						
Paramagnetic oxygen sensor	.										
Particle mass monitor—TEOM									.		
Particle mass monitor—TESS									.		
Particle size monitor-optical Mie scattering									.		
Photoacoustic spectroscopy		.	.	.	.	.	.	.			.
Raman spectroscopy	.	.	.			.					.
Resonance-enhanced multiphoton ionization			.		.	.		.			.
Transmissometry									.		
Thin-film sensors								.		.	
Tunable laser diode spectr.		.	.	.	.	.	.	.			.

Table II. Characteristics of selected techniques.

Technique	Est. Cost (\$K)	Min. response time ^a (s)	Status ^b
Coherent anti-Stokes Raman spectroscopy	120-160	0.1	2b
Degenerate Four-Wave Mixing	140-190	0.1	3
Fourier transform infrared spectroscopy	40-120	10	1
Imaging and thermography	30-120	<0.1	1
Ion mobility spectrometry	60-80	5	1
Laser induced fluorescence	70-140	<0.1	2b
Laser spark spectroscopy	130-150	0.1	2b
Mass spectrometry	30-120	1	2a
Multiplex infrared emission/absorption	70-90	0.1	2b
Particle mass monitor - TEOM	10-50	1	1
Particle mass monitor - TESS	30-50	1	1
Particle size monitor - optical Mie scattering	75-95	30	1
Raman spectroscopy	80-140	0.1	2a
Resonantly-enhanced multiphoton ionization	130-150	0.1	3
Thin-film sensors	20-40	5	2b
Tunable diode laser spectroscopy	60-120	<0.1	2b

Notes:

^a Does not include time for data processing, which varies widely depending on the application.

^b Status codes:

- 1 Instruments commercially available and either in routine use or suitable for use at thermal processing sites. Further development (field hardening, miniaturization, optimization) may be required for ATPW applications, but fundamental technology is mature.
- 2a Instruments commercially available for laboratory use. Has not been applied routinely in the field, but no significant technical obstacles to field applications exist. Technology reasonably mature, although significant advances are still being made.
- 2b Fieldable prototypes have been constructed and demonstrated, or laboratory instruments have been demonstrated in simulated field environments. Technology is nearing maturity, but development still needed. Some research issues remain.
- 3 Instruments have been constructed for laboratory use only. Technology is not mature and significant research and development is continuing.

5.4 Selected Sensing Techniques

5.4.1 Coherent Anti-Stokes Raman Spectroscopy

Contact: R. L. Farrow, 8351, (510) 294-3259

Description

In Coherent Anti-Stokes Raman Spectroscopy (CARS), two or three laser beams are focused through the sample gas. They interact in a small volume to produce a signal beam that is spectrally bright and highly collimated. For this reason, CARS is virtually immune to interferences from flame luminosity and even particulates, and can provide *in situ* measurements in harsh environments. The CARS process is a type of four-wave mixing which depends on Raman resonances in the third-order nonlinear susceptibility of a medium. Typically, one laser is narrow in frequency (the pump laser) and the other (Stokes) laser is either broad in frequency or is tuned during measurements such that the frequency difference between the pump and Stokes lasers excites Raman resonances in the target species. The first method, termed "broadband" CARS, provides instantaneous (~10 ns) measurements; the second method, termed "narrowband" or "scanning" CARS, requires many minutes for tuning the Stokes laser and thus cannot be used quantitatively in unsteady flows. For temperature and/or concentration measurements, a CARS spectrum of a major molecular species such as nitrogen is obtained and analyzed by least-squares fitting to a theoretical spectrum. For broadband CARS, the time to transfer and analyze the data effectively determines the measurement time. In conventional CARS, where the laser frequencies are far from any direct absorptions in the medium, sensitivity is limited to concentrations of ~0.1% by volume for a species mixed with other gases, or 10^{13} - 10^{15} molecules/cc for a pure species and for scanning CARS. Sensitivity is about a factor of ten worse for conventional broadband CARS. For "resonance" CARS, where the lasers excite direct absorptions in the target species, much greater sensitivity (possibly 10^4 - 10^5 greater) can be obtained.

Measured quantities

Temperature and concentrations of Raman-active species in harsh gaseous or liquid environments, with high spatial and temporal resolution. Under favorable conditions, flame temperatures can be measured with an accuracy of $\pm 3.5\%$ using a single laser pulse. Major species concentrations can be measured with an accuracy of roughly $\pm 10\%$ by volume.

Purpose

To obtain gas temperature and major species concentrations with high temporal and spatial resolution in harsh environments, especially in flame or hot exhaust regions.

Sampling type and location

In situ, in any locations where physical probes would be damaged by heat or particulates. Requires minimal (but double-ended) optical access.

Measurement time and frequency

Raw broadband CARS spectra can be obtained at rates limited by the laser pulse repetition rate (prf) or the detector read-out time, typically a few tens of Hertz. However, analysis of a single spectrum to deduce temperature or concentrations requires at least a second. In most applications, raw data is acquired and stored for subsequent analysis. An advanced variation of CARS, currently under development, allows for temperature determinations at real-time rates (limited by the laser prf).

Issues and limitations

- CARS is primarily used for thermometry of gases at high-temperatures, where thermocouples or other physical probes would be inaccurate or intrusive. The ability to measure species concentrations is less well developed, and is limited to relatively few species where theoretical spectral models have been developed (e.g., N₂, CO, H₂O, H₂, O₂). The ability to analyze N₂ spectra is by far the most mature.
- A theoretical understanding sufficient for truly quantitative analysis of CARS spectra, especially for concentrations, is limited to a few species (e.g., N₂ and CO). Spectral models for many species are in preliminary stages or are limited to certain temperature and pressure ranges.
- Sensitivity of conventional CARS is limited to major species (> 0.1% by volume). Resonance CARS provides greater sensitivity but is still in the early stages of development for most species of interest.
- CARS instrumentation is notoriously expensive and complicated. The equipment requires "hardening" for application in most real-world environments.
- The spatial resolution of CARS is not easily controlled. Lack of signal strength prevents the probe volume from being as small as needed for certain applications (e.g., in the presence of large gradients). Where a spatially averaged measurement is desired, the nonlinear nature of CARS signal generation prevents the use of a large probe volume to obtain this averaging.
- CARS temperature accuracy is roughly 3-4% for single-pulse measurements at flame temperatures (or about half this for time-averaged measurements). The best CARS concentration measurements are in the range of $\pm 5\%$.

Status

An advanced technique in a relatively mature state of development. Due to its complexity and cost, CARS is a tool used by personnel with considerable laser training, for combustion research or combustion system design.

5.4.2 Degenerate Four-Wave Mixing

Contact: R. L. Farrow, 8351, (510) 294-3259

Description

Degenerate four-wave mixing (DFWM) is a nonlinear optical technique similar to CARS (see above) in which three laser beams are focused through the sample gas. They interact in a small volume to produce a signal beam that is spectrally bright and highly collimated. For this reason, DFWM is virtually immune to interferences from flame luminosity and even particulates, and can provide *in situ* measurements in harsh environments. DFWM is capable of much greater sensitivity than CARS, although DFWM cannot be easily used to measure homonuclear diatomics such as N_2 . The DFWM process is a type of four-wave mixing which depends on one-photon resonances (direct absorptions) in the third-order nonlinear susceptibility of a medium. DFWM requires only one laser and is thus less complex experimentally than CARS. The laser frequency is tuned into resonance with a direct absorption in the target species, which is typically at a uv wavelength for electronic transitions. Alternatively, infrared lasers can be used to excite rotation-vibration transitions; in this case, DFWM can potentially probe the same wide class of species detectable with Fourier transform infrared spectroscopy (FTIR). To obtain a spectrum (necessary for most measurements), the laser frequency is usually scanned, which can require several minutes. The scanning form of DFWM cannot be used quantitatively in unsteady flows. An alternative method (broadband DFWM) has been demonstrated that uses a broadband laser to obtain a spectrum in a single laser pulse.

Measured quantities

Temperature and concentrations of absorbing species in gases or liquids. Owing to the immature status of the DFWM technique, temperature accuracy is estimated to be 100-200 K in flames. Concentration accuracy has not been established. The sensitivity of scanning DFWM can be in the few ppm range for detecting a small diatomic species in an atmospheric-pressure flame. In liquids, better than ppb sensitivities can be achieved.

Purpose

To obtain gas temperature and minor species concentrations with high temporal and moderate spatial resolution in harsh environments, especially in flame or hot exhaust regions. A relatively undeveloped technique.

Sampling type and location

In situ, in any locations where physical probes would be damaged by heat or particulates. Requires minimal (but double-ended) optical access.

Measurement time and frequency

Scanning DFWM measurements require several minutes to obtain, and at least a few seconds to analyze. Broadband measurements, obtained with a single 10-ns laser pulse, have sampling rates of tens of Hertz, limited by detector readout time or the laser pulse repetition rate. However, spectral analysis may require up to a few seconds.

Issues and limitations

- The potential of DFWM for combustion diagnostics has only recently been demonstrated. The technique is not as mature as competing methods such as laser-induced fluorescence (LIF) and FTIR. Thus, the reliability of DFWM measurements have not been fully established, and results should be regarded as qualitative in most cases.
- A theoretical understanding sufficient for truly quantitative analysis of DFWM spectra, especially for concentration measurements, has not yet been developed. For a handful of diatomic species, e.g., OH, NO, and CH, applicable theories are in various stages of development.
- Compared to its closest competitor (LIF), DFWM has less detection sensitivity (the precise amount varies with conditions). However, in situations where optical access is limited or significant background emission is present, DFWM could offer superior sensitivity due to its coherent signal beam.
- DFWM instrumentation, while not as expensive and complicated as that of CARS, is nevertheless significantly more complex than, say, FTIR. Fairly sophisticated tunable lasers are required. The equipment requires “hardening” for application in most real-world environments. Practical applications of both uv and infrared DFWM, particularly where cost and size of the equipment is an issue, are limited by current laser technology.
- There are issues concerning the spatial resolution of DFWM that are not well understood. DFWM probe volumes are typically on the order of $1 \times 1 \times 10 \text{ mm}^3$. Measurements in the presence of strong gradients often require probe volumes well below 1 mm^3 . However, when the laser beams are made this small (usually by focusing), unwanted saturation and photochemical effects can occur. These effects may be less problematic for infrared DFWM. As with CARS, the nonlinear nature of DFWM signal generation prevents the use of a large probe volume to obtain a spatially averaged measurement.

Status

A potentially powerful technique that is currently the subject of much research and development at many laboratories. It has been demonstrated to work in laboratory flames, welding torches, and the like, but has not been applied in a large scale thermal processing facility.

5.4.3 Fourier Transform Infrared Spectroscopy

Contact: L. R. Thorne, 8102, (510) 294-2552

Description

In Fourier transform infrared spectroscopy (FTIR), spectrally broad light is passed through the sample medium, located in one leg of a Michelson interferometer. Some of the light is also passed through a reference leg. Infrared-active species in the sample absorb the light at various wavelengths and intensities. An absorption spectrum is obtained by performing a fast Fourier transform on an interferogram of the sample. The interferogram is obtained by moving a retroreflector in the sample leg of the interferometer, thus changing its path length, and recording the light intensity obtained by combining both beams on a detector by means of a beamsplitter. The transformed absorption spectrum is typically analyzed by comparison with reference spectra. FTIR provides great improvements in measurement time, spectral resolution, and signal-to-noise ratio compared to other forms of broadband IR spectroscopy. FTIR can also be used when the broadband light source is background light. The infrared active species are then detected in emission if the infrared-active species are at a higher temperature than the background, or in absorption if the background is at a lower temperature.

Measured quantities

Concentrations of infrared-active species, including most organics and some inorganics. Accuracy can be quite high under favorable conditions, in the range 1-2% by volume. Typical sensitivities are 10-100 ppm-m, so concentrations in the ppb range can be achieved with sufficiently long path lengths. Temperature can be measured if the spectra are understood in sufficient detail. Multiple species can be measured simultaneously.

Purpose

Continuous, near real-time monitoring for a wide variety of mostly molecular species.

Sampling type and location

Conventionally, measurements are performed on gas samples. However, FTIR is now being developed as a real-time process monitor. In these applications, the infrared beam is passed through the process stream to obtain a line-of-sight measurement. Open beam FTIR (i.e. when no cell is used, and air can move in and

out of the beam path) is being developed as a fence line monitor for industrial fugitive emissions and for very long path lengths (up to 1 km).

Measurement time and frequency

Typically, measurement times are on the order of seconds to minutes, due to the time required to vary the optical retardation in the interferometer and to Fourier-transform the data. The measurement time depends upon the resolution required and the signal strength. High resolution and weak signals require longer acquisition times. Acquiring and transforming a 4-cm^{-1} resolution spectrum over the entire mid-infrared ($400\text{-}4000\text{ cm}^{-1}$) in less than five seconds is typical of commercially available spectrometers.

Status

Relatively new for use with process stream analysis. Has been used extensively in laboratory settings and as a chemical emissions monitor at a few chemical/thermal processing sites. Commercially available from several manufacturers.

Issues and Limitations

- The time required for measurements may be too long for many applications, e.g., when rapid feedback is required.
- Long path lengths (hundreds of meters) are generally necessary to achieve ppb sensitivity. Sensitivities in the ppm range can be expected for path lengths < 1 meter.
- Measurements are subject to spectral interferences from other species, as with any absorption method. Interferences by H_2O and CO_2 are problematic due to their common occurrence, usually high abundance and strong absorption lines. In measuring hydrocarbon species, the strongest absorptions (involving C-H vibrations) tend to occur in the same spectral region. Solutions to this problem include shortening the optical path length of the sample leg to reduce absorption or increasing the spectral resolution. Both approaches have tradeoffs with respect to sensitivity and measurement time.
- Reference spectra are sometimes not available. Moreover, such spectra are unlikely to be available for the high temperatures found in waste processing, but may be obtained with only modest research effort.
- Non-infrared active species (homonuclear diatomics and most metal atoms) cannot be detected.

5.4.4 Imaging and Thermography

Contact: Robert Hurt, 8361, (510) 294-3707

Description

Imaging, both qualitative and quantitative, within high-temperature furnaces can play an important role in process monitoring, control, and fault diagnosis. Images can be used to inspect solid surfaces for deposition, erosion, corrosion; to inspect incoming solid or liquid streams; or to inspect/monitor flames. Quantitative techniques, such as imaging pyrometry or digital thermal imaging (thermography) can be used to measure radiation levels or temperatures from solid phases, or gas phases with entrained particulate matter.

Imaging within furnaces is complicated by several factors: (1) the hostile environment, which makes optical access difficult; (2) stray reflected radiation from flames, hot surfaces; (3) light attenuation by particulate matter or metal vapors which obscures distant objects; (4) the large dynamic range needed to accommodate the range of temperatures normally encountered in furnaces. There is no general solution to the problem of temperature measurement in complex radiative environments—a careful assessment of the above factors must be made for each application. These combined constraints will in general dictate the spectral range, pyrometric technique (single or multicolor), as well as the sensor components to be used.

Infrared systems are better suited for imaging through particle-laden gases, as particle scattering efficiency decreases sharply with increasing wavelength. Infrared detector arrays can be expensive, however, and emission from gaseous species can interfere in the mid-infrared. Near-infrared imaging systems based on vidicons ($\lambda < 2 \mu\text{m}$) or CCD detectors ($\lambda < 1 \mu\text{m}$) represent a compromise between cost and image quality for particle laden streams. Optical access can be provided by windows, purged ports, or instrumented probes. Instrumented probes offer the most control of the optical path length and field-of-view, but typically do not maintain their performance during long-term operation in hostile environments. Ports or windows offer less control over path length, field-of-view, and optical interferences (e.g., reflected flame radiation), thus placing more constraints on the performance of the imaging system.

Measured quantities

Radiance levels from solid surfaces, temperatures and temperature fields for objects with known optical properties and object sizes.

Purpose

To inspect solid surfaces for deposition, erosion, corrosion, degree of combustion (of solid waste exiting furnace); to inspect/monitor flames (for flame shape, impingement on solid surfaces, balancing of multiple burner systems); to measure the temperatures of solid phases, or gas phases with entrained particulate matter for use in process control.

Sampling type and location

This technique requires optical ports or ports for insertion of instrumented probes in the furnace proper or the downstream ductwork. Many applications require only a single optical port with quartz windows. Mid-infrared imaging requires salt windows, or (more practically) purged holes or slits.

Measurement time and frequency

Video format CCD cameras are available that provide full frames at 30 Hz for display or tape storage. Quantitative digital imaging is now possible at near video rates (15 Hz) although some systems such as slow-scan CCDs with large dynamic range have full frame acquisition rates as slow as 1 Hz. Sampling is generally rapid and light levels in combustion applications are often high enough that extensive time averaging is not required to achieve a usable signal-to-noise ratio. On-line image processing (for image enhancement, object identification, thermography) may require longer times (on the order of seconds).

Issues and Limitations

- Infrared array detectors are expensive and cannot be used in sensor batteries for inspection from multiple locations in a large boiler. Visible and near-infrared imaging systems based on silicon detectors are much less expensive (many consumer components can be used) but do not offer comparable penetrating power through scattering particulate matter or emitting gases (CO_2 , H_2O ...). Visible and near-infrared systems are also limited in low-light applications, such as tube inspection in ductwork.
- There is no general (application-independent) solution to the problem of temperature measurement by radiation thermometry in complex environments. Optical and physical properties of the target needed for temperature determinations (emissivity, surface roughness, size) may not be available or well known.
- Optical interferences (e.g., from hot walls) can make temperature measurement impossible without the use of instrumented probes or intrusive optical baffles to control the field of view and background radiation. Models of furnace radiative transfer can also be used to correct for various optical interferences.

Status

Although most of the fundamental principles of thermal imaging are well established, significant development work is needed to produce low-cost field-hardened systems tailored for specific applications. Several commercial enterprises offer products for qualitative and quantitative imaging inside furnaces and combustion systems. Current applications include recovery boilers in the pulp and paper industry and coal combustion systems. Instruments are not available for many specific applications in thermal waste processing. There is also a general need for low-cost thermal imaging systems for inspection of large areas with

temperatures < 300°C, where emission in the near-infrared is insufficient for image formation.

5.4.5 Ion Mobility Spectrometry

Contact: F. J. Conrad, 9548, (505) 844-4190

Description

Ion mobility spectrometry (IMS) is used to identify gaseous chemical compounds by measuring their ionic mobility. It is similar in concept to time-of-flight mass spectrometry, which measures the transit times of ions accelerated by an applied field, except that in IMS the ionized gases are at or near atmospheric pressure. Thus, rather than charge-to-mass ratios, IMS measures ion mobilities, which are similarly used to distinguish chemical species. IMS measurements are accomplished by:

1. Mixing the sample gas with a carrier gas (usually air);
2. drawing the gases into a reaction chamber containing a radioactive source; ionization of carrier-gas species (e.g., H₂O) occurs, together with ionization of the unknown species by ion-molecule interactions or directly by the source;
3. temporally gating the ions into a drift tube subjected to a DC electric field;
4. collecting the arriving ion packets with a Faraday plate, which produces a current pulse proportional to the net ion charge; and
5. analyzing the resulting IMS "signature" to determine chemical composition.

Step 5 is performed by examining the arrival times of the various current peaks relative to the gate time, as well as the peak heights and areas.

Measured quantities

Concentrations of a variety of chemical compounds: heavy organics, some light inorganics such as HCl, HF, HCN, and NH₃, halogens such as I₂, Br₂, and Cl₂, nitro compounds (very well suited for detecting vapors from explosives), PCBs, and a variety of solvents. Sensitivity is typically ppb. Under favorable conditions (well-calibrated instrument and well-understood sample), accuracy is ±10% by volume.

Purpose

To detect low-level emissions of targeted species; has been widely used for "sniffing" explosives, drugs, and chemical warfare agents. IMS works best at detecting a few well-understood species in well-characterized gas mixtures.

Sampling type and location

Extractive; sometimes requiring filtration and scrubbing to minimize interferences. The sample line may require heating to keep sampled gases above the dew point.

Measurement time and frequency

IMS instruments respond to changes in sample composition in 5 seconds or less. Continuous measurements are possible.

Issues and limitations

- Detected species must be ionizable. Many small hydrocarbons and light gases, e.g., NO and CO, cannot be easily ionized and are thus not detected.
- Interferences are a significant problem due to the inherently low resolution of IMS. IMS peaks may be broadened by tailing, clustering (attachment of H₂O molecules), and space-charge effects. In addition, interfering species can "steal" charge from reactant ions, reducing the net charge available for ionizing the target species.
- Quantification can be a significant problem. The IMS signature is a complex function of the chemical and physical nature of the input gases. Ion mobilities depend on pressure, temperature, and composition of collision partners. Chemical reactions in the reaction tube, especially ion-molecule reactions, determine the ionization efficiency and distribution of charge among species. The peak heights and areas in the signature are a nonlinear function of the input species concentrations. In addition, the dynamic range of measurements is limited to 100:1.

Status

IMS has been the subject of research and development as a chemical analyzer since 1976. Portable IMS detectors have been developed for detecting controlled substances in field applications. These systems are less than 1 m³ in volume, have sensitivities in the low ppbs, and have response times on the order of seconds. However, further development will probably be required for ATPW, depending on the application.

