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TITLE: DEVELOPMENT OF INHERENTLY SAFE AND ENVIRONMENTALLY ACCEPTABLE INTELLIGENT PROCESSING TECHNOLOGIES FOR HTS MATERIALS

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DEVELOPMENT OF INHERENTLY SAFE AND ENVIRONMENTALLY ACCEPTABLE INTELLIGENT PROCESSING TECHNOLOGIES FOR HTS MATERIALS

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ABSTRACT

The Los Alamos National Laboratory, as a national scientific resource, should be a major participant in the development of new technologies and the improvement of existing technologies that will enhance the nation's industrial competitiveness. Because the Laboratory is a national resource we also must take the broadest view of technology development and technology transfer. As we endeavor to convert our basic research into useable technologies that can be transferred to the industrial sector, we must recognize that the job is not complete when the product engineering phase is accomplished. A technology or product application that cannot be implemented by industry because of health and environmental constraints will not contribute to our industrial competitiveness. In a similar fashion, a sophisticated technology that is not accompanied by the appropriate expert knowledge base and process control strategies when technology transfer is attempted will be of marginal use to industry. Thus, it is essential for the Laboratory to take a multidimensional approach to technology development and transfer to the industrial sector.

The development of new processing technologies for the production, fabrication, and application of advanced materials proceeds through several complementary dimensions. The advanced materials dimension includes basic research on materials synthesis, composition, and properties; materials processing research; engineering characterization and materials applications; and product and process engineering. The health and environmental dimension includes identification of potential health and environmental constraints; characterization of candidate processes for waste and effluent quality; process optimization for both economic and environmental benefit; and development of control strategies to deal with health and environmental problems that cannot be solved through process modification. The intelligent processing dimension includes application of available sensors and the development of new diagnostics for real-time process measurements; development of control strategies and expert systems to use these process measurements for real-time process control; and development of capabilities to optimize working processes in real-time for both product quality and environmental acceptability. This paper discusses these issues in the context of the Laboratory's efforts to develop technologies based on the processing of the new high temperature superconducting ceramic oxides.

I. INTRODUCTION

A coordinated approach to research and technology development directed toward advanced materials involves a number of research dimensions that should be pursued in parallel. Some of the general considerations that must be addressed in an integrated effort to develop new technologies that are environmentally acceptable, inherently safe, and do not pose health risks are discussed in this section.

Industry in this country is becoming increasingly aware of the cost of not maintaining high levels of quality and efficiency in the production of goods and materials. Those costs are evidenced by lost markets, below-specification products, and waste. These problems are endemic in our industrial base, including the materials processing, chemical, energy, and other manufacturing and production-oriented industries. When all of the cost factors associated with the production of below-specification products are listed according to significance, lack of understanding of current processes and ineffective process control top the list. A recent report in *Science* (Vol. 232, 1986, p. 968), adopted from a keynote address to the National Conference on the Advancement of Research, states that "Indeed, the process industries have been implementing higher and higher levels of control and optimization for several decades. But as the industry has pursued the task, its difficulties have mounted, because it has such imperfect knowledge of its processes. The need for knowledge is most acute in regard to main reaction pathways; mass transfer effects; operability phenomena like coking, foaming, fouling, and agglomeration; and the failure modes of modern process plants. Better knowledge could be the key to increased yields, efficiencies, selectivity and safety."

The primary reason given for not understanding chemical processes is the lack of reliable chemical sensors and process analytical instrumentation that can measure the concentration of raw materials, products, impurities, by-products, and effluents in real time. The reason is that industry has not needed detailed process information to be competitive in national and international markets. However, this is no longer the case and the issue of national industrial competitiveness has become a recognized concern of our political leadership. We have the technical capabilities to automate and control processes with considerable sophistication, but we do not have the real-time process knowledge needed to know what adjustments to make.

Process chemistry is by its very nature a multidisciplinary field centered around physical chemistry and chemical engineering, but requiring expertise in other fields including statistics, electrical engineering, optical engineering, and materials science. It will be through synergistic research in all of these areas that new methods for measuring the chemical composition of process streams and a more thorough knowledge of reaction chemistry will be developed. Los Alamos can mount a successful program in process chemistry (e.g., the Exploratory Research and Development Center for high temperature superconductor materials processing) because it can develop and bring together expertise in various technical areas which will incorporate the above and other disciplines. These technical areas will include: physical chemistry; chemical engineering; chemical diagnostics, instrumentation and sensor development; data acquisition and analysis; and process control, feedback and adaptive learning. The ultimate goal of process understanding and advanced diagnostics is to provide real-time chemical measurements for improved process control, leading to safer, more efficient, and environmentally acceptable processes. Research in this field should go beyond the traditional control strategies to include control systems based on artificial intelligence and pattern recognition.

Our limited experience at Los Alamos with energy extraction processes in the late 1970's and our continuing commitment to special nuclear materials processing suggests that enormous benefit can be derived by investigations at the intersection of process research and environmental research and control. Process research and development that incorporates a health and environmental dimension ensures that processes are optimized for both economic and environmental benefit

Conversely, the effectiveness of health and environmental research is maximized by understanding the interactions of raw materials and processing parameters that generate products, effluents, and wastes. Integration of these approaches provides a greater degree of control over the identity and environmental behavior of effluents and wastes, minimizes the costs of environmental control technologies and waste disposal strategies, and defines the environmental research and monitoring required to predict the ultimate ecosystem and human health impacts associated with the processing and use of the desired products. Since this approach minimizes costs associated with environmental control and waste disposal, it complements research directed at better process understanding and control for more efficient materials processing.

The high temperature superconducting ceramic oxides provide an excellent opportunity to further explore and validate these concepts. The materials processing issues are currently the focus of a great deal of research internationally, and also at the Laboratory through the ERDC. Because these studies are in their infancy, there is ample opportunity to influence processes, processing technology, process analytical requirements, process control and feedback issues, and the environmental acceptability of these processes. There is much more flexibility at the earlier stages of development to make changes that improve efficiency and environmental acceptability, as compared with existing processes where major changes require plant and hardware modifications.

The following sections describe the baseline information required for assessment of future research and requirements, the technical activities that should be pursued, and the industrial interactions that are necessary to define the importance of a health and environmental dimension in HTS ceramic processing. The technical activities include: (1) materials processing research directed at correlating composition, properties, synthetic routes, and waste and effluent generation; (2) materials characterization; (3) effluent and waste characterization from proposed processes; (4) health hazard identification and characterization; (5) process diagnostics and control required for real-time information and processing efficiency; and (6) process optimization and engineering for both economic and environmental benefit. These technical activities will be implemented in parallel with other materials processing research that is pursued with ERDC resources. The emphasis for these technical activities will be responsive to industrial input about relative importance of the activities.

II. BASELINE INFORMATION REQUIREMENTS

We recognize that the ERDC's industrial partners will be quite diverse both in size and depth of experience in chemical and materials manufacturing. Thus, the information needs of various industrial organizations will be varied. Some of the industrial partners will have extensive chemical and materials processing operations, and thus will be quite familiar with such things as best available environmental control technologies and environmental regulations. Other industrial partners may not have much experience in these matters. In addition, the ability of the industrial partners to cope with the unique requirements defined by the HTS materials processing operations will probably be a function of the resources of the organization. The health and environmental dimension of the ERDC must be flexible in dealing with the industrial partners, to provide the level of support required to complement each industrial partner's capabilities and experience in these areas.

A. Best Available Control Technologies. An important information need that will require a significant level of attention is the health and environmental control technologies that are available for application to high temperature superconducting ceramic oxide processing. It will be important to develop an information base that will parallel developments in HTS materials processing. Comparable activities in the bulk ceramic materials processing industry, the microelectronics device fabrication industry, and other similar industries should yield insights into both the environmental concerns and environmental control technologies that are currently used to mitigate identified concerns. Of course, because of the unique and different properties of these HTS materials compared with other ceramic materials, new control technology requirements may necessitate additional research.