5.4.6 Laser-Induced Fluorescence

Contact: P. H. Paul, 8351, (510) 294-1465

Description

In laser-induced fluorescence (LIF), a laser beam is used to excite electronic transitions in any species which absorb at that wavelength. Upon relaxing back to their ground states, a fraction of the excited species emit the absorbed energy as radiation, with a spectrum characteristic of the species. The amount of this fraction is termed the fluorescence yield and depends on the chemical composition of the sample, its temperature, and pressure. The radiated light is collected and directed upon a sensitive detector, usually a photomultiplier tube. In one form of LIF, termed "dispersed LIF," the exciting frequency is kept fixed and the emitted light is dispersed and its spectrum recorded. In another form, spectra are obtained by scanning the laser excitation frequency and recording the intensity of the

undispersed emission; data obtained in this manner are termed "LIF excitation spectra." Another form of LIF, planar LIF (PLIF), can provide images of the target species.

Measured quantities

Concentrations of any species which absorb and emit light. Examples include most organics, metal vapors, and some other inorganics, e.g., SO₂. LIF is typically quite sensitive; detection levels can exceed ppb. Under favorable conditions, measurement accuracy is roughly ± 5 % by volume. Temperature can sometimes be obtained from spectral analysis, although accuracy (estimated at ± 100 -200 K in flames) is subject to errors from saturation and spectral throughput variations.

Purpose

Continuous, real-time monitoring of a wide variety of species, typically in the gas phase. LIF can also be applied to measurements of solids and liquids.

Sampling type and location

Extractive or *in situ*. The location can be anywhere accessible by a laser beam and from which emission can be collected.

Measurement time and frequency

Real-time monitoring is possible. However, near-real-time response is typical, due to signal averaging and data analysis requirements.

Issues and limitations

- The most well-known limitation of LIF is imposed by quenching, which refers to the rate at which excited species are deactivated by radiationless processes. The quenching rate determines the fluorescence yield and hence the signal strength. If sufficient information is not available to determine the quench rate, such as the temperature, pressure, and chemical composition of the medium containing the emitting species, then the LIF data cannot be analyzed quantitatively for concentration. In most cases, the quenching rate cannot be reliably determined even if complete information on the medium is available.
- The LIF spectroscopy of many species is not well understood, particularly for large organic molecules. Often the spectra of such species are broad and featureless, leading to poor speciation and low sensitivity.
- Optical access can be a problem since LIF is emitted over a large solid angle, usually requiring large windows for the collection optics.
- LIF can be adversely affected by background thermal emission, chemiluminescence, and by LIF interferences from other species.

Status

A technique commonly used in laboratory research. Relatively mature as far as experimental technique, but there are gaps in the ability to quantify measurements due to incomplete knowledge of spectroscopy or other physical parameters. For certain species, e.g., NO and OH, the technology is mature enough to consider LIF-based sensors for practical applications.

5.4.7 Laser Spark Spectroscopy

Contact: N. B. French, 8113, (510) 294-3185
W. Flower, 8111, (510) 294-2046
D. K. Ottesen, 8713, 520-294-3567

Description

The LASS technique relies on a pulsed laser to rapidly heat either a single particle or an ensemble of particles to produce a plasma (or laser "spark") that contains excited-state ions. As the plasma cools, the excited-state species relax and emit photons at frequencies that are characteristic of the emitting elements. Spectrally resolved measurements of this emission can then be used to identify and quantify the elements that are present.

Measured quantities

Concentrations of metals and certain other inorganics present in solid or liquid aerosols. Toxic metals (such as Hg, As, Be, Pb, and Cd) can be detected in airborne particulates at the ppm level; sodium can be detected in liquid aerosols at concentrations below a part per billion. Multiple species can be detected simultaneously. Measurement accuracy for absolute volume concentrations is dependent on knowing the size of the particles.

Purpose

Continuous emissions monitoring for metals and possibly other inorganics.

Sampling type and location

In situ measurements in combustion regions or exhaust gases are possible. Can also be used on extracted aerosols suspended in a carrier gas.

Measurement time and frequency

Capable of nearly continuous, real-time measurements (the sampling rate is determined by the pulse repetition rate of the laser, at tens to hundreds of Hertz). If measurements at only one wavelength are required, then the measurement time is determined essentially by the laser pulse repetition rate. If spectrally dispersed measurements are necessary, then spectra must be captured using a diode array or CCD camera, limiting the data acquisition time to fractions of a second, and analysis time to fractions of a second.

Issues and limitations

- Sensitivity limits have not been explored for field applications, particularly for *in situ* measurements. An underlying background signal has been observed in emission spectra from pure-water aerosols, which limits the sensitivity and accuracy of results.
- Spectral interferences are a potential problem. While atomic spectra often consist of relatively narrow, isolated lines, molecular spectra exhibit broad, diffuse bands which cause problems. The severity of this problem has not been fully investigated.
- Provides elemental, but not chemical, composition of particulates. Thus, LASS is most useful for species for which information on atomic abundance is useful (e.g., metals, sulfur, carbon, but not nitrogen).

Status

Potentially powerful technique currently undergoing research and development, mainly at Sandia. Has been demonstrated in laboratory flames and furnaces but has not been applied in a large scale thermal processing facility.

5.4.8 Mass Spectrometry

Contact: J. V. Volponi, 8353, (510) 294-3292

Description

Mass spectrometry is an analytical method used to identify gas species. A typical mass spectrometer consists of a sampling system, an ion source, an analyzer and a detector. A gas sample at atmospheric or lower pressure passes into the ion source pumped at less than 5×10^{-6} torr, where sample molecules are formed into positive ions by electron bombardment. The ions are then directed into the entrance of the analyzer where they are separated according to their individual mass-to-charge ratios. A quadrupole mass filter is a commonly used analyzer configuration. In the quadrupole, consisting of four cylindrical rods, RF and DC voltages are varied keeping their ratio constant while maintaining a constant frequency. This allows particles of a specific mass to pass through the filter while others are unstable in the field. Thus, separation of the masses occurs as the RF and DC voltages are varied. After the ions are mass separated in the analyzer they are directed to a detector that measures the number of ions exiting the analyzer per unit time. A mass spectrum is obtained from the detector by recording the ion current as a function of mass number obtained by scanning through all or part of the mass range. This spectrum contains all of the gas species present in the sample. Alternatively, a time-of-flight (TOF) mass spectrometer separates ion masses by applying an electric field to the ions and recording the transit time for the ions to strike a detector (lighter masses arrive sooner than heavier masses). Qualitative and quantitative analysis is possible because molecules have a characteristic spectrum, cracking pattern and sensitivity. The output at any given mass number

is proportional to the number of ions formed, which in turn is proportional to the inlet concentration (partial pressure of the species in question).

Measured quantities

Concentration measurements of multiple gas species, simultaneously. Concentrations of stable gas species, detection limit in the low ppm range. Accuracy for detection of species is $\pm 10\%$ when calibration gases are available. Species that cannot be calibrated directly have a detection accuracy within a factor of three.

Purpose

Continuous qualitative and quantitative analysis of multiple gas phase species.

Sampling type and location

Extractive sampling with a physical probe. Source may be at atmospheric or lower pressure. The probe extracts a sample and directs it to the mass spectrometer chamber that must be kept at less than 5×10^{-6} torr. The mass spectrometer chamber may be positioned at a distance from the source to be sampled.

Measurement time and frequency

A scan of a number of masses using a quadrupole system can take minutes. A single mass can be monitored continuously. However, a TOF spectrometer can obtain a complete mass spectrum in 200 ms. Masses can be continuously monitored to detect changes occurring with time or reaction. The main issue is measurement time lag dictated by the extractive sampling system (time to travel from probe tip to ionization chamber).

Issues and Limitations

- To obtain gas species concentration measurements the mass spectrometer must be calibrated. This involves sampling calibration gases with known constituents through the sampling system and determining a sensitivity of the spectrometer to that gas relative to an inert gas. For many gases it is possible to buy calibration mixtures and the procedure is straight forward resulting in a detection accuracy of $\pm 10\%$. However, for gases that are difficult to obtain in calibration mixtures mass spectrometer sensitivities are estimated and this greatly decreases the accuracy to within a factor of three.
- Gas molecules are fragmented into their various constituent masses due to electron impact ionization. Consequently, a mass spectrum will contain overlap of all gas spectrums found in the original gas sample. It is very difficult to discern species that appear at identical masses (for example, CO and N₂ at m/e 28). Also, corrections must be made to specific mass peaks from other gases having interfering peaks at the same position.

- The probe used to transfer sample gas to the mass spectrometer can interact with the sample causing changes in composition. Care must be taken to assure that the design of the sampling system does not cause major disturbances.
- Concentrations of reactive species (radicals) are difficult to obtain. Only stable gas species can be analyzed using a physical probe attached to a mass spectrometer. Molecular beam mass spectrometry is a highly specialized and difficult technique that can be employed to determine both stable and radical species.

Status

A standard laboratory technique. Use of mass spectrometer and analysis of mass spectral data is well developed. Sampling systems must be studied carefully to assure integrity of the sampled gas.

5.4.9 Multiplex Infrared Absorption/Emission

Contact: D. K. Ottesen, 8713, (510) 294-3567
S. W. Allendorf, 8361, (510) 294-2895

Description

Infrared emission or absorption by flame-heated molecules is measured using an array of infrared-sensitive diodes. At flame temperatures, infrared-active molecules in thermal equilibrium both absorb and emit infrared radiation, with a spectrum that is characteristic of the species and its temperature. The spectrum is measured by dispersing the collected radiation using an infrared monochromator. For emission measurements, the sample is viewed against a cold background (either at room temperature or actively cooled), so that light emitted from molecules in the sample is detected with minimal background interference. Alternatively, absorption measurements can be obtained by viewing the sample against a hot background (a heated plate, glowbar, or high-pressure lamp); the difference between the background infrared spectrum with and without the sample gas gives the absorption spectrum.

Measured quantities

Concentration and temperature of infrared-active species, including organics, oxides of sulfur, nitrogen, and carbon, water vapor, and more (same as FTIR). Vibrational temperatures of NO have been reported with accuracies of a few percent, with column or number density accuracies of about 10% or less, depending on calibration.

Purpose

To measure infrared-active species concentrations in real time. This technique would be complementary to FTIR; it would measure the same species with much lower spectral resolution but with potentially much faster response. One important

application would be real-time sensing of puffs of products of incomplete combustion for use in a control loop.

Sampling type and location

In situ, line-of-sight sampling. Requires double-ended optical access.

Measurement time and frequency

Real time. Update rate and response time limited by combination of sensor readout and data processing rates. Rates of up to 125 kHz have been reported for the former. Using optimized software (*e.g.*, look-up tables), data processing time could possibly be reduced to fractions of seconds.

Issues and limitations

- Spectral resolution is low, as a result of the relatively large size and small number of diodes in the detector array (early demonstrations of this technique had only 0.2 mm resolution. Thus, spectral interferences could be a major problem, depending on the species of interest and the composition of the surrounding gas.
- Only line-of-sight measurements are obtained in absorption. However, for emission measurements, some depth resolution can be obtained by limiting the depth of focus of the detector.
- For emission measurements, relatively large size windows are required since the signal strength varies in proportion to collection solid angle. For transmission measurements using a collimated beam of light, the windows can be much smaller.

Status

- This technique has only recently been demonstrated for the first time. Further development is required for waste-stream monitoring applications.

5.4.10 Particle Mass Monitor — TEOM

Contact: J. C. F. Wang, 8713, (510) 294-2786

Description

A new real-time particulate mass monitor has been developed by combining an isokinetic sampling probe with a tapered element oscillating microbalance (TEOM). The particulates from a process stream are extracted through the sampling probe and collected on a positive filter which is oscillated at a low frequency (about 200 Hz) initially on the top of the tapered element in the TEOM detector. As the particles deposit on the filter, the mass increase of the filter is reflected in a frequency reduction which yields the collected particle mass directly in real time. The TEOM detector normally has a high mass resolution (10^{-9} g) and

wide dynamic range (10^5 – 10^6). It can also be desensitized for high particle loading and/or high temperature applications.

Measured quantities

Mass loading of particulates and concentrations of volatile gases evolved from the particulates can be measured in harsh gaseous or liquid environments at a wide range of dust loading, temperature and pressure conditions.

Purpose

To monitor particulate mass loading in process streams and effluents, e.g., combustor and fluidized-bed exhaust regions, and to monitor the presence of volatiles in the particulates.

Sampling type and location

Extractive, from locations where a physical sampling probe can be inserted. Requires minimal single ended flange type access.

Measurement time and frequency

The time resolution of the TEOM detector system depends on the speed and accuracy of the frequency counter and the mass resolution required. However, a measurement time constant of 1 second or less is normally obtained with a reasonably high mass resolution.

Issues and limitations

- TEOM is primarily used for real-time solid particulate mass and concentration measurements in a gaseous flowing stream where a physical sampling probe can be accessed.
- The measurements have to be calibrated with similar type of particulate and flow conditions. However, a relative measurement can be obtained without the calibration.
- The filter needs to be flushed or self-cleaned periodically to avoid plugging. The frequency of this cleaning process depends on the particulate loading in the measured stream and the capacity of the filter.
- Concentration measurements are derived from the mass and flow rate measurements.
- Mass and concentration measurements of volatile gases in particulates are obtained by mass differences in the particulates before and after heating. The frequency of measurements is generally much lower than those for particulates.

- Chemical composition of the volatile gases can be measured if a mass spectrometer is connected to the TEOM detector during the sample heating process described above.

Status

TEOMs have been available as commercial instruments for many years. Many types of TEOMs are available for various applications. However, commercial TEOM detectors are not applicable in the high dust loading and harsh environments encountered in most combustor and fluidized bed exhaust regions. Development efforts are needed to advance the TEOM technology to those harsh environments.

5.4.11 Particle Mass Monitor — TESS

Contact: D. R. Hardesty, 8361, (510) 294-2321

Description

TESS, an acronym for "Transform method for Extinction-Scattering with Spatial resolution," is based on a patented (patent numbers 5, 101, and 113) theory and design developed by Insittec Measurement Systems. (Insittec is a company founded by a former Sandia staff member to develop and market particle measuring systems originally based on Sandia technology.) TESS determines both absolute concentration and mean diameters in a way that is nearly independent of the particle size distribution and particle composition over the size range of ~0.5-10 microns (PM-10) configuration. At the same time, the technique remains relatively simple so that it can be implemented in a low-cost hardware package.

The instrument uses a probe, 6 cm in diameter. Independent 1.3 m long sections can be joined together to form a probe having a total length of 4 m. The probe is inserted into the process stream and the particulate flow passes through a laser-illuminated 3x10 cm slot. A receiver lens collects both transmitted and scattered light. Physically, the TESS method intelligently weights the scattering information from all particles passing through the illumination beam so that the measured scattering is directly proportional to the particle volume concentration and not to any size changes that might occur in a process stream. Laser and optics are protected from the flow using a gas purged window system. Diode lasers are used for illumination, incorporating the combined benefits of small size and long laser lifetimes. The probe also carries an integral water cooled jacket for high temperature and high pressure applications.

Measured quantities

Particle volume concentration and, if the particle loading is sufficiently high (10-20 percent extinction over a 10 cm path length), particle mean diameter. Typical configurations encompass a size range of ~0.5 microns to 10 microns. Substituting different light collection optics can increase the top size to 20

microns. Measurable particle concentrations range from 1 to 10,000 ppm by volume. Measurement time is 1-2 s.

Purpose

The TESS system has been configured primarily for use as a CEM for particles.

Sampling type and location

The water-cooled TESS probe can be inserted in stack or duct flows at ambient or elevated (but less than flame) temperatures and pressures. In situations where *in situ* measurements are not feasible, sample extraction is necessary.

Measurement time and frequency

Measurements are continuous, updated every two seconds using a 486 based micro-computer.

Issues and limitations

- The sensitivity of the TESS probe for very small particles has not been well established. Based on measurements made in flows carrying predominantly sub-micron particles, the lower limit sensitivity of TESS has been estimated as 0.5 microns. As the sub-micron regime becomes an increasingly important source of emissions the lower limit sensitivity of the TESS probe should be more accurately defined.
- For long term applications, especially in high temperature environments, the measurement probe is susceptible to failure in the event of cooling water stoppage. Optical geometries that more closely replicated those of traditional opacity monitors, i.e., a laser beam traversing the flow without the use of a probe, could extend the measurement capability of the system and greatly extend its lifetime.

Status

The TESS system, in its current configuration, represents a maturing technology for particle CEMs. Field and laboratory based studies have confirmed measurement linearity with particle loading over the working range of the instrument as well as its ability to track changing process conditions over a wide range of particle concentrations.

5.4.12 Particle Size Monitor — Mie Scattering

Contact: D. R. Hardesty, 8361, (510) 294-2321

Description

In this method, focused laser light randomly and singly illuminates particles passing through the measurement volume of the instrument. Light scattered by

these particles is collected with appropriate optics and converted to a Gaussian-shaped voltage pulse. Light collection is in the near-forward direction, minimizing sensitivity to changing refractive index and particle non-sphericity. According to the Lorenz-Mie theory for scattering from single particles, the particle size is proportional to the amplitude of the voltage pulse. Particle velocity is determined from the slope of the down-going edge of the voltage pulse and the diameter of the measurement volume. Particle concentration (number density) is determined from the rate at which particles are detected.

Measured quantities

Particle size, concentration and velocity over a size range of 0.25-200 microns at particle concentrations as high as 10^7 particles/cm³. Sizing accuracy is typically $\pm 10\%$ of indicated particle size. Particles can be spherical or non-spherical with aspect ratios less than two. Equivalent spherical diameters are reported for non-spherical particulates.

Purpose

To measure particle size, concentration and velocity in dilute, two-phase flows. Potential applications in effluent monitoring, e.g., to verify the proper operation of air-pollution control systems, and possibly in process control.

Sampling type and location

Two instrument configurations are available commercially: 1) a completely non-intrusive system that probes the flow over a long laser path length and, 2) a probe version that is inserted directly in the flow for measurements in larger scale systems. The non-intrusive instrument can be used to probe open flames, ducts and high pressure/high temperature systems through gas purge windows. The probe form has been used extensively in the power industry to examine particle flows in combustor sections in downstream gas clean-up systems. For high temperature applications, the probe is enclosed in a water cooled jacket.

Measurement time and frequency

Measurement time is a function of particle loading. For heavily loaded flows, such as those at the entrance to a gas-cleaning system, measurement time is on the order of 30 s. For lightly loaded flows, the statistical rarity of the larger particles in the flow require longer counting periods to accurately characterize the large end of the distribution.

Issues and limitations

- The particle size range is limited to 0.25-200 μ m. Some ATPW applications may fall outside this range.
- The measurement time is long (typically greater than 10 sec) in order to build up an accurate size distribution. This time lag may limit applicability, especially in process control or upset sensing.

- The complex refractive index of the particles must be known. While the real part (index of refraction) generally does not vary dramatically, the imaginary part (absorption cross section) can have large excursions. This has the greatest impact on Mie scattering for small absorption values, when the particles are nearly transparent. As absorption increases, the particles become less transparent, dramatically modifying the Mie scattering distribution. Thus, the technique will work best for particle distributions that have fairly uniform absorptivity.

Status

Single particle counting and sizing technology is mature and well known. The PCSV (particle concentration, sizing, and velocity) technique originally developed at Sandia has been developed into a commercially available system. Multiple units have been serving industry and the R&D community for nearly ten years.

5.4.13 Raman Spectroscopy

Contact: R. L. Farrow, 8351, (510) 294-3259

Description

In Raman spectroscopy a laser beam is directed into the sample and the resulting scattered light is collected and spectrally analyzed. Raman-active molecules or atoms can be viewed as absorbing photons of the incident radiation and emitting photons of a different frequency (usually lower) while undergoing a transition to a different energy level. From conservation of energy, the difference in frequency between incident and scattered photons is proportional to the energy difference between initial and final levels. The energy-level differences corresponding to Raman-active transitions are usually a characteristic of each species. From the Raman spectrum, one can determine the species concentration, temperature, and possibly other conditions, such as pressure. Since the entire Raman spectrum is generated with a single laser pulse, multiple detectors or detector arrays can be used to measure several species simultaneously (multi-channel Raman spectroscopy). Raman scattering, however, is an inefficient process, resulting in very low scattered light levels unless very intense lasers are used.

Measured quantities

Concentration and temperature of Raman-active species (this includes homonuclear diatomics, which are not generally detectable by direct absorption). Sensitivity is relatively low compared to methods such as LIF or FTIR; unless conditions are optimal, only major species can be detected in a mixture (>a few volume percent). Under favorable conditions in flames (i.e., nonluminous, clean gases) measurement accuracy is roughly $\pm 5\%$ by volume for major species concentrations, and $\pm 3-5\%$ for temperature.

Purpose

Used for analysis of gaseous and liquid mixtures in research laboratories, though not to the same extent as non-dispersive or Fourier-transform infrared spectroscopy. Also used to perform *in situ* measurements in very clean and non-luminous combustion gases. Concentration measurements of all major species and temperature have been obtained with 10-ns resolution in certain flames.

Sampling type and location

Both *in situ* and extractive measurements are possible. High spatial resolution is obtained; spatially averaged measurements can also be obtained.

Measurement time and frequency

With multi-channel Raman spectroscopy, measurement time for raw data is generally limited by the time for detector read-out and data processing or the laser repetition rate, at tens to hundreds of Hertz. Under ideal conditions it is possible to obtain analyzed results in fractions of a second, providing real-time, nearly continuous monitoring capabilities.

Issues and limitations

- The most significant limitation is sensitivity, which is largely determined by background luminosity. In completely clean and non-luminous samples, e.g. extracted gases) sensitivity is limited by photon noise and can be relatively high (ppm). However, for *in situ* measurements in reacting gases, sensitivity is typically limited to major species, or, in cases of sooting or particle-laden flows, measurements cannot be obtained at all. An additional interference can result from laser-excited fluorescence in the sample.
- Under favorable conditions, Raman scattering is an extremely powerful technique owing to its simplicity and ability to measure many species simultaneously.

Status

Used in research laboratories for analysis of extracted samples, and in limited cases, for *in situ* measurements. Still under development as a CEM.

5.4.14 Resonantly Enhanced Multiphoton Ionization

Contact: E. A. Rohlfig, 8353, (510) 294-2289

Description

In resonantly enhanced multiphoton ionization (REMPI), a laser is tuned to an n-photon molecular resonance and the electronically excited molecule is ionized by additional absorption of m photons. Thus a general REMPI scheme is denoted as n+m REMPI; 1+1 REMPI is sometimes also denoted as resonant two-photon

ionization since the overall process involves absorption of two photons. REMPI detection depends on the collection of the molecular ions or electrons formed by the ionization process. Ion detection is often performed in low-pressure or molecular-beam environments with a mass spectrometer (typically a time-of-flight instrument) in order to provide additional species selectivity. Electron detection is typically used for *in situ* flame diagnostics. REMPI spectra are molecular excitation spectra obtained by scanning the laser frequency and collecting ion or electron signals. Additional information can be obtained from mass spectra (i.e. ion fragmentation patterns) or from kinetic energy analysis of the photoelectrons (i.e. photoelectron spectroscopy). Variations of REMPI include the use of two different lasers (two-color REMPI) to separate the excitation and ionization steps. REMPI is often coupled with molecular-beam cooling to simplify spectra of large molecules.

Measured quantities

Concentrations of species in the gas phase. REMPI sensitivity depends strongly on the order of the resonance (i.e. one-photon, two-photon, etc.). 1+1 REMPI is usually the most sensitive scheme with detection limits that can exceed 1 ppb. Temperature can sometimes be obtained from spectral analysis. REMPI can be applied to nonfluorescing species. Quantitative measurements are typically difficult to obtain, owing to uncertainties in relating ion current to ion yield and finally to ground-state concentrations. For the most part, REMPI results should be considered as qualitative.

Purpose

Near real-time monitoring of a wide variety of trace species in the gas phase.

Sampling type and location

Typically extractive for REMPI with TOF MS; can be *in situ* with electron detection. Collection of ions or electrons requires the presence of electrodes; thus, *in situ* measurements risk perturbing the flow and are limited by the ability to introduce electrodes into the environment.

Measurement time and frequency

Near-real time monitoring is feasible. The precise time delay will depend on constraints imposed by sample extraction, signal averaging, and data analysis. Under favorable conditions (e.g., the laser wavelength need not be scanned), the response time would be on the order of fractions of a second, with repetition rates of tens of Hertz (determined by the laser pulse repetition rate).

Issues and limitations

- The acronym REMPI covers a broad range of molecular excitation and ionization phenomena. The sensitivity and applicability of a given REMPI scheme depend strongly on the order of the molecular resonance and the number of photons required to ionize the molecule. 1+1 REMPI is usually

the most sensitive scheme since it involves two one-photon steps. REMPI schemes that utilize higher order resonances (i.e., 2+1 or 2+2) will generally be significantly less sensitive and will also require higher laser intensities. The advantage of the higher-order schemes is the ability to access high-lying states with usable laser wavelengths.

- REMPI can be applied with success to species that cannot be detected with LIF because of their low quantum yield of fluorescence. Large aromatics and halogenated aromatics typically do not fluoresce with reasonable quantum yield due to rapid nonradiative relaxation. The ionization rate in the REMPI process can often dominate the nonradiative rate and thus efficiently produce ions. However, the spectral selectivity for such species may be poor due to excessive lifetime broadening in the excitation spectrum.
- The combination of REMPI with time-of-flight (TOF) mass spectroscopy (MS) provides a powerful tool for sensitive and selective detection of trace species. The coupling of mass selectivity to REMPI spectral selectivity greatly enhances one's ability to identify trace species in complex mixtures. Mass spectrometry also allows one to characterize the ion fragmentation channels for a particular species as a function of REMPI scheme, wavelength, and laser intensity. Sandia staff in the BES Chemical Sciences program have considerable experience with, and facilities for implementing, both techniques. The downside of the REMPI/TOF MS combination is that it almost certainly requires sample extraction. The upside is the high sensitivity and chemical specificity.
- The combination of REMPI/TOF MS with molecular-beam sampling provides further selectivity and sensitivity, especially for large molecules. The adiabatic cooling due to free-jet expansion greatly reduces spectral congestion for large molecules (thus improving selectivity) and also condenses the number density into far fewer quantum states (thus improving sensitivity). Again, the addition of molecular-beam sampling further removes the technique from real time and adds additional concerns over sample preparation. For example, the presence of particulates is undesirable since they may promote condensation in the free-jet cooling process.
- *In situ* use of REMPI in flame environments is limited to detection of electrons. The sensitivity of this detection scheme is generally poorer than for ion detection in low-pressure samples. However, the measurement time can be closer to real time. The sensitivity of the method is often limited by background ions in the flow produced by thermal ionization.

Status

REMPI is increasingly popular in laboratory research due to its sensitivity. It is less mature than LIF and the development and understanding of REMPI schemes is an active area of research. Because of the wide range of processes described generically by $n+m$ REMPI, there are substantial gaps in our knowledge of the molecular spectroscopy and ionization dynamics that contribute to specific REMPI schemes. Only recently has REMPI begun to be quantified in terms of

detection limits for trace organics and chlorinated organics in simulated "real-world" environments.

5.4.15 Thin-Film Sensors

Contact: J. J. Wiczer, 1315, (505) 844-5672

Description

Thin-film sensors are semiconductor devices that sense changes in the acoustic or electrical properties of thin films which are sensitive to specific chemical compounds. In surface acoustic wave (SAW) sensors, a thin film is deposited on a piezoelectric quartz substrate, between two transducers termed input and output. The transducers respectively launch and detect surface waves that travel across the substrate and thin film. When the film is exposed to certain chemicals, the velocity and often, the attenuation, of the SAW is affected, resulting in detectable changes in the output- transducer signal. Analysis of these changes can often determine the chemical which caused the response. Arrays of SAW sensors can be manufactured, each with a different thin film, to allow the identification of multiple chemical species. Another type of thin-film device uses thin films composed of special catalytic alloys (PdNi). In the presence of H₂, the electrical properties of these films are modified. By fabricating the films directly on the substrates of complementary metal oxide semiconductor devices, the changed properties of the films can be detected, converted into an electrical signal, and amplified. A third type of thin-film device uses thin coatings of special materials applied to the end of an optical fiber. The thin film acts as a chemical transducer in response to contact with certain chemical species, through changes in the optical properties of the film. These changes alter the reflectivity of the end of the fiber, which is sensed by shining light into the fiber and measuring the intensity of the light reflected from the coated end. Different materials may be used for the coating to sense particular species.

Measured quantities

Concentrations of a wide variety of chemical species for which chemical transducers based on thin films are available. Examples include H₂, H₂S, volatile organics, and Hg vapor. Part per million sensitivity is possible for detection of H₂, with accuracy better than 2% in some cases (clean samples with no interferences).

Purpose

Potential applications in process and continuous emissions monitoring.

Sampling type and location

Sensors must be in contact with the gases to be analyzed and cannot tolerate flame temperatures or extremely corrosive gases. In the latter case, gases must be extracted and possibly processed before analysis; otherwise, the sensors are

generally compact enough be placed in the desired measurement location. Note that electrical leads will be required to connect the sensors to electronics packages.

Measurement time and frequency

Response time can be under one second, providing near-real-time readout. Measurements are continuous. Note that the contact nature of thin-film sensors will require gas extraction and clean-up in some cases, greatly lengthening the response time.

Issues and limitations

- Thin-film sensors must be in contact with gases being analyzed, limiting applicability to less-than-flame-temperature, non-corrosive flows (or to extractive sampling with gas clean-up).
- Thin-film devices must be designed to detect a particular species or a class of chemically similar species since the composition of the film plays a major role in chemical specificity. Thus, these sensors are not as versatile or general-purpose in nature as, say, an FTIR or mass spectrometer. They will be most useful for specialized applications involving relatively simple, well-understood mixtures.
- For analyzing complex mixtures, especially when the species likely to be present cannot be anticipated, there is an issue of susceptibility to interferences. It is unlikely that the chemical speciation provided by the thin films alone (or even combined with the acoustic-wave signature of a SAW device) will be adequate for such cases. Thus, thin-film devices may have to be used after an additional separation process (e.g., a filter) in these cases.

Status

SAW detectors are well developed for a few specialized applications. For example, a portable SAW instrument (termed PAWS) has been developed and demonstrated by Sandia for monitoring volatile organic compounds at hazardous waste sites.

5.4.16 Tunable Diode-Laser Spectroscopy

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Description

Tunable diode-laser (TDL) spectroscopy uses solid-state, semiconductor lasers to emit lines which are spectrally extremely narrow (typically $< 0.001 \text{ cm}^{-1}$). The wavelength of the laser is tuned by controlling the diode current and temperature; depending on the composition of the diode material, laser emission can be obtained in many portions of the near-infrared (0.8-1.6 μm) and mid-infrared (3-25 μm) regions. This method is ideal for performing high-resolution absorption spectroscopy of infrared-active gas-phase species down to trace levels. Scans

through the laser tuning range for a given resonance mode can be quite rapid and very reproducible which allows coherent time-averaging of the absorption spectrum in noisy environments. Sensitivity to trace species can be further improved by modulating the diode current and employing phase-sensitive detection.

Measured quantities

Line-of-sight temperature and concentrations of infrared-active species in gaseous environments with high spectral resolution. Measurements of species concentrations in liquids and thin solid-films have also been made. Transitions detected are usually vibration-rotation fundamentals in the mid-infrared and combination modes in the near-infrared. Low-lying electronic transitions of atomic species can also be measured for purposes of elemental analyses. Under favorable conditions (*i.e.*, involving a species with a well-understood spectrum free from interferences) measurement accuracy can approach $\pm 1\%$ by volume for species concentrations, and $\pm 2-4\%$ for temperature in flames.

Purpose

To obtain gas-phase concentrations at trace levels with particular emphasis on environmentally regulated air-toxic species.

Sampling type and location

In situ, in any locations where physical probes would be damaged by heat or particulates. Requires minimal (but double-ended) optical access. Where optical access is not possible or additional absorbing path length is necessary for trace species, samples may be extracted into a multiple-pass gas cell.

Measurement time and frequency

Individual scans of the TDL over a resonant laser mode can be done in less than 1 ms. Since the scanning conditions can be controlled very precisely, coherent time-averaging of successive scans is possible for quasi-steady-state processes to improve resulting signal-to-noise ratios. Depending on the nature of the measured spectra, near-real-time analysis of the absorption data may be possible (fractions of a second) which permits process control applications.

Issues and limitations

- TDL spectroscopy in the near- and mid-infrared has undergone intense development over the past fifteen years. Useful sensitivities of less than 1 ppm per meter of absorbing path length have been demonstrated for many species. For some highly absorbing species, sensitivities below 1 ppb have been demonstrated over an absorbing path length of tens of meters.
- Equipment costs for TDL spectroscopy are modest (typically tens of \$K). Expenses are relatively evenly spread over a variety of hardware (laser

diodes, temperature and current controllers, detectors, lock-in amplifiers, mode selection filters, data acquisition and analysis systems).

- Theoretical understanding is sufficient for quantitative analysis of TDL spectra of simpler species for temperature and concentrations. Concentrations of larger molecules may be extracted by experimental calibrations at known, constant temperature. Problems in data analysis may arise due to non-uniformities in both concentration and temperature along the absorbing line of sight.
- Tuning ranges of TDLs are limited, particularly in the mid-infrared region. As a result, only a few absorbing species of interest may lie within the tuning range of any particular laser mode which creates the necessity of sequential tuning of several modes in a single TDL, or additional TDLs to provide wide spectral coverage for the detection and analysis of a large number of molecular species.
- Resonant cavity emission from TDLs is often multi-mode, particularly in the mid-infrared region, which may require complex mode filtering using a low dispersion monochromator. Output modes from TDLs are highly divergent and are collimated over very long distances with some difficulty which may limit some remote sensing applications. Operation of mid-infrared TDLs at cryogenic temperatures is tricky and expensive, although this is being improved by new molecular beam epitaxy processes of TDL production resulting in devices which operate at temperatures above 80 K.

Status

TDL is a developing technique which is approaching maturity. Advances in materials and processes for the fabrication of laser diodes will continue to widen the available wavelength range accessible by this method. The range of stable mode, continuous tuning is also being increased. These improvements will enlarge the number of absorbing species detectable by TDL spectroscopy and widen its field of application.

5.5 Conclusions and Recommendations

Summarized below are sensing needs, Sandia capabilities, and development opportunities that we have identified as key for ATPW.

5.5.1 Process sensors

Gas temperature

There is a lack of *in situ*, gas-temperature diagnostics that are rugged and sufficiently simple for operation by unskilled personnel in the field. Fine-wire thermocouples are adequate in many cases for temperatures up to ~1900 K, but cannot be used in corrosive or particle-laden flows. While many optical techniques can provide temperature measurements, most depend on the presence of transient species such as OH, metal atoms, or hydrocarbons that may not

persist in the flow under all conditions. On the other hand, Raman-based techniques such as CARS are more generally applicable since temperature can be probed via N_2 (a ubiquitous, relatively inert molecule). CARS provides point-resolved measurements with potentially fast response (see Sec. 5.4.1). Moreover, Sandia has considerable expertise in experimental and theoretical aspects of CARS. Present CARS instruments, however, are too expensive, bulky, and complex for routine use in thermal processing. The large size and cost of CARS setups, however, is mainly a result of its prototype nature; individual components are purchased from scientific suppliers and assembled on large optical tables. With the rapidly shrinking costs and dimensions of modern lasers, detectors, and computers, rugged and compact CARS systems could be engineered by Sandia for ATPW demonstrations. With future advances in laser price/performance ratios, reliability, and miniaturization, the instrument could become feasible for widespread application.

Hydrocarbons, CO, O₂

Approaches to mitigate upset conditions such as "puffing" in incineration systems (see Sec. 4.2.3) require fast sensors for detecting fuel-rich conditions within the primary combustion chamber or its outlet. Such sensors need not be highly quantitative but should be capable of reliably indicating a fault condition. Speed of response, however, is critical; the sensors must provide an indication with a delay < 1 sec. The fuel-rich condition can potentially be detected by monitoring total hydrocarbons (THC), CO, or O₂, and, possibly, temperature. While physical probes exist for detecting various hydrocarbon species, CO and O₂, their use is precluded by the need for fast response times and measurement locations in the primary combustion zone or immediately downstream.

We have identified two promising approaches based on optical probes that could be pursued. For THC or CO detection, an infrared multichannel detector could be used to analyze optical emission from gases exiting the primary combustion chamber (multiplex infrared emission; see Sec. 5.4.8). This method would require optical access to the flow as well as a cold (relative to the gas temperature) field of view behind the flow, as viewed from the access port. Depending on the collection optics and detector array employed, the emitted radiation could be imaged to obtain a concentration map, or it could be collected from a selected volume of gas to obtain the desired amount of spatial averaging. The advantage of this scheme is simplicity, relatively low cost, and rapid response time. Tunable diode laser spectroscopy (TDL; see Sec. 5.4.15) could also be applicable if path averaging is acceptable and broad wavelength scanning is not required.

Another approach would make use of a KrF excimer laser to excite LIF from O₂ (see Sec. 5.4.5). Such lasers are rugged, reasonably compact, and widely available. This method would also require optical access, and because of the need to collect the LIF with fast optics, the required size of the port might be too large to be used in the primary chamber. An imaging configuration can be used to obtain a concentration map. Since O₂ is excited from high vibrational levels in this scheme, a decrease in the LIF signal cannot be distinguished from a decrease in temperature. However, both of these conditions are consistent with the

presence of puffs. Thus, one or more additional sensors (temperature, pressure, or flow rate) might be needed to confirm the latter.

Note that the sensors discussed above could be suitable for use in intelligent control systems or as part of an upset processing system involving rapid detection followed by diversion and further processing or storage.

5.5.2 Continuous emission monitors

The development of faster and more sensitive CEMs is receiving much attention from industry, spurred by ever stricter emissions regulations. However, ATPW often demands capabilities that are not yet commercially available, especially with respect to response speed and sensitivity. These properties are required of CEMs for upset processing schemes (see Sec. 6.2) or for monitoring species with extremely low allowable emissions (e.g., toxics or chemical/biological warfare agents). Many of the techniques described in Section 5.4 present excellent potential for development as CEMs. *The development of advanced CEMs should therefore be a major component of any comprehensive ATPW research and development program.* Listed below are some key ATPW needs for effluent monitoring, together with applicable Sandia capabilities.

Toxics, metals, chlorinated and fluorinated species, etc.

Resonance-enhanced multi-photon ionization (REMPI) spectroscopy is one of the most sensitive of the optical techniques (see Sec. 5.4.13). Combined with mass spectrometry and molecular beam sampling, REMPI has been demonstrated to provide 10-100 ppb sensitivity for chlorinated hydrocarbons and aromatics in gas mixtures simulating waste-processing exhaust streams. Sandia has considerable expertise and facilities for working with this technique. Moreover, promising opportunities exist for developing the combination of time-of-flight (TOF) mass spectrometry and molecular-beam sampling to obtain enhanced selectivity and sensitivity.

Sandia has considerable expertise with mass spectrometry (MS) for characterizing the chemical constituents of flames. These capabilities and facilities could be exploited in a program to develop MS techniques and instruments for ATPW. Issues involving response speed, sample preparation, speciation, and quantitation could be addressed. Time-of-flight MS is a potentially powerful method for improving response times, as complete mass spectra can be obtained on millisecond time scales. Applying TOF MS and using methods developed for flame sampling (heated sample lines and filtration systems), could result in very capable, nearly real-time instruments for simultaneously monitoring key species. Note however, that both of the above techniques will be subject to lag times associated with extractive sampling. This delay will limit applicability in some cases, but may be dealt with by proper system design in others.

Metal species are especially suitable for detection by optical techniques owing to large absorption and emission cross-sections. Currently, most sensitive detection methods are based on extracted samples subjected to chemical analysis by approved EPA methods. Some ATPW applications will acquire continuous, on-line monitoring of metal emissions with sensitivity comparable to the EPA

methods. Optical techniques with the required sensitivity include LIF, REMPI, and optogalvanic spectroscopy (analogous to REMPI except that the species of interest are excited by one-photon resonant radiation). While REMPI and optogalvanic methods require the use of electrodes for detection, LIF has the advantage of working without requiring physical probes. By implementing LIF in a lidar system, the species of interest can be monitored above the stack, or concentration maps can be measured in the vicinity of the processing plant. For analyzing the metal content of aerosols and particles, the laser spark spectroscopy (LASS; see Sec. 5.4.6) technique has been shown to detect metals at levels below Clean Air Act standards.

NO_x, SO_x, hydrocarbons

Currently, CEMs for these species are typically based on physical sensors (e.g., solid-state or electrochemical devices) placed directly in the flue or used to analyze extracted gases. Optical techniques such as Fourier transform infrared spectrometry (FTIR; see Sec. 5.4.3) and flame ionization spectrometry (FIS) are beginning to be applied for external analysis. A difficulty with using these methods in some ATPW applications is inadequate response speed. Solid-state and electrochemical sensors involve diffusional processes that impose minimum lag times of ~5 sec or greater. Other instruments such as FTIR, FIS, and MS have lag times approaching 1 sec, but the time involved in extracting and possibly processing the sample must also be considered. Since species such as NO_x and hydrocarbons are often produced by process conditions that are correctable (e.g., stoichiometry, dilution), exceptionally fast sensors for these species may be required for use with control loops.

In cases where path averaged measurements can be used and when wavelength scanning is not necessary (mainly in the absence of interferences), tunable diode laser (TDL) spectroscopy is a promising approach. Sandia is developing TDL monitoring technology for process control in steelmaking furnaces, with the goal of obtaining information on the composition and temperature of gases in the process exhaust stream. Another project involves the development of CEMs for volatile organic compounds and simple inorganic molecules in the effluent of DOE waste-treatment facilities. Clearly, this technology is extremely well-suited to monitoring thermal waste processing and it should be considered for support under ATPW programs.

The multiplex infrared absorption/emission technique (Sec. 5.4.8) also presents interesting possibilities for development as a CEM. This method is perhaps more applicable for monitoring flue gases than process gases as described above, since flue gases can be more easily viewed against a low-temperature background. The advantages of this method over TDL and FTIR instruments is response speed (measurement time much less than 1 sec), improved quantitation since a broad infrared spectrum is obtained, and the ability to conveniently measure multiple species.

Miniature lidars using infrared or ultraviolet wavelengths could provide site-wide maps of NO_x or SO_x. Ultraviolet wavelengths have not been widely used in traditional (long-range) lidars due to problems with absorption and mie scattering.