Another valuable source of information will be the ERDC industrial partners. Most of these companies will have extensive experience with control technology requirements for chemical and materials processing activities. Through collaboration with the industrial partners the current state of technology can be defined, and new issues and requirements for the HTS materials will be identified. These identified concerns can be resolved through collaborative technical efforts. Many of the occupational health issues that must be resolved by our industrial partners for the safe and efficient processing of these materials can be handled in a similar fashion.

B. Health and Environmental Regulations and Requirements. In order to match technical efforts with the health, safety, and environmental needs of these materials processing activities, it will be necessary to have a thorough understanding of the health and environmental regulations that require compliance, including a thorough knowledge of the toxicology of these materials. Regulations dealing with air quality, water quality, and solid and hazardous waste disposal have been growing rapidly in the last ten years, and careful compliance with these regulations must be designed into our integrated processes. It is important to understand air quality standards and their impacts on emissions, the requirements for liquid and wastewater discharges and disposal, and the strict requirements for hazardous waste handling and disposal. Because of our interactions with a wide range of industrial partners it also will be necessary to understand individual state regulations and requirements, that are in addition to federal requirements. This is particularly true for toxic air pollutants, since the Environmental Protection Agency (EPA) has delegated these compliance issues to the states. With this type of knowledge, the materials processing research can be directed toward development of efficient and environmentally benign processes. At Los Alamos, several organizations, including the Health, Safety and Environment (HSE) Division and the Assessment (A) Division, can contribute greatly to this information gathering process.

C. Health and Environmental Effects. It also is important to be thoroughly knowledgeable concerning the potential health and environmental effects that may be encountered, if the HTS precursor materials or waste and effluents generated during processing are mistakenly released to the environment. Plant upsets or accidental spills or releases of wastes will first impact the occupational work force. It is necessary to design inherently safe processes, but it also is important to be prepared with emergency procedures to protect the workforce from unforeseen circumstances. These procedures must be designed cognizant of the potential health effects that are associated with the materials being process. These same concerns are important for the protection of the public health, if plant upsets or accidental contamination incidents transport beyond the plant boundaries. Literature searches and systems analyses will be required to assess the possible effects, and to design strategies to deal with unforeseen consequences of HTS materials processing. We anticipate that each industrial partner will have a great deal of experience in these areas, but there may be unique problems and requirements that are associated with the HTS materials.

It also is important to assess the potential environmental impacts on ecosystems that may come about from HTS materials processing operations. If environmentally acceptable processes are designed with appropriate control technologies to mitigate the effects of the wastes and effluents, the potential environmental consequences will be minimized. However, it is still necessary to understand the environmental behavior of these materials (wastes and effluents), including their ultimate fate and uptake in the biosphere. This information is necessary to define appropriate responses, in the event of unexpected environmental releases.

III. TECHNICAL ACTIVITIES

The technical activities of the ERDC include basic research, materials processing research, configured conductor development, engineering characterization, device applications, and product and process engineering. The health and environmental dimension of the overall technical program contributes to each of these endeavors. Four families of high-temperature superconducting ceramic oxides are currently being investigated both at the Laboratory and internationally. These ceramic materials are: (1) the 1-2-3 materials, $YBa_2Cu_3O_{7-\delta}$; (2) the bismuth-based materials, $Bi_2Ca_2Sr_{n-1}Cu_nO_{4+2n}$; (3) the thallium-based materials, $Tl_2Ba_2Ca_{n-1}Cu_nO_{4+2n}$; and (4) the non-copper-based materials, $Ba_{1-x}K_xBiO_3$. Clearly, the health and environmental implications associated with processing of these materials and disposal of the wastes generated from these processes must be addressed because of hazardous nature and potential toxicity of the elements involved in these materials. Some of the generic steps in bulk processing and thin/thick film processing are described in Figures 1 and 2, along with the types of wastes and effluents that will be generated by each process step. Each process that is researched must be evaluated in terms of the intermediate products and wastes that are generated. Alteration of process operations to minimize wastes, optimize recycle strategies, and employ environmental control technologies are all potential steps that can be taken to mitigate adverse environmental consequences of the integrated processes. The Laboratory currently has materials synthesis efforts designed for device-oriented thin film applications and monolithic ceramic powder processing for high-current conductor applications. We have extensive characterization efforts directed at correlating electronic and magnetic properties of these materials with their chemical, physical, and synthesis parameters. This approach is leading to an understanding of the sensitivities of the important materials properties to the processing parameters that must be controlled in large-scale manufacturing operations.