However, for short-range (<1 km) probing, these effects are less important. The use of ultraviolet radiation in lidar is sometimes preferable over near-infrared radiation as the former is more immune to background interference, more easily implemented in tunable configurations, and probes stronger transitions. Moreover, LIF-based, uv or visible lidars offer exceptional sensitivity for such species as NO, SO₂, and NO₂. Sandia has ongoing lidar development programs, including "mini" lidars at the California and New Mexico sites for climate research and environmental monitoring.

Particles

As result of diagnostics developed for coal-related combustion research, Sandia has capabilities for monitoring properties of particles in reacting flows. Particle diameters and number densities can be determined *in situ* using optical Mie scattering (Sec. 5.4.11), while particle mass loading can be measured by passing gases extracted from the flow through a filter whose mass increase is dynamically measured (Sec. 5.4.9). Such methods may have applicability for continuous monitoring of the effectiveness of air-pollution-control filtration systems.

6.0 UPSET PROCESSING

6.1 Introduction

Upset processing is defined to be the means to prevent excessive emissions exiting the air pollution control (APC) system during upset conditions from being released to the environment. We propose to do this by sensing the upset, diverting the effluent stream to a storage tank for the duration of the upset, and recycling the stored effluent back to the ATPW system after normal operation is restored. We will refer to this technique as Divert, Store, and Recycle (DSR).

Most present day incinerators rely on heavily instrumented trial burns to characterize the emissions to be expected from routine operation with known waste streams. Because of the difficulty in characterizing waste input, however, "upsets" often occur which result in the release of air pollutants at unacceptable levels, even on incinerators equipped with air pollution control systems. Combustible liquid wastes are normally mixed with an absorbent and sealed in a drum made of cardboard, plastic, or steel. These drums are fed to a rotary kiln incinerator where they are heated until the vapor pressure of the liquid causes them to burst. The supply of combustion air is often insufficient to completely oxidize the large amount of combustible vapors suddenly released into the incinerator with the result that a "puff" of toxic organic vapors is discharged into the environment. These upsets are generally short in duration (less than a minute) but can occur as frequently as several times per hour. Current regulations allow incinerator emissions due to upsets to exceed permitted limits only if the hourly rolling average emissions remain within those limits. Incinerator operators often have to scale back operations after a severe upset in order to reduce the chances of another upset making it impossible for them to meet their hourly rolling average emissions limit.

The ability to assure the public and the regulatory agencies that emissions from any given incinerator are *always* within established guidelines would be very helpful in getting new incinerators permitted and allowing old incinerators to continue operating. This is especially true for incinerators which burn hazardous wastes. Incorporation of an upset processing system would achieve this goal and could also have economic benefits. It is very expensive to sort and characterize wastes. Having the means to handle upsets would allow the incinerator operator to greatly reduce his waste characterization costs and to operate near design capacity a much greater fraction of the time.

6.2 The Divert, Store, and Recycle System

Figure 2 shows schematically how a DSR system might work.

Figure 2. Schematic of DSR (Divert, Store, & Recycle) System

The waste stream undergoes thermal processing and the effluent enters the air pollution control (APC) system where, under normal conditions, the gas is cleaned to releasable standards and vented to the stack. If, however, the continuous emissions monitors (CEMs) detect excessive emissions or there are other indicators that the process is not operating normally, the effluent stream is diverted to a storage tank. Simultaneously the process controller, using feedback from the CEMs, the thermal process diagnostics, and the APC diagnostics, attempts to recover from the upset condition. When the CEMs and other diagnostics indicate that the process is again operating normally, the effluent stream is again vented to the stack and the storage tank gas is recycled. The schematic shows the contents of the storage tank being recycled to the APC system because it was assumed that the APC system would be able to handle the relatively small concentration of contaminants in the storage tank gas and that recycle through the thermal process would not be necessary. Alternatively, the storage tank gas could be recycled through the thermal process by valving-out the main combustion-air stream and valving-in the storage tank gas (into which enough oxygen had been blended to bring it up to combustion air standards). This option would minimize the time required to empty the storage tank and would be less perturbing. For certain circumstances a small dedicated system to process the tank gas in a closed loop mode might also be considered.

If the process controller cannot restore normal operation within the allotted time, the incinerator is shut down. This would most likely occur only during a major malfunction of the incinerator or the APC system rather than as a result of "puffs" generated by variations in the waste stream. The maximum time allowed for the process controller to restore normal operation equals the time it would take the diverted effluent to fill the storage tank minus the time required to shut down the thermal process.

There are a number of possible variations to this basic scheme, but the essential elements are:

1. CEMs or other process diagnostics to signal when an upset occurs;
2. a storage tank to which the effluent stream can be diverted during an upset;
3. process diagnostics/controls to allow recovery from upsets with minimum impact on operations;
4. a means to process the gas collected in the storage tank, either by recycling or by a small dedicated system.

Development of real-time CEMs for all species of interest is unlikely in the near future. However, a system could be developed very soon which would provide increased assurance over present-day operations and *would be the first step in the evolution of advanced effluent control systems*. CEMs and process diagnostics which indicate only whether or not the thermal process and APC system are operating normally could be used to trigger diversion to a storage tank. It is important that the "indicator" CEMs do not provide false assurance that the effluent is clean. As better CEMs and process controls/diagnostics are developed it should be possible to sharpen the criteria for diversion, resulting in fewer diversions and smaller storage tanks without any increase in risk.

Although this approach is not restricted to any particular thermal process, a liquid waste stream being fed to a liquid injection incinerator or a gaseous stream being fed to a fume incinerator would be easier candidates for a proof-of-concept demonstration than a rotary kiln being fed municipal wastes. However, application of this approach to rotary kilns would have much greater potential impact because of the widespread use of rotary kilns, the varied and relatively uncharacterized waste streams fed to them (leading to more frequent upsets), and the long time required to shut them down.¹

6.3 Technical Issues

There are relatively few technical obstacles to implementation of a DSR-based upset processing system. The most important enabling technology is development of appropriate upset indicators to trigger diversion of the puff to the storage tank. The storage tanks themselves are proven technology, as are the blowers and diversion valves.

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¹ David J. Hanson, "Hazardous Waste Incineration Presents Legal, Technical Challenges," Chemical & Engineering News P. 6, March 29, 1993.

We need to determine performance characteristics of CEMs or other upset indicators necessary to enable upset processing. Although most upsets last less than one minute², we need to learn more about upsets so that we can set storage tank capacities and effluent recycle rates with confidence. If we intend to prevent emissions due to upsets, we need CEMs or upset indicators that respond in a matter of seconds. We need to determine what existing CEMs or process diagnostics would allow design of a first-generation upset processing system in the near future. Is it necessary to actually measure excessive emissions exiting the APC to trigger diversion or can other indicators, such as an oxygen deficiency in the incinerator, a pressure pulse, or an abnormal temperature profile be correlated with an upset condition? CEM development will be a continuing need. Better CEMs and process diagnostics will allow more accurate determinations of when effluent diversions to storage/recycling are needed and will allow better dynamic process control.

The Longwell committee reports that very large, near-atmospheric-pressure gas-holding tanks are proven technology³. The systems use concentric vertical cylinders that telescope to expand or contract the tank volume as needed. Two positive seal systems considered for possible use in chemical demilitarization are the water seal and the Wiggins (bellows) seal. Water seal systems with usable capacities up to 10 million cubic feet have been built. Brown Minneapolis holds the patent rights to the Wiggins seal systems and has sold units as large as two million cubic feet. The safety of these tanks does not appear to be an issue. They have been used to store natural gas, industrial gases, and town gas (mostly CO and hydrogen).

An issue which has both technical and economic ramifications is whether we should limit our attention to puffs resulting from waste feed variations and temporary process irregularities or whether we should also try to mitigate emissions resulting from equipment failures in the incinerator and/or the APC system which require shutting down the incinerator for repairs. In principle, the DSR system should be able to handle these, but it would be costly. Whereas a storage tank designed for puffs may need to contain only a few minutes worth of effluent, one designed to contain the effluent generated during the hour or so it would take to shut down a rotary kiln could be prohibitively expensive. The cost/benefit analysis needed to decide that issue is beyond the scope of this study.

6.4 Relationship of DSR to other Upset Processing Techniques

An upset processing system based on waste stream characterization, understanding of the thermal process, real-time diagnostics, and intelligent process control might seem to be an ideal alternative to DSR, but with today's technology it can realistically only complement DSR for most processes and waste streams. Nevertheless, continued development of the elements of intelligent process control are very important for several reasons. For waste streams which are easily characterized, intelligent process control without DSR backup may be a realistic goal in the not too distant future. For processes and waste streams requiring the assurance offered by DSR, intelligent process control offers the

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² Private communications: Jerry Cole & Steve Lanier, EER; Dave Dalton, SAIC.

³ Committee on Alternative Chemical Demilitarization Technologies chaired by John P. Longwell, *Alternative Technologies for the Destruction of Chemical Agents and Munitions*, National Academy Press, Washington, D.C. 1993.

potential to reduce the frequency and duration of upsets, thus reducing the size and cost of the DSR system and allowing the incinerator to operate closer to design capacity.

A puff mitigation scheme has been proposed which relies on passing the effluent stream through a copper oxide bed to oxidize unburned hydrocarbons.⁴ After the process returns to normal, the excess oxygen normally present in the effluent reoxidizes the bed. This concept has been tested in the laboratory with good results, but the economics of the scheme have not yet been evaluated. Energy is needed to continuously maintain the bed at more than 800°C and to compensate for the pressure drop resulting from always passing all of the effluent through the bed, even though the bed is needed only for puffs. If the bed were to be kept at temperature in a standby mode to avoid the pumping losses, upset indicators would be needed to trigger effluent diversion to the bed. There is the additional question of whether there would be other emissions resulting from the upset which would not be removed by the copper oxide bed.

6.5 Economic Issues

We need data on the frequency, duration, and severity of upsets for operational incinerators in order to quantify the benefits of DSR. This data is also needed to estimate storage tank requirements. Anecdotal evidence indicates that most upsets are due to "puffs" and last less than a minute, but estimates of the frequency of upsets range from several times an hour to several times a month. The frequency is not so important as long as the time between upsets is long compared to the time needed to recycle the storage tank gas. Fairly small storage tanks could be used if the only upsets of concern were the puffs. However, if a major incinerator malfunction occurs, the upset would last as long as the residence time of the fuel in the incinerator. In the case of a rotary kiln, this would be of the order of an hour and requires a much larger storage tank.

It is reasonable to assume that data on frequency and duration of upsets, operating and capital costs of various incinerators, and costs of APC systems are available; but they were not obtainable in time for this report. Believing that a rough estimate is better than nothing, we attempted to estimate the cost of adding a DSR system to a rotary kiln incinerator. We found the capital cost of a Municipal Solid Waste (MSW) plant burning 100 tons of MSW per day to be \$12,250,000⁵. The energy produced per ton of MSW is given to be 10.3 million Btu. Burning natural gas with 100% excess air yields about 1 cubic foot of effluent for every 50 Btu produced. Using this relationship gives 206,000 ft³ of effluent per ton of MSW leading to about 14,300 ft³ of effluent produced per minute.

Chicago Bridge and Iron Works, Inc. fabricates near-atmospheric pressure gas holding tanks and gave the following rough estimates for tanks operating at 6.5 to 7 inches water column.

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⁴ Richard K. Lyon, "Unmixed Combustion: A New Technology for Prevention of Puffing by Rotary Kiln Incinerators and other Applications", Preprints of Papers presented at the 205th ACS National Meeting, Denver, CO, March 28-April 2, 1993, p. 688.

⁵ *Data Summary of Municipal Solid Waste Management Alternatives Vol. I: Report Text*, October 1992, NREL/TP-431-4988A, prepared by SRI International for NREL.

<u>Capacity (std cubic feet)</u>	<u>Cost (\$)</u>
36,000	500,000
72,000	780,000
100,000	950,000
108,000	1,000,000
145,000	1,250,000

The biggest uncertainty in estimating the cost of the DSR system is in deciding how big to make the tank. Based on the anecdotal data giving upset durations of less than a minute, we assumed that a five minute holding capacity would be realistic. Using the cost estimates listed above, a tank with the capacity to hold five minutes worth of effluent would cost about \$780,000 or about 6% of the total cost of plant. The cost of auxiliary equipment, such as valves and pumps, is small compared to the uncertainty in whether to size the tanks to collect one minute or ten minutes worth of effluent.

6.6 Summary and Conclusions

Current thermal treatment installations do not incorporate upset processing systems, but we believe that a Divert, Store, and Recycle system is feasible with today's technology for certain thermal processes and waste streams. Advances in continuous emissions monitoring will make such systems more generally applicable in the near future and more stringent regulations may make them necessary. There are relatively few technical obstacles to implementation of a DSR-based upset processing system. The most important enabling technology is development of appropriate upset indicators to trigger diversion of the puff to the storage tank. The storage tanks themselves are proven technology, as are the blowers and diversion valves. The biggest uncertainty in estimating the cost of the DSR system is in deciding how big to make the effluent storage tank. Using very rough estimates, a tank with the capacity to hold five minutes worth of effluent from a 100 ton per day MSW incinerator would cost about 6% of the total cost of plant.

There are economic incentives for developing DSR and the elements of intelligent process control. It is very expensive to sort and characterize wastes. Having the means to handle upsets would allow the incinerator operator to greatly reduce his waste characterization costs and to operate near design capacity a much greater fraction of the time. For processes and waste streams requiring the assurance offered by DSR, intelligent process control offers the potential to reduce the frequency and duration of upsets, thus reducing the size and cost of the DSR system.

It may be possible to sell DOE or EPA on the idea of attaching a DSR system to an existing burner (e.g. one in CRF). Studies of upset conditions, surrogates, etc. could be conducted without releasing pollutants to the atmosphere. In addition, the effluent collected in the storage tank could be analyzed using EPA methods and correlated with real-time process diagnostics. This could be the basis for a subsequent partnership in which Sandia would install diagnostics and intelligent process control along with a DSR system on an industrial incinerator.

7.0 SYSTEMS ANALYSIS AND INTEGRATION

7.1 Introduction

This section of the database deals with systems analysis and integration issues associated with thermal processing of waste. This section identifies three systems analysis and integration tasks as they might be identified by a user of the analysis: *Technology Screening and Selection*, *Technology Integration*, and *Risk Management*. These are ordered by scope. The first is relatively narrow in its outlook and seeks to direct those beginning to develop technologies in response to broadly defined goals. Technology integration supports the development of complete systems that address specific goals. Risk management supports the overall definition and description of the goals in the first place, but includes technology aspects as well.

There is considerable overlap in the tools used to address each of these tasks. For example, risk analysis may be an input to all three. Decision analysis and quality tools applicable to the first may both be applicable for structuring risk management activities. Similarly, process simulations developed for the technology integration may be very useful tools for the more quantitative risk analyses or cost/benefit studies than make up part of the risk management. In some cases the tools themselves—simple fault trees, decision matrices, etc.—look rudimentary. It is the data collection and its integration into a form that is meaningful and useful to all parties that is important. Often an analysis has to be structured around the data available and the specific task at hand.

7.2 Technology Screening and Selection

Many technology development activities start with a general statement of the problem but without a clear single best means to address it. One of the most fundamental systems analysis activities is to translate a general problem statement into terms relevant to technological choices and then to develop means to assess how effectively the different choices address these. This analysis is often needed both for an initial screening of technologies and for a later selection of those to explore in depth. The user of such an analysis can be either internal or external to Sandia. In the first case, externally and broadly specified goals are given and systems analysis tools are used to most efficiently channel Sandia resources to meet those goals. In the second case, our analysts work directly with the ultimate user of Sandia technology to best match his or her needs with our capabilities. Technology screening and selection analyses are often relatively small studies in which the challenge is to integrate data of limited detail from widely disparate sources.

A technology screening or selection analysis generally consists of three steps:

1. Define alternatives;
2. establish measures of effectiveness;
3. assess alternatives against the measures

The first, defining the alternatives, may be straightforward, but sometimes a problem-specific structuring is needed to make sure the less obvious (and sometimes the simplest) alternatives are not lost. The second step, defining measures of goodness (or satisfaction, or effectiveness), must capture the user's overall goals against which

technological alternatives can be measured. There are often multiple measures that have to be balanced. For example, in allocating developmental resources amongst different emissions monitoring approaches, there may be a desire to minimize cost, minimize technical risk (i.e., the chance that the development will not succeed), maximize sensitivity and response time of the sensors, and still have the sensors be small, unobtrusive, and reliable. These multiple objectives are often guaranteed to conflict, so a method for balancing these choices must be developed which reflects the overall needs of the program. The third step of the analysis is, of course, to rate alternatives against the measures and to identify the most and least promising alternatives. Usually the result of a quantitative technology screen/ selection analysis is only one input to a decision process that includes hard-to-quantify or non-quantifiable organizational or social issues.

There may be many opportunities for the ATPW program to make use of this kind of short, focused study. It is, however, difficult to anticipate exactly when or where. Such studies are driven by sponsor-specific needs or problems, not by issues generic to the technology as a whole. Thus, rather than concoct exemplary but artificial examples beyond the sort of study alluded to above, it might be best to review how such studies have been used in other Sandia areas.

This sort of technology screening has been one of the traditional SNL/CA systems analysis activities in support of defense programs. Measures related to military effectiveness have historically been the dominant measure of goodness, with trade-offs of various features against cost measured in weight, volume, or development time being common. We have also applied this sort of technology screening to more strictly internal technological issues.

Since much of the discussion above is generic, the following case history may help to illustrate how this kind of analysis works. We assisted in the definition of system safety tests for a weapon system. We developed a list of over 100 potential tests (the alternatives). First we had extensive interviews with different parties with interests in the information that could be developed from such a test program. We then structured the kind of tests available in an organized outline format to make sure that all reasonable combinations of test attributes were included. At the next step we defined six measures of goodness, including items such as the likelihood of the environmental conditions the test was examining and the breadth of the test's applicability to other issues. We rated each test against each criterion and derived several rankings by considering different weightings of the criteria that captured different stakeholders' views of the relative importance of the issues. This analysis was then the basis for a final *qualitative* review and test selection process in which the hard-to-quantify issues were discussed and incorporated.

Modern quality techniques, such Quality Function Deployment (QFD), have been widely used at Sandia—and, of course, not only in the systems analysis organizations—to carry out this sort of technology screening analysis. As an example, Sandia, in conjunction with the other weapons laboratories and the Department of Energy, just concluded a study of potential architectures for next-generation, extremely safe, weapons. Measure for such diverse issues as safety, effectiveness, and impact on military operations were all included in the QFD framework. A team that included members from SNL/CA and SNL/NM carried out the risk assessment that provided the rating of architectures against one safety criterion. That risk analysis included a simple system response model in the form of a fault tree for each design, together with order-of-magnitude estimates of environmental

exposures and responses to them. This risk assessment was, it should be noted, only one input into the larger analysis.

7.3 Technology Integration

As the problem formulation matures, the systems analysis task often changes to one of systems integration, where the goals are to choose the proper mixture of technologies to meet a specific need and to measure the overall effectiveness of that system. The distinction between technology integration and the technology screening and selection described earlier is often one of degree. Here, the problem and overall approach toward solution are better defined, but now an optimum, and potentially complex, coupling of technologies for a specific application is needed. This might be coupled with a model for the potential variability in the inputs. The tools for this sort of technology integration are process simulations and analytic models. These can range from the very simple to the extraordinarily finely resolved.

The tasks in building such models are two-fold: 1) understanding the substantive issues in the problem and 2) representing those issues in a model—typically on a computer—which captures the situation and provides analyses that communicate useful information about the process (via, for example, graphic displays, user interactions, or reports).

Clearly there is considerable overlap between developing these sorts of process models and the development of process control strategies as discussed in Section 4. In some cases, process models may be used as a testbed for potential control algorithms and features.

Several of the Sandia ATPW areas raise technology integration issues. One example is provided by two- or multi-stage thermal processes, such as rotary kilns, that may include feedback control systems and that may have to deal with variable input streams. In these, modeling process interactions can help guide system development and measure potential performance. Process modeling can also assist in the choice of whether it is economically and technologically better to deal with widely varying input streams and upset conditions with an automated pollution control system or to divert and hold emissions for subsequent treatment. Process modeling can assist in the sizing of these systems.

Complex process simulation modeling has also been one of the strengths of the SNL/CA systems analysis organization. In the defense world, we have developed highly resolved models to support combat logistics analyses (SCABBARD) and ballistic missile defense applications (AURORA). These tend to be multi-year, multi-person efforts, so undertaking a high resolution model is a major commitment.

Working with industrial partners, we have developed an object based user interactive code for simulation of power utility generation systems. Combustion processes are modeled with Sandia's CHEMKIN chemical reaction kinetics codes. Because these tools simulate the production and destruction of individual chemical species, we are able to perform emissions analyses as well as thermodynamic efficiency analyses for complex systems configurations.

In all these cases, we have relied heavily on project sponsors and users for the substantive data about the problem at hand. We have been able to structure the data into computer models and provide graphical tools to interact with this data and understand its implications.

7.4 Risk Management

Risk management is the process of making technical and nontechnical decisions in the presence of risk. Very often, the first and most important function is to clearly define the problem or decision to be addressed. The technical screening and integration tasks discussed above may be inputs into a risk management process, but the scope here is broader. Risk management supports those who define and enforce environmental priorities and regulations as well as the industries and technologies that respond to them.

One critical element in risk management is *risk analysis (or assessment)*, the quantification of risks or hazards associated with or removed by a particular action. Risk analysis itself involves several elements. First is identifying the hazards associated with a given action. Second is analyzing the exposure to these hazards that a particular action presents. With a chemical or radiological toxin, for example, this involves both understanding the source of the toxin (the "source term") and the pathways by which it reaches individuals and the environment. Third is understanding the consequences of this exposure. For chemical or radiological toxins this typically involves understanding the dose/response relations in humans, but broader environmental measures are often of interest. Finally, there is risk characterization and communication.

While risk analysis quantifies the risk presented or removed by a particular action, the broader concept of *risk management* seeks to deal with decisions in the presence of this risk. One of the fundamental tasks of risk management is to clearly *structure the decisions and alternatives*. In addition to risk analyses, *cost and cost/benefit analyses* are needed for a rational decision process. Risks reduced and costs incurred both involve quantitative best estimates and uncertainties. Both must be folded into the decision making. There are also *non-quantitative factors*. Public expectations and education will affect how quantitative risk and cost numbers are evaluated. A regulator's ability to enforce decisions made or regulations proposed may be an issue. The impact of a given regulatory decision on other regulations may be a consideration.

Analytical tools are useful throughout risk management. Detailed quantitative tools have primarily been applied to the *risk analysis* part of the problem. Tangible costs and benefits studies are also obvious candidates for analytic treatment. In addition, less quantitative decision analytic methods may be use in structuring some the qualitative considerations.

While it is recognized that public policy cannot be reduced to a series of formulas, the need exists for a better structured decision process that integrates costs, benefits, and non-quantitative factors. By working with the public and its representatives, regulators, and industry to provide an objective assessment of the amount of system improvement added by technical improvements, we may be able to establish a baseline for informed decision making about the acceptability of thermal processes. This may prove central in defining what really constitutes assurance in the context of the ATPW program. One fundamental question underlying assurance, "*What must our technological systems*

demonstrate in order to assure all parties that thermal waste processes are indeed acceptable?" is ultimately a question of risk management.

Sandia has contributed to and expects to contribute in the future to several parts of the risk management process.

Risk analyses have been undertaken at both SNL/CA and SNL/NM. Risk analysis at SNL/CA has generally been done in the context of technology screening and selection as was discussed earlier. These have generally been of relatively small scale, addressing proposed systems where many design decisions were still outstanding. One exception to this was the probabilistic risk assessment begun for a now-canceled weapon system. This joint activity of SNL/CA, SNL/NM, and LLNL, had as one of its ultimate goals to understand the interaction of design, operations, and emergency response on system safety—a risk management goal. Risk analyses at SNL/NM, done for the Nuclear Regulatory Commission, have been of much larger scale and have been done explicitly as one part of the risk management process.

The structuring of decisions and alternatives will certainly be a cooperative undertaking of all involved in risk management. We have many of the tools available to support this process. We have used a variety of formal (and less formal) decision analysis tools for internal studies. Nonetheless, what is probably needed here is a large integration activity to which we could contribute but which requires the participation of many parties.

Cost and cost/benefit studies have been undertaken by the systems analysis organizations at both SNL sites. In general this is a research task combined with some structuring of the problem at hand. Since the actual approach used for a cost or cost/benefit study depends strongly on the specific situation, it may be best to illustrate this capability with an example. SNL/CA recently reviewed factors that could affect future costs for hazardous, mixed, and low-level radioactive wastes. Our goal was to understand the sources of variations that earlier studies had identified. We began with existing DOE work and reviewed available source material rather than relying on the summaries derived from it. We interviewed people involved in handling wastes at the three DOE weapons laboratories. We used our own site as a detailed case study. In the process, we were able to better describe the factors driving costs for treatment of hazardous wastes and the disposal of mixed and low-level wastes. We also made observation on storage and on-site transportation costs that had not been raised in other reviews. We identified some of the key cost drivers (and issues that were not key drivers even though they might have been expected to be) and areas that needed further work.

7.5 Points of Contact

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8.0 INDEPENDENT ASSURANCE

8.1 Introduction

A critical concept in the Assured Thermal Processing of Wastes (ATPW) program is **ASSURANCE**. By assurance we mean: *the integrated procedure involving all elements necessary to allow stakeholders to know that all effluents are, and always will be, continuously maintained within acceptable levels*. It is through assurance that the thermal processing method, whatever this method may be, is permitted to be used on wastes. The processing operator has to be assured that the process is working correctly, the regulating and governmental agencies have to be assured that the process is complying with the law and regulations, and the public has to be assured that they and their interests are secure.

In practice, assurance is a two-step procedure. First, it must be *ensured* that the thermal process works properly, and this is accomplished through correct engineering. Second, and just as important, the interested parties must be *assured* that the process is working properly. For the first, other sections of this report address how this ensuring can be achieved and how Sandia can effect its realization. In this section, we discuss how assurance can be provided to the interested and mandated parties

Assuring that the thermal process is working as intended can be a complex problem. Technical people, however, must take account of assurance, for it can greatly impact the technology they are trying to implement. For instance, assurance may require additional instrumentation, access to data, transmissibility of data, translation of data, public control features, and others.

Assurance is multi-faceted. It can be viewed and approached in a number of different ways, but for our discussion we have subdivided the considerations into four different areas. First, and of primary importance, is assuring those parties responsible for enforcing the regulations and the laws that they have been complied with. Second, and perhaps of equal weight, is assuring the public that their safety is not in danger and that the environment is being protected. Third, the individual thermal processes themselves must be reviewed to determine the critical aspects that need to be assured. The fourth area deals with the mechanics of assurance. These four areas are discussed below.

8.2 Regulatory Assurance

A number of agencies must be considered in providing regulatory assurance, the principal party here being, of course, the federal Environmental Protection Agency (EPA). They see that such laws as the Clean Air Act are complied with. Often enforcement responsibility is passed to state EPAs. In addition, there can be additional regulation at the state or the regional level. In California, regulation for air emissions occurs through the California Air Resources Board, the South Coast Air Quality Board, and others. For air emissions, there are now 189 species that are regulated by the Clean Air Act Amendments of 1990. There are also regulations on the ash or solid residue from processes, a critical area, but the ATPW emphasis has been on air emissions.

An additional consideration for a process is the destruction and removal efficiency (DRE) for the hazardous waste that is being removed. In this case, chemicals are being

dealt with that do not appear on the standard regulatory list. An example of this is the chemical warfare agents that the U. S. Army is destroying. Here it must be assured that a certain destruction efficiency is reached. Required destruction efficiencies are often greater than 0.9999 (referred to as four 9s).

Permitting to allow commercial or governmental use of a thermal processor is done on the basis of "trial burns." In these burns, either the actual waste or surrogate materials are used to test the process. These burns are managed by the EPA or the appropriate regulation agency. If the agency passes the trial-burn, a permit is issued.

Some continuous monitoring is done on most thermal processes, especially for CO. Besides being regulated for incinerators, it is a measure of the efficiency of the combustion process. For hazardous wastes, representative molecules are also searched for. In addition, data about the waste feed stream, supplementary fuel, and combustor operation are all acquired and would be available for public review.

There is a pressing need for more extensive continuous emission monitors (CEMs). These monitors need to encompass a broad range of molecules, two key examples being furans and dioxins. The next level of regulatory assurance will almost assuredly encompass a broader range of continual assurance techniques for metals, mercury, organics, particle matter, chlorine, and hydrochloric acid.

There are two key ways that Sandia can help the EPA and other regulating bodies to provide regulatory assurance. First is defining what the level of assurance should be. An example of which is embodied in a proposal that Sandia has already submitted to EPA. Here we propose to assist EPA by helping them decide what instrumentation should be used for CEMs for particular regulated species and provide a risk analyses for thermal processing units being used for the destruction of hazardous wastes. We would be part of the process that determines the means of regulation assurance. Sandia can effectively do this job because we have the technical background and we have the impartiality of a government laboratory. Other possibilities for regulatory assistance might arise such as providing thermal process understanding, selecting key measurables, etc.

The second area that Sandia can provide assistance to regulating bodies is through technical advancement. This is particularly true with CEMs. A number of instrumentation advancements are discussed in the sensor section.

8.3 Public Assurance

How to provide public assurance is definitely a more sophisticated issue than providing regulatory assurance. For regulation, the engineering and scientific requirements are prescribed. For the public, what is necessary to provide assurance is not at all clearly defined. In fact, to proceed with public assurance it is necessary to obtain public testimony.

We have considered several ways of obtaining public testimony or information to provide guidance in how public assurance should be provided for thermal processing of wastes. This task is difficult because of the catholic character of this program. The public prefers to deal with real situations: actual processors, a specific location, selected operators. With this program, we are trying to obtain broader and more encompassing perspectives.

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With this as background, we discuss some of the public testimony options considered and give an opinion about their usefulness.

1. Confer with Livermore public officials about their sense of what is needed for assurance.

We suggest that this not be done. It would be difficult for them to relate to our more universal question; there are no specific issues that they need to deal with in this regards.

2. Confer with California public officials about their sense of what is needed for assurance.

This might provide useful information. It might still be difficult to bring people to the table because of the lack of specificity. We would have to do this carefully, because of all of the California relationships we are trying to foster.

3. Join with ES&H center as they initiate public discussions about ES&H issues at Sandia.

This would be a good opportunity to be part of a local public forum. There are three difficulties with this idea, however. First, the purpose of the forum is not ATPW; it is the discussion of site-specific issues. Second, there is no need for the forum to focus on ATPW scientific and engineering work apart from the general nature of the research work done at Sandia. Third and again, there are no specific waste processing issues at this site from ATPW. (Our incinerator might be counter to this comment.)

4. Participate with the Western Governor's Association and their DOIT program as they determine public policy and position with regards to hazardous waste disposal.

This idea has a lot of merit. We already have good connections with this organization through Nina Bergan-French and Sally Raubfogel. This is a formal collaboration between public entities and the DOE. It has a broad enough perspective that many of the issues that ATPW are interested in would be included. It also is in contact with many public elements. Public forums have already been conducted and others are planned.

5. Contact representative organizations such as the City Manager Association.

This could provide a useful view point. Will require careful preparation and DOE concurrence.

6. Conduct facilitated meetings with particular organizations.

Sandia has experience in conducting such meetings and they have turned out to be very useful for special situations. This would require DOE's concurrence and sponsorship. It is worthwhile to pursue this idea for selected organizations.

8.4 Process Assessment for Assurance

Assurance of regulatory compliance is being addressed in other sections and again, of course, this means the application of sensors. For public assurance, this is a different matter. The public may wish to have several levels of assurance, and, of course as discussed above, the proper procedure here is to ask the public what assurance is necessary. Nevertheless, several process assessment issues can be anticipated for public assurance.

The public needs to know that the regulations and the laws are being complied with. They probably wish to be informed regularly. This is, of course, the responsibility of the regulating and governing agencies. So, whatever information that is provided to these agencies should be passed onto the public. The issues here would be the frequency of this information passthrough, the immediacy of the passthrough, and the hierarchical nature of the information, i.e., what detail is needed.

In addition to the regulated information, process condition information may be requested. Is the processor operating? If not, why not? Are hazardous materials involved? What is the nature of the hazardous materials? Are there special environmental conditions for operation? Then there may be specific information about the processor that is such as temperature, feedrates, etc. Admittedly, this may be too much information but requests like this might arise.

An interesting question arises as what the public should do with this information. Should this be for information only? Should it be used as an alert if the process goes awry? Should the public have some control of the operation? Could it be used for legal purposes? Such questions would have to be addressed.

Sandia can provide technical assistance here in three ways. First, as already mentioned we can provide the CEMs necessary for the monitoring. Second, we can help select the information and/or determine how best to supply the required information. As an example, maybe a range of operating temperatures are needed. Third, Sandia can assist in interpretation, or translation, of the technical information to the level required for the public need. This could be nothing other than a statement that the operation is working satisfactorily or unsatisfactorily.

8.5 Transfer of Assurance Information

There are two issues relative to the transfer of assurance information. The first is the means of information transfer. Electronic systems exist today such that with proper engineering and development the necessary information can be transferred reliably and quickly to the necessary members of the public and governing agencies. This information may be made available at a local site or one somewhere else in the nation. A feature that might also be built into the system is for the public to query about the status of the processor for more detailed information. And as mentioned, control issues might also be important.

Sandia through its computer and design departments is heavily involved in nationwide information transfer for weapon design, virtual manufacturing, and high performance

computing and, hence, is well qualified to help build the appropriate electronic data transfer network. To achieve assurance information transfer, there are four information-access or network-base options: leased line (LL), dial-up (DU), cable TV (CATV), and wireless-personal data assistant (PDA). LLs are the only private option, but they are expensive. With T3 lines, data transfer up to 45 million bits/sec is available, more than adequate for public communication. DUs are simpler and less costly. They are useful for data management with query, where public officials would not wish to be continuously informed, only when there is the need. CATVs have the advantage of being able to provide a continuous visual display that is a vivid and easily comprehensible form of information. They are, however, expensive. With PDAs, movable inspections can be conducted, as hardwiring is not necessary. Voice transmission can be done with 16 kilobits/sec. This option is not private. Regardless of the option chosen, and it may be site specific, Sandia has the technical capabilities to develop the assurance information transfer.

The other issue is who should receive the information. Should this be designated public officials, environmental monitoring organizations, regulation bodies, the public at large, or some combination? Such a question can not be answered straight-forwardly. It will definitely be dependent upon the process, the physical environment, and the public attitude in the area. Some of the answers can be provided through the public testimony phase of this assurance element.

8.6 Conclusion

Assurance of thermal processing of wastes is a complex issue. Sandia, however, through its technology, its scientific understanding, and possibly facilitation of public forums can provide the needed elements to achieve the necessary assurance.

9.0 APPENDIX

Included in this appendix is a listing of capabilities and activities at both the SNL California and New Mexico sites that have applicability to the ATPW project. The listing was current as of August, 1993. With a number of the sections, there are comments about application of the capability; these comments were made by Jerry Cole of Environmental Energy Research, Inc. Also listed for the various capabilities, where appropriate, are contacts, their organization, and telephone number.

9.1 General Summary of Advanced Control Concepts

9.1.1 Systems Science and Intelligent Control

Figure 3 is a simple representation of the essence of an intelligent control system. Briefly, an intelligent control system uses on-line measurements along with prior information (a model) about the system to be controlled to generate high level strategies or plans and lower level detailed commands which will cause the system to behave in a desired manner over time. The system to be controlled can be simple such as the temperature in a room or as complex as the national health care system. In any case, the systems scientist makes a number of assumptions about the system. For example, the system is assumed to be subject to inputs, only some of which are under the control of the system designer (for example, outdoor temperature is an uncontrolled input while valve position on a heater is a controlled input). It is also assumed that measurements can be made of variables meaningful to the desired performance of the system. Both input and output variables are functions of time and the structure and parameters of the system determine how input time functions are transformed into output time functions. The goal of the intelligent controller is to generate decisions, as a function of time, that result in satisfactory (perhaps optimal, provided a performance index can be defined) system performance. The role of time and sequential decision making is central to the concept of control. In particular, current decisions (and inputs) affect the system outputs only after some time. Thus subsequent decisions act on a system that is still responding to the effect of earlier decisions. This complication differentiates the systems science approach from approaches taken in static optimization or artificial intelligence.

In general, an intelligent control system is a continuous automated system and the "intelligence" resides in the computational resources processing the measurement data. However, there is wide scope for a complete system to integrate the decision making of a human operator and the automatic decision making of the machine. Some of the complexities that can exist in a real application will be identified following a brief discussion of conventional feedback control.

Figure 3. An Intelligent Control System.

9.1.2 Background on Feedback Control

The control of physical systems using feedback has existed for centuries, with simple float regulators controlling fluid levels being a typical example. More sophisticated controllers were designed and built for mechanical systems (e.g. flyball governors for steam engines) and process control (e.g. temperature, pressure and flow regulators) well before any systematic analysis of the feedback principle was begun in the mid-twentieth century. The rationale for such controllers was obvious and compelling—physical variables could be maintained within desired limits, even when subjected to disturbances, without the need for a human operator.

A simple feedback control system—A feedback control system consists of sensors, actuators, decision logic and a communication pathway to carry information among these components (Figure 4).

Figure 4. A Simple Feedback Control System.

The feedback concept shown in Figure 3 is present as well in Figure 4. The basic idea is that of error-correcting; the decision logic (controller) generates a signal to the actuator which in turn affects the system so that the difference between the desired value and the actual value (as measured by the sensor) is continuously reduced. It is assumed in this simple control system that “good performance” can be defined simply in the form of a

desired value. In general the system is subject to disturbances so that even if the error becomes zero at one instant, the controller must continue to operate to counter the effect of the disturbances. As in Figure 3, the system to be controlled is assumed to contain dynamics, implying that an input to the system at any time T is reflected in the output of the system for all future time $t > T$. It is this delayed input-output response that can cause problems when the system is placed in a feedback loop such as that in Figure 4. The purpose of the decision logic is to compensate for the system dynamics so that the overall system is both stable (no "vicious cycles" develop) and optimal with respect to a performance index.

Limitations of the simple feedback system—Simple feedback control systems like that shown in Figure 4 have had a tremendous impact in industry, with hundreds of applications ranging from aircraft and spacecraft control to regulation of diverse manufacturing processes. However, such controllers are not adequate in many situations. Why is this so? There are many ways in which the system to be controlled can be complex. Sources of complexity include nonlinearities in the system, uncertain or widely varying environments, unavailability of sensor data at a centralized location and the need for distributed decision making, complex or multiple performance goals, difficult to quantify constraints, need for different decisions to be made on different time scales, and the importance of complex patterns of sensor data in addition to the raw data itself.

In the case of nonlinearity, for example, conventional feedback controllers are based on linear models. This implies that the process can be described by linear differential or difference equations. The model comes from either fitting the parameters of an assumed linear structure using input-output data or from linearizing an assumed nonlinear structure which was derived from first principles. In fact, many systems cannot be satisfactorily controlled using controllers designed with linear models. Even if the behavior is adequate in the vicinity of a nominal operating point, large excursions from nominal (common in practice) render the fixed control logic inappropriate.

A second source of complexity is uncertainty. Since dealing with uncertainty is one of the principal challenges of intelligent control, this subject is discussed at more length in the following section.

9.1.3 Dealing with Uncertainty: Adaptation and Learning

Numerous extensions of the basic feedback system in Figure 4 have been made to address the problems noted above. The most successful of these have been directed toward making the control system perform well under larger uncertainties than a simple feedback controller can accommodate. One common source of uncertainty is due to the inherent randomness in many physical processes. Statistical fluctuations in the underlying process and instrument noise are two examples. If analysis can be done to characterize the noise statistics, then techniques known as stochastic control can be applied. Generally the same assumptions and designs carry over from the deterministic case, except that now the control logic optimizes some statistical measure of system performance. Since stochastic uncertainty by definition cannot be eliminated, controllers can be designed which minimize expected value or variance of a cost function.

Adaptive control—Another type of uncertainty demands a fundamentally different approach. This uncertainty stems from lack of prior knowledge about the structure of the

system or even parameter values for a known structure. Or it could be that such information is known initially, but changes as the process evolves. In any of these cases, the uncertainty is due not to randomness but to missing information which in principle can be obtained. If this information were revealed, then deterministic or stochastic control could be successfully applied. It is in such cases that the biological and psychological concepts of adaptation and learning have been brought to bear. The basic idea in an adaptive system is to introduce a higher level of feedback which continuously adjusts parameters built into the controller. Figure 5 shows a standard form for an adaptive control scheme.

The model in Figure 5 is selected by the designer to exhibit desirable output behavior for a certain class of inputs. It is assumed that the performance of the system would be satisfactory if the system output were the same as the model output when subjected to the same input. As in Figure 4, an error signal representing the difference between model and system outputs is used in a feedback loop. However, instead of the controller output being a fixed function of the error, in the adaptive system the error causes an adjustment of control parameters which in turn determines the controller output. This seemingly simple modification introduces major analytical difficulties, but theoretical advances have provided assurances that systems controlled in this manner can maintain predictable stable behavior.

Figure 5. A Common Adaptive Control Structure.

Adaptive methods of this type provide an effective means of dealing with parametric uncertainty about the system.

Learning—A related approach, inspired by research in psychology and animal behavior, is that of learning. As developed in the systems engineering context, learning refers to deciding, on the basis of past experience, which action out of a finite set of actions results in the best performance in a given environment. The underlying model is quite different from that of adaptive control, but the essential property of feedback and sequentially improving performance remains, as indicated in Figure 6. The environment is assumed to be stochastic in relating performance obtained to action chosen. In contrast to the feedback systems in previous figures, the information fed back in Figure 6 is the actual measure of performance (e.g. “good” responses or “bad” responses in a binary case). The job of the controller here is to learn to choose over time that action which maximizes the probability of evoking a “good” response. Effective learning algorithms have been

developed for deciding how to choose the next action based on the results of previous choices. Systems exhibiting such a learning behavior can be considered intelligent in an environment about which little is known. The model of the environment still must include a description of what actions are appropriate and what constitutes a useful measure of performance. This learning paradigm, while effective in environments that are largely unknown, must be modified to incorporate more information about the process if it is available. Integration of prior information into learning schemes is a major topic in learning research.

Figure 6. A Learning Model for Highly Uncertain Environments.

9.1.4 Intelligent Control

The use of the term *intelligent* only compounds the problems encountered with the introduction of the terms adaptive and learning into the control vocabulary. It is assumed that one knows what is meant by *intelligent*, but in fact defining intelligence is even more daunting than defining adaptation or learning. Dictionary definitions such as “the ability to learn or understand or to deal with new or trying situations” or “the ability to apply knowledge to manipulate one's environment” are useful, but of little value in differentiating among levels of intelligence whether in humans, animals or machines. For the present discussion, we assume that intelligent control refers to the above definitions of intelligence when applied to environments or new situations that are dynamic and require sequential decision making. Clearly, simple feedback, adaptive and learning controllers all could qualify as intelligent controllers according to this definition. However, we will arbitrarily refer to intelligent control as what is used when the complexities present exceed the capabilities of what we call feedback, adaptive and learning controllers today.

Systems can become complex in infinitely many ways. Adaptive and learning controllers deal with complexities that simple feedback controllers cannot. However, there remain complexities for which even higher levels of information processing are needed. For example, the uncertainty about the process may be more than that it is linear with unknown parameters. Nonlinearities pose a problem in that there currently is no design basis for adaptive controllers for nonlinear systems. Other examples of complexities beyond the scope of adaptive and learning controllers are listed below.

1. Adaptive controllers adjust continuously, but have no memory. When an environment for which satisfactory control parameters have already been found is revisited, the adaptive process makes no use of this fact.

2. Different reference models used in the adaptive system of Figure 3 may be appropriate for different conditions. Making this decision would require a higher level logic.
3. Different algorithms may be appropriate under different conditions. This would imply switching among algorithms rather than adjusting the parameters of a given algorithm.
4. Patterns of sensor measurements may be more useful for determining control actions rather than the raw measurements.
5. Other high level tasks such as planning, scheduling and resource allocation may be needed as a preliminary step prior to generating lower level control signals.
6. Upset conditions or unusual events may need special action. A "flag-raising" capability or even a switch-throwing capability may be required.

A common theme throughout the above list is the importance of recognizing useful patterns. The operator of a complex manufacturing process routinely recognizes and analyzes a wide array of patterns. In addition, a human demonstrates robustness by being able to respond satisfactorily to many different types of events. Examples of a response include adjusting control parameters, collecting additional information, or calling a supervisor. One goal of intelligent control is to make explicit use of these patterns in a control strategy. Indeed, a possible measure of success of an intelligent control system is the degree to which it can emulate the performance of a skilled human operator, and this depends critically on pattern recognition.

There are many legitimate approaches to intelligent control. Control theory provides an understanding of dynamic system models and techniques for designing suitable controllers for certain classes of disturbances and performance criteria. Artificial intelligence contributes models of higher level reasoning and rule-based methods effective for dealing with unusual events. Operations research offers optimization models and methods for solving resource allocation and scheduling problems. The ability to plan ahead and schedule is necessary for providing appropriate inputs (e.g. set point changes) to lower level controllers. Recent developments in artificial neural network models of biological information processing systems show encouraging promise for intelligent control applications. By exploiting the unique contributions from each of these approaches, it appears possible to create systems capable of intelligent behavior beyond that possible with a single approach.

Neural networks for intelligent control—To the extent that intelligent control seeks to emulate human behavior, it is reasonable to consider an information processing paradigm that is based on the human physical information processing system. This premise has led to the development of artificial neural network models that are at least crudely derived from the components of real nervous systems. Such models include representations of neurons (processing nodes), synapses (connection links) and the rules for information flow through the network. Despite painfully simple approximations, neural networks have demonstrated impressive abilities to learn complex associations and to generalize to similar but new situations. This feature is the heart of pattern recognition and, at least in constrained situations, neural networks have been able to emulate visual pattern recognition and speech

recognition. In addition, neural networks can be trained to implement nonlinear mappings required for controlling a nonlinear dynamical system. The integration of static neural network models and dynamical system models is currently an active research area.

Other research has shown the effectiveness of neural networks for solving combinatorial optimization problems, which arise often in the context of efficient resource allocation. Thus, many of the complexities described above can be addressed by the neural network paradigm. While it is unlikely that a practical intelligent control system will take the form of a single huge neural network, it is very likely that neural networks will be used as components, perhaps for pattern recognition, optimization or nonlinear control, within the overall intelligent control system.

9.2 Air Pollution Control

9.2.1 Introduction

The elements of an air pollution control system (sometimes referred to as an off-gas treatment system) will vary depending on the thermal process to which it is connected, the waste stream being treated, and the emissions requirements for the particular installation. It is assumed that an APC system can be designed to meet all emissions requirements during normal operation and can demonstrate this during trial burns. A definitive and extremely well-organized report⁶ on APC devices is available and will be the primary reference for the APC section of this report. Another good reference, which contains much more detail but little evaluation, is a book called *Air Pollution Control and Design for Industry*⁷.

The referenced report by Dalton *et al* contains practically all of the information we might want to include in a data base on air pollution control technologies. It discusses the types of air pollutants emitted by thermal treatment processes and how the waste stream characteristics and thermal system effects influence their generation. It discusses current regulatory requirements and anticipated changes. It discusses APC technologies and describes a basic process for selecting APC devices. Finally, it evaluates APC devices and systems for hypothetical waste streams. The 71 page report contains a 73 page appendix describing each of the 40 APC device technologies evaluated in the report. The technologies are grouped according to the type of pollutant removed (e.g., acid gas, particulate, heavy metal, PICs, NO_x). It also lists the principle of operation, advantages, disadvantages, and research needs for each of the 40 technologies.

The authors stress that the actual selection of APC devices for a given application depends on waste streams, locations, and thermal technologies.

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⁶ J.D. Dalton, R. L. Gillins, T.L. Harris, and A. L. Wollerman, *An Assessment of Off-Gas Treatment Technologies for Application to Thermal Treatment of Department of Energy Wastes*, DOE/MWIP-1, Martin Marietta Energy Systems, Inc., Oak Ridge National Laboratory, Oak Ridge, Tennessee, September 1992.

⁷ Paul N. Cheremisinoff, *Air Pollution Control and Design for Industry*, published by Marcel Dekker, Inc., 1993.

Following is the list of APC devices evaluated by Dalton *et al.* along with some additional information for those technologies where there is a need for substantial development.

9.2.2 Acid-Gas Removal

All acid-gas removal technologies rely upon converting the acid to a salt by reacting with an alkali reagent. Once converted, the salt can be collected as a dry particulate or dissolved in a liquid solution.

9.2.2.1 Wet acid-gas removal devices

- Packed-bed scrubbers
- Tray scrubbers
- Wet fluidized bed scrubbers
- Spray scrubbers

9.2.2.2 Dry acid-gas removal

- Dry sorbent injection
- Dry fluidized-bed scrubbing

9.2.2.3 Semi-dry acid-gas removal

- Spray dryer absorber

9.2.3 Particulate Removal

The amount of particulate in the off-gas and the size distribution of the particulate are the most important issues from the standpoint of equipment performance and public protection. High particulate loadings can result in excessive particulate releases and can shorten the useful life of the particulate removal devices. Submicron particles are more difficult to collect, contain higher concentrations of toxic compounds, and can more easily enter the lungs. Particulate removal is currently a high priority so that even though many of the listed technologies have been around for a long time there is a great incentive to improve on them.

9.2.3.1 Dry particulate removal

- Baghouses
  - Lengthen life of bags
  - High temperature bags
  - Coatings and surface treatments for mitigation of bag blinding (small particles penetrating fabric pores and plugging the filter)
- Electrostatic precipitators
- Ceramic candles

- High Efficiency Particulate Air (HEPA) filters
  - Increase durability of filtration medium and seals used to isolate dirty side from clean side
  - Develop cleanable filters
  - Higher temperature filters
- Metal filters
  - Proof of long term reliability on various thermal units
- Nested fiber filters
  - Proof of long term reliability on various thermal units
  - Tests of mechanism used to clean filters
  - Optimize needle length, bed density, and gas velocity
  - Study operation under vacuum at varying temperatures
- Gravity settling chambers
- Cyclone separators
- Mechanical centrifugal separators
  - Better construction materials and design to lessen wear and erosion
- Impingement separators
- Barrierless ultrasonic cleaners
  - Optimize power level, residence time, chamber geometry, temperature, and ultrasonic frequency

9.2.3.2 Wet particulate removal

- Venturi scrubber
  - Need improvements in sub micron particulate removal
- Other high-energy scrubbers
  - Need improvements in sub micron particulate removal
- Self-induced scrubbers
- Rotary atomizing wet scrubbers
- Free-jet scrubbers
- Ionizing wet scrubbers
- Flux force/condensation/collision scrubbers
- Froth scrubbers

9.2.4 Toxic Metals Removal

Toxic metals are present in all waste streams and are released from thermal treatment units by entrainment as particulate matter or by volatilization. When acid-gas removal and particulate removal devices are combined, 90 to 99% of the metals (with the exception of mercury) can be removed. Because toxic metals removal is a relatively recent concern, there is a lack of data for many toxic metal removal techniques. More research is needed.

9.2.4.1 Activated carbon adsorption

The use of activated carbon absorption is simple and well-tested. Its primary research need is to resolve the issue of secondary waste treatment and disposal.

The following three devices are all for mercury removal.

9.2.4.2 Selenium filters

Developed in Sweden and uses a reaction between selenium and mercury to contain the mercury. Little is known so much research is needed. Filter blinding and poisoning need to be investigated.

9.2.4.3 Sodium sulfide injection

This process typically removes 50 to 90% of the mercury—not as good as activated carbon systems, but better than acid-gas and particulate removal systems alone. Improvements are needed in the atomization process, which is the mechanism for mass transfer between the sodium sulfide solution and the mercury vapor.

9.2.4.4 Mercury scrubbers

This is a relatively new technology which reacts mercury with chemicals such as sodium hypochlorite or with a chelating agent and cupric chloride to form water soluble mercury species. Mercury can then be removed from the flue gas using conventional wet scrubbing technologies such as packed beds or spray towers. Research needed to find and test potential chemical reactions.

9.2.5 Treatment of Products of Incomplete Combustion

According to Dalton *et al*, the best method for control of hydrocarbons is to design and operate the thermal treatment unit properly. A secondary combustion chamber will minimize the production of PICs and some PICs will be removed by the acid-gas and particulate removal equipment. Many of the PICs, such as the dioxins, furans, and polyaromatic hydrocarbons are becoming a major obstacle to building waste treatment facilities and require additional treatment and detection capabilities.

9.2.5.1 Activated carbon

9.2.5.2 Catalytic destruction

Catalytic destruction of hydrocarbons is well tested, but use of process on PICs is virtually untried. There is concern over catalyst erosion, poisoning, and deactivation.

9.2.6 NO_x Abatement

NO_x abatement is generally divided into two categories. Primary technologies involve treatment prior to or during the combustion process and are not considered a part of the APC system. The primary methods achieve only a 20 to 70% reduction, so secondary technologies, which are a part of the APC system, are often necessary.

9.2.6.1 Dry NO_x abatement

Dry NO_x removal techniques involve the reduction of NO_x into molecular nitrogen and other non-polluting gases.

- Selective catalytic destruction
- Selective non catalytic destruction
- Non selective catalytic destruction
- Direct decomposition
- Electron beam process

9.2.6.2 Wet NO_x abatement

- Oxidation and absorption
- Scrubbing with chelating agents

9.2.7 Summary

According to Dalton *et al*, each APC device/technology has one or more limitations that could be improved with further research. Particular areas in which further R&D are needed are: treatment and disposal of secondary wastes, ability to remove multiple pollutants, mass-transfer rates, optimizing multiple APCDs used in an integrated off-gas train, process control, catalyst activity and resistance to degradation, and materials of construction for APCDs.

9.3 Sandia Capabilities for ATPW at the California Site

9.3.1 Combustion Chemistry

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Both fundamental experimental and computational research in combustion chemistry provides information needed to understand the complex chemical processes involved when fuels are burned. In order to understand the complex chemical processes that occur when a fuel is burned, it is necessary to determine the rates of elementary processes using state-of-the-art diagnostics and to integrate the results through the close coupling of experiment, theory, and modeling.

In combustion chemistry, we possess skills in physical chemistry, theoretical chemistry, and chemical applications of lasers. Expertise is available on ultrafast

intramolecular processes, state-to-state chemistry, molecular spectroscopy, thermal reaction kinetics, flame chemistry, thermal decomposition of energetic materials, fullerene structures, potential-energy surfaces, complex reaction modeling, and the coupling between chemistry and fluid dynamics. Experiments that characterize individual chemical reactions in detail are emphasized. Optical and mass spectrometric analysis techniques are available. Computer simulations that model idealized thermal processes are pursued. Efforts to include detailed chemistry in turbulent reacting flow models are ongoing.

Elementary reactions important to the burning of fuels or the production of pollutants are studied by utilizing slow-flow reactors to determine accurately the consumption rates of reactants or flow-tube apparatus to measure product distributions. Kinetic mechanisms involved in prototypical combustion systems using mass spectrometry and laser-induced fluorescence to probe low-pressure flames are an important part of the research. Fundamental questions of molecular dynamics are investigated using state-of-the-art laser-based techniques in order to develop complete models of kinetic processes.

Theoretical calculations of potential energy surfaces enable predictions of the reaction rates and product distributions that result when reactive species interact. These calculations are useful in extrapolating measured reaction rates and are crucial for estimating rates of elementary reactions that have not been studied experimentally. Computer modeling of the complete kinetics for combusting systems defines the dominant reaction pathways.

The experimental, theoretical, and modeling efforts focus on topics of importance to energy-producing technology. Themes of current emphasis include the formation and destruction of nitrogen-containing pollutants, the oxidation of hydrocarbons, and the kinetics of carbonaceous species related to soot.

In addition, logical extensions of our activities center on applications where molecular-level information is critical. Examples include incineration and/or supercritical oxidation of toxic materials, combustion modification using chemical additives, analytical and spectroscopic detection of trace contaminants, chemical vapor deposition, chemical lasers, laser-induced biological processes, and computer modeling of complex reactive environments.

ATPW opportunities:

- Advanced combustion system development. For example, existing burners and secondary oxidation chamber designs are based on good engineering knowledge of combustion systems. A better understanding of combustion kinetics when different waste products are involved could lead to improvements in areas such as flame stability, efficient burnout, NO_x emissions control, CO oxidation, and reduced PIC formation.
- Advances in combustion control, heat release, radiation heat transfer. Efficient heat transfer is critical to most thermal processing technologies. In waste processing this can be especially crucial for separating potentially valuable byproducts or value-added products from non-usable toxic contaminants. Simple improvements in design and operation of conventional combustion equipment could make important cost differences in waste processing

technologies, especially those involving fluid heating, as found in the plastics recycling industries.

- Primary emissions control (CO, HCs, NO_x, etc.) technologies. While there is considerable demand for improved emissions control outside the ATPW arena, many of the processes of interest to ATPW require combustion conditions that are at odds with good emissions control practice. Better understanding of combustion chemistry will be critical to meeting the demands of many ATPW technologies without incurring an emissions or APCD cost penalty.
- Improved post-treatment APCDs. Afterburners, flares, hot cyclones, and ceramic filter baghouses are examples in which combustion participates in the final destruction of organic wastes or processing byproducts. Better understanding of combustion, and formation during combustion, of larger and more complex organic molecules will support developments in this area.
- Primary support tools for most other non-diagnostic ATPW developments.

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Chemical kinetic models of turbulent jet flames are being developed under the sponsorship of the Gas Research Institute (GRI). The models use simple submodels for turbulent mixing in order to retain complete description of the elementary chemical reaction mechanism. The empirical mixing models are derived from laboratory flame experiments, which GRI is supporting at Pennsylvania State and Stanford

ATPW opportunities

- Improved combustor design. Flame-mode processing and flame-mode destruction of waste materials is conducted primarily with turbulent diffusion flames. Present understanding of these flames is mainly empirical, and even simple chemistry, such as that of NO_x formation is difficult to predict. Improved understanding and prediction algorithms could lead to better hardware designs and improvements in efficiency, heat release patterns, process/destruction efficiency, and reduced pollutant emissions.
- Advanced afterburner development. Afterburners operate in a special regime where bulk oxygen concentrations are low, and temperatures are high. In addition, the concentration of the target species (pollutant or combustion byproduct) is generally low. Auxiliary fuel and/or oxidant generally burn under conditions of stretch and strain and with free boundaries, leading to turbulent conditions during combustion. Advances in predictability for turbulent combustion modeling could lead to improvements in afterburner efficiency in terms of compound removed per unit fuel consumed.
- Improved understanding and design of incinerator primary and secondary oxidation chambers. Conventional practice in incinerator design uses a few rules to define l/d, refractory thickness, and exit port size and location. The effects of far-field boundaries on turbulent combustion are rarely, if ever,

considered. Heat transfer between furnace walls and the primary combustion zone, and reentrainment of burned gases have impacts on flame stability, combustion temperature and flame structure. Improvements in these models may lead to advanced designs for primary and secondary oxidation chambers in waste incinerators incorporating non-intuitive geometries and heat-transfer materials and surfaces.

- Possible spin-off applications in high-temperature thermal treatment/recycle/recovery technology development (e.g. recycling of plastics, tires, lubricating oils, etc.) More discussion under “Reacting Flows,” below.

9.3.2 Turbulent Combustion Measurement and Modeling

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Extensive experimental and theoretical capabilities exist for fundamental studies of the coupling and interaction of fluid dynamic mixing and chemical kinetics in turbulent reacting flows.

The experimental facilities include the Turbulent Diffusion Flame laboratory, the Planar Imaging laboratory, and the Turbulent Flame Structure laboratory. Each laboratory allows a high degree of optical access for laser diagnostics and has the flexibility to support a variety of fuels and burner geometries for both premixed and nonpremixed flames. Simultaneous point measurements of NO, OH, major species, and temperature provide detailed information on the chemical structure of reaction zones in turbulent flames. Planar imaging capabilities are used to determine the spatial structure of turbulent reacting flows. Techniques include simultaneous two-dimensional imaging of CH₄, CH, and OH in turbulent methane flames, simultaneous imaging of NO and temperature, simultaneous imaging of OH and acetone (a fuel marker), and imaging schemes to measure molecular mixing and differential species diffusion.

The reacting flows modeling capabilities include computational fluid dynamics, direct numerical simulation of turbulence with chemistry and detailed modeling of mixing and reaction. The one-dimensional linear eddy mixing model, unique in its representation of the distinct influences of convective stirring and molecular diffusion, has been used to interpret measurements of chemical reactions in spatially homogeneous turbulent flows. Direct numerical simulation of three dimensional turbulence with a passive flame propagation model has shown that the flame geometry is related to the structure of the turbulence. Multi-step chemistry in curved diffusion flamelets is being compared with the established planar, strained flamelet results, in particular modeling of NO formation. Direct numerical compressible flow simulations show the interaction of flow and chemistry in a reduced chemical kinetic scheme.

ATPW opportunities

- Combustion control.
- Positive feedback/forward control system development.
- System performance analysis.

9.3.3 Reacting Flows

"This section intentionally left blank." Refer to Section 9.4.2.

9.3.4 Combustion in Engines and Furnaces

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A broad program of research on the combustion processes in internal combustion engines and furnaces is being pursued. In the engine area, the program focuses on the application of advanced laser diagnostics to provide insight into critical problems impeding the development of improved engine concepts. The problem areas under investigation include the interaction between precombustion fluid mechanics and combustion, end-gas autoignition leading to engine knock, and the autoignition and combustion properties of alternative fuels for diesel applications. Research involves the development of nonperturbing, laser-based methods that provide time- and space-resolved measurements inside combustion engines. A continuing focus is the application of these diagnostics toward more practical engine configurations.

A complementary activity that focuses broadly on continuous combustion systems for furnace and boiler applications, which have major implications for ATPW, has produced interesting new results. The program focuses on the application of advanced laser diagnostics to provide insight into critical problems impeding the development of improved furnace concepts. Initially, the intent of this program was to perform fundamental investigations of the pulse combustion process and to incorporate this new understanding into a physically based computer model. The model that has evolved is being used by industry to speed the design of compact, high efficiency, multifuel pulse combustors. More recently pulse combustion has been demonstrated as an effective technology for the destruction of chlorinated VOC's, and a field demonstration unit is under development. In addition units producing ultra-low emissions of NO_x and CO have been demonstrated.

The Sandia Research Furnace is used to study the critical processes of group combustion in steady spray flames. Laser imaging techniques provide new insight into the controlling processes to enable combustor designers to meet future needs for increased fuel flexibility and efficiency, increased industrial productivity, and control of emissions.

The Burner Engineering Research Laboratory is being used to apply advanced diagnostics to the characterization and development of industrial scale gas burners.

ATPW opportunities

- Incinerator design and analysis. Interestingly, an internal combustion engine can be operated to act as both a vacuum (suction) pump and combustion device. Research into how introduction of moisture and organic soil contaminants affect combustion efficiency and engine emissions would be of use. Also, study of incinerator geometry and its effect on heat and mass transport.
- High-temperature separation process technology development. Empirical developments in heat distribution during combustion in conventional and

advanced burners could be used to improve energy efficiency and emissions control as well as product quality in fluid-heating separations processes.

- Combustion/heating/incineration processes utilizing advanced heat and mass transfer concepts such as pulse combustion. Acoustic stabilization of heat release and mass transfer processes could be used to improve burnout, reduce auxiliary fuel consumption, and reduce combustor size.

9.3.5 Coal Combustion

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A broad program of research is underway to gather fundamental information on important features of pulverized coal combustion processes and to develop improved *in situ* sensors to monitor coal utilization process streams. The combustion studies are aimed at acquiring extensive qualitative and quantitative experimental data and at using the data to develop predictive models that describe the combustion behavior of the organic and inorganic constituents of commercially important steam coals.

The experiments use well-controlled laboratory flow reactors to obtain spatially and temporally resolved data during the combustion of well-characterized coals under conditions of practical industrial importance. Several of the reactors are instrumented with modern optical diagnostics for *in situ* observation of the size, temperature, and velocity, or residence time, of individual reacting particles for narrowly size classified coal samples. The experiments are designed to measure the kinetic rates, chemical mechanisms, and products of devolatilization of raw coals and of the subsequent oxidation of the residual chars. These data are providing critical ingredients to new predictors—useful engineering models—of the processes of devolatilization and char oxidation, based upon chemical and physical descriptors of the raw coals and of the combustion environment.

Considerable resources are also being devoted to determining the high temperature combustion transformations, subsequent evolution, and ultimate deposition on heat transfer surfaces of the inorganic species imbedded in the coal matrix. Our newest facility, the Multifuel Combustor, allows realistic simulation of both the combustion and deposition environments in a full-scale industrial boiler for typical power-plant grinds of pulverized coals. This pilot-scale combustor is being used to conduct measurements of the transformation and deposition of mineral species on simulated boiler steam tubes during coal combustion.

In addition to these measurements, extensive chemical analyses of isokinetically captured samples are conducted off line. Specific attention is being devoted to improving and quantifying the accuracy and precision of computer-controlled scanning electron microscopy for quantitative measurement of the morphology and composition of these captured samples. Data from these three reactors are being used to develop an industrially oriented engineering model to predict ash deposition rates, as well as to predict the character (e.g., chemical composition, emissivity, tenacity, and removability) of ash deposits formed under conditions representative of both conventional boilers and of advanced, 21st century, coal utilization equipment.

In addition to this problem-driven, coal combustion research, work continues at the CRF on the development and validation of advanced optical diagnostics for application to particle-laden, coal combustion flows. Two of these techniques, Fourier transform infrared spectroscopy (FTIR) and laser spark spectroscopy, are proving useful for direct, *in situ* measurements of the chemical species and the elemental constituents, respectively, within coal ash deposits.

ATPW opportunities

- Advances in metals emissions monitoring and controls. Spinoffs into solids feed stream characterization. Could be applied to cement kiln incinerators for on-line control of alkali metals feed rate. Also useful for biomass incineration if coupled with advanced combustor process control algorithm. Current biomass combustion processes have problems with slagging that could be mitigated by active control of stoichiometry and temperature, or by active control injection of auxiliary fuel if on-line real-time flame-zone detection and determination of ash composition could be effected.

9.3.6 Solid-fuel Combustors

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Sandia, California has four laboratories for studying the combustion behavior of pulverized solids in entrained flows. The Coal Combustion Laboratory houses a bench-scale gas-flame-supported laminar flow combustor with optical access for particle diagnostics. This facility is primarily used for fundamental studies of the heterogeneous kinetics of solid-fuel combustion. The Coal Devolatilization Laboratory houses a similar reactor in which inert carrier gas is electrically heated to study the pyrolysis behavior of pulverized solid fuels. The Burner and Diagnostics Development Laboratory houses a third similar reactor, equipped with an FTIR and long path-length heated cell for analysis of combustion processes. The fourth laboratory contains the Multi-Fuel Combustor, a two-story refractory-lined pilot-scale furnace designed to produce particle loadings and residence times simulating those found in suspension-fired boilers. The Multi-Fuel Combustor is equipped with independently-controlled electrical heating segments that allow tailored temperature profiles, and an open test section for application of optical diagnostics.

ATPW opportunities:

- Advanced separations/recovery processes, especially for low-level mixed wastes. Current DOE mixed wastes contain solid and liquid combustible components that need to be separated from solid, solute, and liquid radioactive materials. Application of these laboratory facilities could answer questions relevant to separation and recovery of radioactive inorganic components of these waste streams.

9.3.7 Supercritical Water Oxidation

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Sandia, California has two research laboratories dedicated to waste destruction by supercritical water oxidation processes. In addition, Sandia has an engineering development reactor that is used to address design issues, materials development, and waste destruction feasibility issues. One laboratory houses a bench-scale tubular flow reactor of approximately 20 ft in length, processing on the order of one gal/hr. The reactor typically operates at temperatures of 450°C and pressures of 4000 psi. The second laboratory houses a reactor with a 1 in³ volume primary chamber with optical access for hydrothermal flame studies.

ATPW opportunities

- Direct applications in toxic substance destruction. This application is already under development.
- Separation and organic destruction in low-level mixed waste treatment. SCWO could be applied to the problems at, e.g. Hanford, where organic compounds need to be oxidized and radioactive compounds separated from the remaining aqueous waste. The effects of SCWO on solubility of inorganic ions could be exploited for specific separation processes.

9.3.8 Plasma Processes

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Sandia, California has bench-scale devices incorporating plasmas (microwave, inductive, capacitive) for diamond deposition and a plasma arc system for waste destruction studies.

ATPW opportunities

- Novel materials and interface surface developments. One area of particular interest lies in biomass processing where heat exchange surfaces are often fouled by low-melting ash (slag). The application of a surface coating such as diamond to heat exchange tubes might change the adhesion of the slag, slowing its buildup and/or making it easier to remove during operation. This would be of especial interest if it could be done in place to existing equipment.
- Specialized waste treatment/recovery technologies. Plasma arc processes have already been demonstrated for incineration/gassification and vitrification of medical wastes. Application could be extended to mixed and radioactive waste streams.

9.3.9 Combustion Diagnostics

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One of the primary thrusts of the combustion research program at Sandia National Laboratories is the development of diagnostic techniques that take advantage of the latest advances in laser and detector technology. This development effort has three objectives: the development of innovative methods for non-intrusive probing of combustion systems, a quantitative understanding of the usefulness and limitations of these methods, and the transfer of technology from research to application environments.

Because of their non-intrusive nature and great versatility, laser-based optical techniques receive the strongest emphasis. Techniques considered include: laser-induced fluorescence, resonant wave-mixing, spontaneous and coherent Raman spectroscopy, laser Doppler velocimetry, and multiphoton optogalvanic spectroscopy. New laser diagnostic techniques for measurements of temperature, species concentrations, velocity flow fields, and other parameters of importance for the understanding of combustion phenomena have been developed. The capabilities of laser diagnostic techniques depend directly on the availability of laser sources with unique spatial, temporal, and spectral properties, and an important feature of the combustion diagnostics program is the development of high-performance lasers that meet the requirements for specialized laser-diagnostic applications.

ATPW opportunities

- Improved process control. Applications exist for development of a range of *in situ* analyzers for primary combustion processes used in waste processing. Most of these would require advanced process control algorithms, and in some cases advanced process control hardware, in order to become effective. Spatial temperature measurement, and in-flame detection of key intermediate species such as 1,3-butadiene, H₂, CO, or benzene could be exploited to improve primary flame control, and also to feed-forward to secondary oxidation chambers or afterburners.

9.3.10 Sensors/Diagnostics

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Sandia has extensive capability in the development and application of sensors and instrumentation, many of which have been directed toward combustion science and combustion application. A large set of these have been based on lasers.

Laser-based techniques that Sandia has developed or have used for research and development purposes include the following:

Raman Spectroscopy—Light scattering that has molecular discrimination, concentration, and localization capabilities; can be used for temperature measurement.

Rayleigh Scattering—Permits measurement of total gas density.

Inverse Raman—Probe laser utilizing the Raman effect for measurements of molecules at reduced concentrations along a line of sight.

Coherent Antistokes Raman Spectroscopy (CARS)—Four wave mixing technique for sensitive molecular identification and temperature measurement within a volume.

Laser Induced Fluorescence (LIF)—Molecular identification that arises from fluorescence induced by incident laser, generally in a plane.

Laser Induced Incandescence (LII)—Particles are heated and detected through optical emission.

Multi Photon Induced Fluorescence—Used to determine atomic concentrations.

Antiresonant Ring Transient Spectroscopy (ARR)—Used to increase signal to noise ratio for detection of minor species.

Spark Analysis—With a laser, metals are excited and their emission lines are measured enabling concentration and identification.

LASS (Laser Spark Emission Spectroscopy)—Laser induced spectroscopy for elemental analysis.

LIDAR—Light scattering techniques for identification of molecules from great distances.

DIAL (Differential Absorption on Line-of-Sight)—Line-of-sight absorption-differencing technique for sensitive molecular identification.

Optical and IR Absorption—Transmission measurements for line-of-sight identification of molecules.

Laser Doppler Velocimetry (LDV)—Seeded flows are used to measure fluid velocities based on frequency shifts.

Flash X-Ray—Can identify density changes in dense matter as a functions of time.

Laser-Induced Gratings or Resonant Wave Mixing—Nonlinear optical techniques usually based on four-wave mixing. Used to detect minor species with high spatial and temporal resolution. Imaging configurations are possible. Both ultraviolet and infrared wavelengths can be used; the latter can also provide major species measurements.

Other optical or infrared techniques that do not include the use of a laser are:

Fourier Transform Infrared Spectroscopy (FTIR)—Thermal emissions in the infrared are used for identification and concentrations.

Optical Emissions—Thermal emissions are used in the optical for molecular identification, concentrations, and temperature; may utilize fiber optics.

One- and Two-Color Thermometry—Intensity measurement(s) enables determination of temperature.

Thermography—Temperature distributions are made in real time.

Measurements are also commonly made that do not depend upon electromagnetic waves:

Time-of-Flight Mass Spectroscopy—Allows species identification based on velocity.

Quadrupole Mass Spectrometry—Ionization and magnetic fields separate various molecules.

Speed of Sound—Provides temperature of the gas.

Isokinetic Probes—Gas concentration measurements can be made based on the speed of sound.

Ion Probes—Localize the position of the flame front.

Ultra Sonic Emissions—Acoustic signature in frequency and intensity identifies temporal features.

Conventional Pressure—As a result of work with high-pressure gas flows and internal combustion engine research, Sandia has extensive experience with conventional gas pressure measurements (up to kilobars).

Conventional Temperature measurements—Expertise exists in thermocouple measurements, pyrometry, soot emissions, and other conventional themometric techniques.

ATPW opportunities

- Tremendous opportunities in process control, monitoring, secondary treatment, emissions inventory control.

Specific opportunities identified with individual diagnostic methods include:

Raman Spectroscopy—Light scattering that has molecular discrimination, concentration, and localization capabilities; can be used for temperature measurement.

Rayleigh Scattering—Indirect estimation/determination of waste feed heating value, when corrected for moisture, in fume incinerators.

Inverse Raman—Probe laser utilizing the Raman effect for measurements of molecules at reduced concentrations along a line of sight.

Coherent Antistokes Raman Spectroscopy (CARS)—Possible applications for *in situ* real-time temperature measurements, particularly in homogeneous fluids.

Laser Induced Fluorescence (LIF)—Identification of PAHs in primary combustion zone of air-starved med-waste incineration systems and in stack gases of all waste combustion processes. *In situ* NO measurements.

Laser Induced Incandescence (LII)—Determination of soot particle concentration. Real time determination of key metals: presence and concentration in dispersed fly ash.

LASS (Laser Spark Emission Spectroscopy)—Good candidate technique for determination of metals concentration and composition in solids feed to thermal desorption, incineration, plasma arc, and other solids processing methods. Also has potential applications for flame zone monitoring for volatile metals concentrations and for criteria metals emissions as particulate matter at the stack.

LIDAR—Remote stack monitoring for key species emissions. Fugitive emissions detection and monitoring from waste handling/processing facilities.

DIAL (Differential Absorption on Line-of-Sight)—*In situ* real-time identification and determination of HCl and organic chlorides in plastics reprocessing operations.

Optical and IR Absorption—QA measurements in tire and plastics reprocessing effluent. *In situ* determination of key species in waste combustion processes, after primary pyrolysis, secondary oxidation and in stack.

Laser Doppler Velocimetry (LDV)—Actual fluid velocity in particulate laden gas and liquid streams.

Flash X-Ray—Potential for identification of metals concentrations in solids and slurry process feed streams in cement kilns, rotary kilns, plasma arc incinerators, and other systems sensitive to metals and fugitive emissions. Also a possible technique for identification of heavy metals in feed to soil thermal desorption processes.

Fourier Transform Infrared Spectroscopy (FTIR)—Process quality control in value-added processing of plastics and other petroleum-based waste streams. Useful for monitoring of process effluent composition when instantaneous information is not required.

Optical Emissions—Process chamber wall temperature.

One and Two Color Thermometry—Potential use for real-time process control in plasma-arc processing. Process temperature is affected by heats of vaporization and fusion of feedstock components. Optimal temperature must be maintained for effective waste stream processing with minimal energy consumption.

Thermography—Has applications for mapping and monitoring temperature distribution in waste incineration and fluid heating systems.

Measurements are also commonly made that do not depend upon electromagnetic waves:

Time-of-Flight Mass Spectroscopy—When coupled with extractive sampling has potential for real-time monitoring of critical emissions in incineration systems.

Quadrupole Mass Spectrometry—Ionization and magnetic fields separate various molecules.

Speed of Sound—Could be applied for process monitoring in incineration systems.

Isokinetic Probes—Gas concentration measurements can be made based on the speed of sound.

Ion Probes—Localize the position of the flame front.

Ultra Sonic Emissions—Acoustic signature in frequency and intensity identifies temporal features.

Conventional Pressure—As a result of work with high-pressure gas flows and internal combustion engine research, Sandia has extensive experience with conventional gas pressure measurements (up to kilobars).

Conventional Temperature Measurements—Expertise exists in thermocouple measurements, pyrometry, soot emissions, and other conventional themometric techniques.

9.3.11 Industrial Processing

Don Hardesty, 8361, (510) 294-2321

Chuck Hartwig, 8366, (510) 294-3047

We are engaged in a variety of projects in areas of industrial processing whose common theme is an emphasis on understanding the behavior of materials undergoing high-temperature conversion processes as a function of the chemical and physical properties of the starting material, as well as the key parameters that characterize the processing environment. Included in this industrial processing research is research on the high-temperature combustion synthesis of new materials, in particular silicon carbide, research and process development on the destruction of hazardous wastes using supercritical water oxidation, and fundamental investigations of the decomposition of energetic materials including propellants and explosives and of the stability of highly exothermic, condensed-phase, thermite reactions.

The experiments employ well-controlled laboratory reactors that simulate the key features of practical industrial processing systems and permit the temporal and spatial resolution required to allow the details of these complex, multiphase, high-temperature processes to be interrogated. Optical diagnostics in these experimental reactors permits application of the wide array of laser diagnostics available in the CRF to measure temperature, velocities, and species compositions. Rapid quench sampling systems are also used in combination with mass spectrometric analysis of extracted materials to obtain detailed information on both reaction intermediates and products.

In research on the high-temperature synthesis of silicon carbide we are developing a comprehensive understanding of processes that rely upon gas-phase and surface reactions, within the silicon-carbon-hydrogen-chlorine system, that yield silicon carbide in the form of surface coatings, powders, and high-density composites. Models are used to describe the chemical vapor deposition of silicon carbide and to understand the behavior of industrial reactors that rely on particle enhancement to augment the rates of silicon carbide deposition. Silicon carbide surfaces are examined with molecular and atomic hydrogen, and quantum chemistry is used to develop the thermochemical parameters required in both the models and the experiments.

Our research on the destruction of toxic aqueous wastes by supercritical water oxidation involves the development and use of unique experimental reactors to investigate key operational features of this promising technology. These reactors permit the application of advanced laser diagnostics in experimental studies of waste destruction efficiencies, chemical reaction kinetics, and hydrothermal flame formation.

Our work on energetic materials and processes includes experimental studies of the complex chemistry associated with the decomposition of propellants and explosives using simultaneous thermogravimetric and modulated beam mass spectrometry. In addition, theoretical research is being done to describe resonant mode interactions in thermite type reactions.

ATPW opportunities

- Advanced materials for, e.g., corrosion resistance, heat transfer, diagnostics hardening, etc.

9.3.12 Experimental Applied Mechanics

Wendell Kawahara, 8746, (510) 294-2614

Laboratories are available for experiments and testing in structural, fluid, and thermal mechanics research and development. For material testing and constitutive model development, loads of up to a million pounds are available on a variety of machines. Stress-strain curves can be obtained at a variety of temperatures, strain rates, and heating rates. Special holographic techniques are available for strain measurements and non-contacting surface strain measurements, such as "hole-burning." Thermography is applied to non-contacting thermal measurements. Lasers are used for fluid measurements through Schlieren and LDV. Flow measurements are available from molecular to viscous to inertial to turbulent. Significant research is done in porous materials and non-Newtonian fluids.

Conventional flow, temperature, strain, pressure, stress measurement packages are available.

9.3.13 Computational Applied Mechanics

Mel Callabresi, 8743, (510) 294-2064
Bob Kee, 8745, (510) 294-3272

Numerical analysis capabilities are available for structures, heat transfer, and flow. Structural analysis features finite element Sandia and LLNL developed codes as well as commercially available codes. These include the DYNA, PRONTO, and ABAQUS suites of codes. Individualized material constitutive models are included with individual failure models possible. Research has focused on structural steels, stainless steels, aluminum, and fiber wound composites.

Three dimensional finite THERMAL analysis is available with TACO that presents conductive heat flow, multiple radiation enclosures, and a variety of means to include heat transfer boundary conditions. Coupled structural/thermal calculations are performed with the commercially available code, ABAQUS, or a new suite of Sandia codes, JACK. A new Sandia code, COYOTE, is being developed to focus on phase changes and other high temperature non-linear heat transfer phenomena.

For gas transfer, the code TOPAZ is used to calculate flow rates, pressure waves, and mass accumulation. Fluid thermodynamic packages are built around CHEMKIN. For flow field and temperature distributions in fluids, the commercially available package, FIDAP, is predominantly used. Specialized numerical application codes are built per need.

9.3.14 Controls and Intelligent Processing

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Bob Hurt, 8361, (510) 294-3707
Richard Wheeler, 8112, (510) 294-2443

Numerical analysis experience exists in control of various chemical synthesis and combustion processes. Applications include chemical vapor deposition in rotating disk reactors and low-pressure diffusion furnaces, diamond growth by plasma torches and premixed flames, coating of parts in high-temperature furnaces, and pulse combustors.

Generally, chemical process models are built upon the CHEMKIN and Surface-CHEMKIN software developed by Sandia. The process models are implemented within the Matrix-X software that provides intelligent control algorithms. Sandia is working with Relman Inc. and Integrated Systems Inc. on projects supported by SEMATECH and DARPA. Sandia works closely with process control designers to insure that the process model provides sufficiently quantitative simulations. Once control of the process model is demonstrated, the controller is applied to the actual manufacturing process.

9.3.15 Materials

Mark Perra, 8714, (510) 294-2093

Jim Wang, 8713, (510) 294-2786

Sandia's Materials and associative Applied Mechanics expertise encompass three interrelated scientific and technical research and development program components: synthesis and processing; materials characterization; and theory, modeling, and simulation.

Materials capabilities that specifically relate to high temperature processing include:

Alloy Design, Development, and Processing

Ceramics/Glass Synthesis and Processing

Materials and Process Modeling

Coating Technology and Interfacial Phenomena

Materials Joining

Materials Reliability, Lifetime Prediction, and Corrosion Kinetics

Materials Characterization and Testing

In materials joining, Sandia has broad-based capabilities in welding, soldering, brazing, glass to metal sealing, and adhesive bonding. Experience in assembly welding spans a size range of three orders of magnitude from explosive bridge wires less than a 0.001-inch to bomb castings of over an inch in thickness. Brazing of advanced metal alloys, graphite, and ceramics to metals represents an area of enduring expertise at Sandia. Numerous CRADA's and industrial partnerships are in-place, including gas-tungsten arc welding of thin-section, Ti alloy sheets with Pratt and Whitney and establishing advanced brazing technology with Allied-Signal Corporation for the joining of silicon nitride to a variety of metal alloys for aerospace applications.

Sandia specific capabilities in high temperature corrosion includes corrosion product analysis (*in situ* and *ex situ*), substrate analysis (e.g., microstructural changes and thermochemical equilibrium studies), materials engineering analysis (e.g., lifetime predictions), and high temperature environmental testing (e.g., non-contact measurements of surface chemistry, materials, deformation, and crack growth).

For material characterization and testing, Sandia has a blend of advanced analytical techniques, process and environmental monitors, and failure analysis. Advanced analytical techniques presently under development include chemometrics, back-scattered electron Kikuchi pattern acquisition and analysis, x-ray topography, and high resolution electron microscopy. Some of the companies with which Sandia is pursuing joining instrument development are Radiant Technologies, Photometrics, and SEMATECH.

Other projects related to ATPW include the development of materials for advanced aircraft engines (\$15M CRADA that includes a consortium of six engine manufacturers), and aluminum alloy casting project, and a project to model the distortions that develop during heat treating.

9.3.16 Design and System Engineering

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Howard Hirano, 8441, (510) 294-2053
Bill Peila, 8453, (510) 294-2077

At the California site, there are 230 members of the engineering organization—management, staff, and technicians. Responsibilities include design, manufacturing coordination, system integration, engineering analysis, materials definition, and test. On site fabrication capabilities include a machine shop, a welding laboratory, an electronic fabrication shop, and a test unit assembly area. There are special laboratories for high pressure testing with hazardous gases (hydrogen and others up to 100,000 ksi), the test and design of telemetry and control systems, the proofing of components and systems with environmental testing, and the testing of explosive components. The principal engineering expertise is electrical/electronic and mechanical.

9.3.17 System Analysis

Richard Wheeler, 8112, (510) 294-2443
Jim Ringland, 8112, (510) 294-3299

System Analysis has played a key role in guiding Sandia programs and in providing a basis for interactions with our external customers. Our goal is to provide critical insights that impact program decisions and directions. We accomplish this by integrating a broad range of technical and non-technical information through the use of computer models and other analytic techniques. Our work is broad based and interdisciplinary. Our studies have ranged from one-person-month reviews of a specific management issue to multi-year, multi-person computer simulations. Specific capabilities include the following:

Strategic Planning Support—We have provided analytical support to both internal and DOE strategic planning efforts. In some cases this has involved directly framing issues and developing planning documents. In others, we have provided supporting studies, have developed metrics, and gathered project data.

Probabilistic Risk/Safety Analysis—We have quantitative risk studies early in program development to help guide initial design choices and during later full-scale development to help maximize the value of testing and analysis activities.

Cost and Cost/Benefit Studies—We have done cost and cost/benefit studies for applications as diverse as the Solar Thermal Program in the late 70's and early 80's to current DOE hazardous and radioactive waste handling and disposal.

System Architecture Definition—We have helped define specific physical and logical elements needed to carry out initially only broadly-defined goals. Applications have ranged from architecture studies of ballistic missile defense in the mid-80's to studies supporting manufacturing needs for Complex-21.

Operations Analyses—Once a system architecture is defined, we have applied models ranging from simple analytic calculations to complex simulations to evaluate the effects of specific engineering design and operational choices on system performance.

9.4 Sandia Capabilities for ATPW at the New Mexico Site

9.4.1 Laser Development (NM)

Tom Raymond, 1128, (505) 844-9166

Sandia is developing solid-state laser technology primarily for applications in remote sensing. Emphasis is on rugged, compact, field-deployable devices. Output is generally pulsed, with wavelengths ranging from the near-ir to the near-uv.

Optical Parametric Oscillators—Broadband, tunable, solid state source of coherent radiation; visible to uv wavelengths. Being developed for remote sensing of complex molecules using laser-excited fluorescence and chemometric analysis.

Ti:Sapphire Oscillators/Amplifiers—Broadly tunable solid-state laser in the near ir, being developed for differential absorption lidar. Stable, single-frequency oscillation.

Compact Single-Frequency Dye Oscillators—Modified Littman-type oscillators emitting short pulses (2-3 ns). Can be scanned over large wavelength ranges while operating in a single longitudinal mode. Well-suited for spectroscopic applications.

Tunable VUV lasers—Very large, complex system of lasers used to obtain VUV radiation using resonant wave mixing in metal vapor. Relatively high pulse energies are obtained.

9.4.2 Controls

At SNL/NM the Intelligent Systems and Robotics Center, 1600, encompasses much of Sandia's expertise in control. Adaptive machining, robotics, and virtual reality are examples of focus areas. Contact to discuss overlap with ATPW has not yet been made.

Kathleen Alam and others in Department 1823 have demonstrated an automated technology for separating plastics. The group has trained a neural network to recognize differences in infrared spectral features of different plastics and to give control signals for sorting. This type of work may have appreciable overlap with ATPW.

9.4.3 Sensors/Instruments at SNL/NM

Art Verardo, 6612, (505) 845-9614

Chemical Microsensors—Chemical sensors that are built from surface acoustic wave (SAW) devices, micromirrors on fiber optics, and silicon based devices. Absorption of molecules change physical properties. Coating SAW devices with

polymers like polyisobutylene make them effective for detecting VOC's. Detection limits can be from 1 to 50 ppm.

Multispectral UV Fluorescence—Fluorescence spectrum is known as a function of excitation frequency. Using two excitation frequencies enable single component detection in multicomponent mixtures. May be used at distances up to 10 km.

Ion Mobility Spectrometer—Has been applied to explosives detection. Works well for most, but not all, halogenated compounds. Can be used at atmospheric pressures. Can have ppt sensitivity.

IR Spectrometry with Neural Networks—Reflectance spectra obtained for various plastics and used to train network. Can be used with trash.

9.5 CRF Basic Research Projects Related to ATPW

The following is a list of basic research projects at the CRF that support competencies required in the area of Assured Thermal Processing of Wastes (ATPW.)

George Fisk, 8353, (510) 294-3376

Project 0425: Combustion Analysis by Advanced Methods plus Combustion Diagnostics Development (\$5,200K in FY93). This is part of the major BES Chemical Sciences project at the CRF. It supports basic research in diagnostics, reacting flow, and combustion chemistry. Some areas of emphasis are indicated below.

- **Laser-Based Diagnostics**
  - nonlinear optical techniques such as coherent anti-Stokes Raman spectroscopy (CARS), degenerate four-wave mixing (DFWM) and multiphoton ionization
  - linear optical techniques such as laser-induced fluorescence (LIF), spontaneous Raman scattering, and Rayleigh scattering
- **Turbulent Combustion Measurements**
  - turbulent diffusion flame experiments
  - planar imaging
  - turbulent flame structure
- **Turbulent Reacting Flow Modeling**
  - computational fluid dynamics
  - direct numerical simulation of turbulence with chemistry
  - computation of turbulent flames with full chemistry using parallel techniques
- **Flame Chemistry**
  - low-pressure, laminar flame experiments
  - modeling of detailed chemistry in these flames
  - determination of pathways leading to pollutants

- **Chemical Kinetics**
  - measurements of rate constants and product distributions for individual chemical reactions
  - theoretical calculations of potential-energy surfaces and reaction paths
- **Chemical Dynamics and Spectroscopy**
  - ultrafast intramolecular processes
  - state-to-state chemistry
  - photodissociation dynamics
  - molecular spectroscopy and structure

Project 1035: Analysis of Turbulent Reacting Flows (\$425k in FY93). This project supports development of numerical simulation techniques for understanding unsteady reacting turbulent flows. Research focuses on detailed mechanisms for the transport of heat, mass, momentum, and chemical species. This project supports our general competency in the theory of turbulent reacting flows rather than a specific element of ATPW.

Project 1153: 1) Mixing and Phase Change During Combustion and 2) Supercritical Water Oxidation (\$250k in FY93). Task 1 supports the linear-eddy approach to issues of molecular mixing in turbulence. Task 2 supports basic research on diffusion flames in aqueous media above water's critical temperature and pressure. This project provides general, core support for areas within ATPW; follow-on research to that in task 2) could give specific support.

Project 4921: Strategic Environmental Research and Development Program: Kinetic Mechanisms for Supercritical Water Oxidation (SCWO) (\$382k in FY93) This project supports basic research aimed at understanding the chemical steps involved in the destruction of material via SCWO. The effort includes flow-reactor experiments and development of improved kinetic models. It supports ATPW generally, and follow-on research could support specific ATPW elements.

Projects 2764 (Mobile testbed), 4912 (CALIOPE), and LDRD (Environmental Monitoring System): Remote Sensing of pollutants, effluents, and trace species in the atmosphere.

- **Mobile Testbed**

A mobile (two semi trailers) UV-Raman Lidar capability has been established and applied to atmospheric water-vapor measurements. The testbed is designed to accommodate the development and testing of future remote sensing applications.

- **CALIOPE**

CALIOPE is the acronym for Chemical Analysis by Laser Interrogation of Proliferant Effluents. Sandia is engaged in a collaborative program with other National Laboratories to conduct a variety of studies in this area.

- **LDRD**

A mobile (van) environmental monitoring system incorporating remote-sensing Lidar technologies is currently being developed. This capability will allow rapid response to needs of industrial partners.

9.6 CRF Applied Projects Related to ATPW

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Chuck Hartwig, 8366, (510) 294-3047

9.6.1 PERF (Petroleum Environmental Research Forum)

For energy, petroleum refineries burn their excess refinery gases. Pending pollution regulations will make it more difficult to use these gases because of their combustion and unburnt products. PERF is a program to improve the burners using refinery gases to enable them to meet their pending pollutant requirements. The program has a scaled approach working from a research burner to BERL to an industrial burner. Both computational and experimental capabilities are included. The program is being done in cooperation with refineries.

9.6.2 BERL (Burner Engineering Research Laboratory)

The BERL laboratory was built in cooperation with EER and is sponsored by GRI and DOE. The laboratory is being used by companies for the design of new burners. The firing rate extends from 100 MBtu/hr to 3 MM Btu/hr. Conventional instrumentation and laser diagnostics, including Schlieren, planar Mie scattering, LDV, Fluorescence, Degenerate Four Wave Mixing, and CARS, are available.

9.6.3 Biomass Combustion: Environmental and Process Performance of Biomass Boilers

Program is being sponsored by DOE through NREL. Research is a joint topic with UCD and Bureau of Mines and is sponsored by a collection of power station operator, boiler manufacturers, EPRI, and Biomass Power Producers. The combustion and ash deposition of various biomasses are being examined.

9.6.4 Coal Combustion: Ash-Related Problems in Utility Boilers

Ash deposition impedes coal-fired utility boiler operation. In collaboration with Northern Indiana Public Service Co. (NIPSCO), Sandia is assessing the causes and consequences of ash deposition in utility boilers. Specifically, blends of eastern and western coals are being studied. Various utilities are utilizing the information from this program.

9.6.5 Coal Combustion: Rates and Mechanisms of Combustion of Pulverized Coals

The burning of individual coal particles is being studied. The goals are the understanding of combustion subprocesses, including char combustion, the fate of mineral matter during combustion, and the behavior of organic toxics during coal combustion. The program is supported by Pittsburgh Energy Technology Center (PETC) and International Energy Agency (IEA).

9.6.6 Pulse Combustion

Pulse combustion uses acoustic modes to induce efficient mixing to ensure complete combustion. A laboratory burner that includes optical instrumentation has been used for fundamental research. The burner is supported by an extensive modeling capability. Applied burners are being developed for volatile organic compounds (VOC) destruction at Savannah River and with the Pulp and Paper Association. An application with Curtiss DYNA FOG is under review.

9.6.7 Spray Combustion

Structure and combustion of liquid sprays used in burners is being studied.

9.7 Other Projects at Sandia, California related to ATPW

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John Vitko, 8102, (510) 294-2820
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9.7.1 Optical Sensors and Controls for Improved Basic Oxygen Furnace Operation (BOF)

The project is sponsored by the American Iron and Steel Institute. The instrumentation goals are to provide *in situ* measurements of off-gas composition and temperature and temperature measurements of the molten bath in Basic Oxygen Furnaces. With this information, an on-line strategy for BOF control will be developed.

9.7.2 ARM (Atmospheric Research Module)

Using remote optical techniques, cloud formation is being studied.

9.7.3 Energetic Materials Destruction

Sandia is responsible for a number of rocket motor propellants, explosives, and explosive components. Sandia has a program studying the preparation of these materials for destruction or conversion and the means of destruction or conversion.

9.7.4 Metals Emission Monitoring

Based on laser spark spectroscopy, a program for elemental analysis of effluents is underway. This has DOE and DoD sponsorship

9.7.5 Chemical Vapor Deposition (CVD)

Studies of chemical vapor deposition processes for the fabrication of silicon nitride insulation, silicon chips, diamond substrates, and metal composites are being sponsored by Advanced Research Program Agency (ARPA). Thermodynamics, heat transfer, species transport, and chemical kinetic models are used to predict performance. Accompanying experimental research provides needed rate constants. Collaboration exists with industry to enable and verify operational strategies. In some cases, control methodology is imposed to improve product.

9.7.6 Chemical Vapor Composite (CVC)

Working with ThermoTrex, Sandia is developing high temperature ceramic composites for industrial applications. A feature of this program is RASSPVDN (Random Sphere model of Simultaneous Particle and Vapor Deposition), a predictive code for the codepositing of particles and vapor for the making of the product. Experimental studies of gas flows with entrained solids is being conducted.

9.7.7 Thermal Decomposition of Energetic Material

Using a microbalance and time of flight spectroscopy the decomposition products of various energetic materials and being studied. These include RDX and HMX.

9.7.8 Mercury Monitoring

A continuous monitor to measure total, elemental, and speciated Hg is being developed. The monitor will be used with gas phase effluents from waste treatment processing. The goal is to attain a sensitivity of 0.1 ppb

9.8 Sandia Environmental Projects

Taz Bramlette, 8106, (510) 294-2299

9.8.1 Site Characterization

A necessary element of any site remediation program is assaying the environmental state of the site. Sandia has projects that provide this site assay through the detection and characterization of subsurface volatile organic compounds (VOC's), the development of methods to predict the subsurface transport of uranium in unsaturated soils, the development of a characterization system to detect heavy metal contaminants in unsaturated soils, and the development of a sample analysis system for heavy metals that allows rapid and precise analysis on field samples.

9.8.2 Site Remediation

There are numerous technical challenges in remediating sites. Sandia is developing electrokinetic methods for removal of chromium, enhanced soil vapor extraction system to reverse subsurface VOC contaminant plume diffusion and remove VOC contamination using steam reforming for the destruction of halogenated solvents, and employing a combination of pulse combustion and catalytic combustion for the destruction of halogenated solvents.

9.8.3 Risk-Based Standards

Sandia also has the capability to evaluate environmental risks. There are efforts at Sandia to organize programs that provide better scientific and public understanding of the risks associated with hazardous agents such as chemical, biological, radiological, and physical agents in the environment and in the workplace.

9.8.4 Robotics

An important tool in dealing with hazardous situations is the use of robotics. Sandia has many leading technologies that are being used in defense programs and environmental programs. These include the reduction of waste streams associated with hazardous materials-handling operations through minimization of direct personnel exposure, increasing sample throughput and reduction of exposure of personnel to hazardous materials and substances during characterization activities at ER sites and D&D remediation activities, the development of modular control and sensing technologies applicable to many ER/WM robotics activities, the development of sensor-based robotic manipulator systems to remove waste from underground storage tanks, and the development of technologies that minimize personnel exposure to radioactive materials during

9.8.5 Other Activities being conducted at Offsite Installations

Several other projects are being conducted at offsite installations. These include optimizing sampling strategies for subsurface contaminant source characterization, development of *in situ* containment and stabilization techniques for buried waste, development of an integrated geophysics program to rapidly and effectively characterize subsurface topographical conditions, and development of enhanced methods for seismic characterization of subsurface conditions.

9.8.6 International Environmental Projects

Technologies from international sources being evaluated for applicability to DOE sites and installations include ER/WM activities in the former Soviet Union, Japan, and the United Kingdom; a German-engineered barrier system to passively control geohydrologic gradients over the long term around a controlled placement of hazardous materials; and identifying technical advances in Germany in the areas of horizontal drilling, borehole stabilization, contaminant sampling, and polymer seals formation and injection.

9.8.7 Transportation Management

Protection of the environment entails shipping products safely. For transportation, Sandia is predicting the behavior of packaging under transport conditions using regulatory-approved analytical computer codes, investigating and developing new systems and components and characterizing packaging materials, certifying and recertifying radioactive material packaging, developing technical data and providing independent review and comment on proposed regulations and standards, analyzing DOE transportation systems for radiological and non-radiological risk, and developing packages to transport liquid and mixed hazardous waste to facilitate DOE site cleanup.

9.8.8 Thermal Processes Underway at Albuquerque

Dale Blankenship, 6623, (505) 844-9694

Catalytic Extraction Processing of Weapon Components

Thermal Process—Molten metals-the catalyst-are used to destroy hazardous wastes and extract inorganics and metals. Waste, gases, and a flux are inputs. Gaseous products are recovered and treated in an air pollution control device. Recovered energy is used for various processes.

Supplier—Molten Metal Technology is the supplier. There are proposals for a cooperative development with Sandia.

Application—Destruction of Sandia weapon components and the recovery of materials.

Status—Demonstration projects are underway.

Plasma Energy Waste Processing System for the Disposal of Weapon Component Wastes

Thermal Process—A plasma arc turns metals into recyclable ingots (or vitrified slag) and destroys hazardous organics.

Supplier—Plasma Applied Energy Technology

Application—Destruction of Sandia weapon components and the recovery of materials.

Status—Demonstration projects are underway.

Destruction of Organics in Mixed Waste by Steam Reforming Destruction of Halogenated Solvents by Steam Reforming Steam Reforming Off Gas

Thermal Process—Steam reforming

Application—Being used at Hanford for the destruction of organics in saltcakes and sludges and elsewhere for halogenated solvents.

Status—Demonstration projects are underway.

9.8.9 Other Projects

Onsite Environmental Projects

Waste Component Recycle, Treatment, and Disposal
Effects of Site Capping on Contaminant Transport
Mixed Waste Landfill Integrated Demonstration
Technology Integration Workshops for Mixed Waste Landfill Identification
Advanced *In Situ* Moisture Logging System
Geochemical Controls on Chromium Mobility
Hybrid Directional Boring and Horizontal Logging
Electrokinetic Remediation
Field Screening Laboratory Systems
Soil Vapor Extraction System
Mixed Waste Landfill
Characterization System for Metal Contamination in Arid Soils
Remedial Options Evaluation
Technology Infusion for the MWLID
Waste Minimization Opportunity Assessment
Cross Borehole Electromagnetic Imaging of Chemical and Mixed Waste Landfills
High Resolution Thermographic IR Imaging

Offsite environmental projects

Process History Methodology
Robotics Advanced Technology
Retrieval Technology Concepts for Tank Waste
UST Waste Dislodging and Conveyance Technology Development
PAWS Off-Gas
PAWS Downhole Liquid/Vapor Phase
Groundwater Flow Sensor/Seismic Imaging
Robotics Waste Minimization
Robotics Decontamination and Decommissioning
Robotics Lab Automation
Robotics
Robotics Buried Waste
Utility Industry Directional Drilling
Robotics Waste Facility Operation

Environmentally conscious electronic manufacturing projects

Fluxless Soldering to reduce Solvent Usage
Dry Process Cleaning of Surfaces
Solvent Substitution Study
On-Line Monitoring of Volatile Organics for Waste Management

Environmentally Conscious Manufacturing

Waste minimization projects

Waste Minimization Opportunity Assessment

9.9 Acronyms and Initialisms

APC	Air pollution control
APCD	Air pollution control device
ARM	Atmospheric Research Module
ARPA	Advanced Research Program Agency
ARR	Antiresonant ring c
ATPW	Assured thermal processing of wastes
BEKP	Back-scattered electron Kikuchi pattern
BERL	Burner Engineering Research Laboratory
BOF	Basic oxygen furnace
CAA	Clean Air Act
CALIOPE	Chemical analysis by laser interrogation of proliferant effluents
CARS	Coherent anti-Stokes Raman spectroscopy
CATV	cable TV
CCD	Charge coupled device
CEM	Continuous emission monitor
CEP	Catalytic extraction processing
CHEMKIN	Chemical reaction kinetics code
CRADA	Cooperative Research and Development Agreement
CRF	Combustion Research Facility
CVC	Chemical vapor composite
CVD	Chemical vapor deposition

D&D	Decomissioning and dismantlement
DC	Direct current
DFWM	Degenerate four-wave mixing
DIAL	Differential absorption on line-of-sight
DoD	Department of Defense
DOE	Department of Energy
DRE	Destruction and removal efficiency
DSR	Divert, store and recycle
DU	dial-up
EER	Energy and Environmental Research (Corporation)
EPA	Environmental Protection Agency
EPRI	Electric Power Research Institute
ER/WM	Environmental restoration/waste management
ESR	Electroslag remelting
FID	Flame ionization detector
FIS	Flame ionization spectrometry
FTIR	Fourier-transform infrared spectrometer
GRI	Gas Research Institute
HEPA	High efficiency particulate air
HRTEM	High-resolution transmission electron microscopy
IEA	International Energy Agency
IMS	Ion mobility spectrometry
ir	Infrared
LASS	Laser spark emission spectroscopy
LDA	Laser Doppler anemometry

LDRD	Laboratory Directed Research and Development
LDV	Laser Doppler velocimetry
LIF	Laser-induced fluorescence
LII	Laser-induced incandescence
LL	leased line
LLNL	Lawrence Livermore National Laboratory
MS	Mass spectrometer
MSW	Municipal solid waste
NIPSCO	Northern Indiana Public Service Company
NREL	National Renewable Energy Laboratory
OPO	Optical parametric oscillator
PAWS	Portable surface acoustic wave sensor
PCSV	Particle concentration, sizing and velocity
PDA	personal data assistant
PEAT	Plasma energy applied technology
PETC	Pittsburgh Energy Technology Center
PERF	Petroleum Environmental Research Forum
PIC	Product of incomplete combustion
PLIF	Planar laser-induced fluorescence
PSR	Perfectly stirred reactors
QA	Quality assurance
QFD	Quality function deployment
REMPI	Resonance-enhanced multiphoton ionization
RF	Radio frequency
SAW	Surface acoustic wave

SEM	Scanning electron microscopy	.
SMPC	Speciality Metals Processing Consrtium	.
SNL/CA	Sandia National Laboratories, California	.
SNL/NM	Sandia National Laboratories, New Mexico	
TDL	Tunable diode-laser	
TEM	Transmission electron microscopy	
TEOM	Tapered element oscillating microbalance	
TESS	Transform method for extinction—scattering with spatial resolution	
THC	Total hydrocarbons	
TOF	Time-of-flight	
UCD	University of California, Davis	
UNM	University of New Mexico	.
uv	Ultraviolet	.
VOC	Volatile organic compound	.
vuv	Vacuum ultraviolet	.

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