In parallel with materials processing research, ongoing efforts have been directed toward the design of a generic intelligent process control system that will be applied to candidate technologies. We envision a multipurpose control system that has four major components: (1) process modeling and optimization software; (2) a health, safety, and environmental regulation rule-based component; (3) real-time feedback and control software that integrates *in situ* process diagnostics and outputs with process optimization and environmental rules; and (4) an adaptive learning module based on neural networks for automated accumulation of additional process operational experience. This approach to process control requires close coordination with Laboratory efforts in the development of diagnostics and sensors for process monitoring. Advanced control systems are required for materials process technologies to optimize process performance, reproducibility and economics; insure that materials are produced in an environmentally acceptable manner; and to guarantee efficient technology transfer of advanced production technologies. Laboratory or bench-scale processes are good prospects for testing our system, because they provide challenging control problems without overwhelming a developing control system with shear numbers of processes to be controlled and alarms to be answered. Also, high levels of control on our experimental materials processing research allows us to learn how to produce materials reproducibly, a problem at any scale in ceramics processing.

A. Materials Processing Research. From experimental studies conducted at Los Alamos and other research laboratories it is apparent that the electronic and magnetic properties of the various families of high temperature superconducting ceramic oxides are very sensitive functions of the chemical composition and crystalline structure of the solid phases. The composition and structure are, in turn, very sensitive to the synthetic routes, including synthetic precursors, high temperature chemistry (solid phase reaction chemistry), and annealing schedules and atmospheres. Clearly, the sensitivity of the desired materials properties, as a function of the preparative schemes, may leave few alternatives for procedural changes in synthetic pathways that will improve environmental acceptability of these processes. However, each high temperature superconductor family has its own characteristics and processing requirements, and parametric studies on a research scale to understand tradeoffs

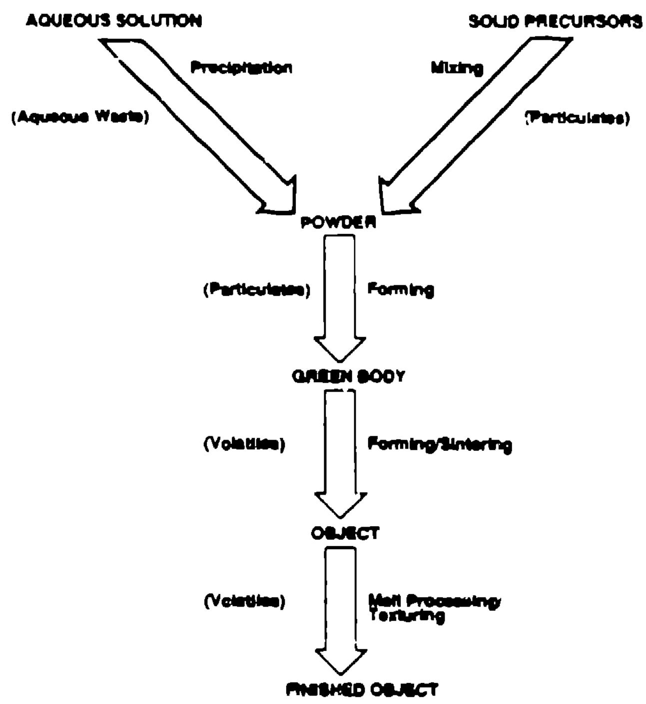

Fig. 1. Bulk processing.

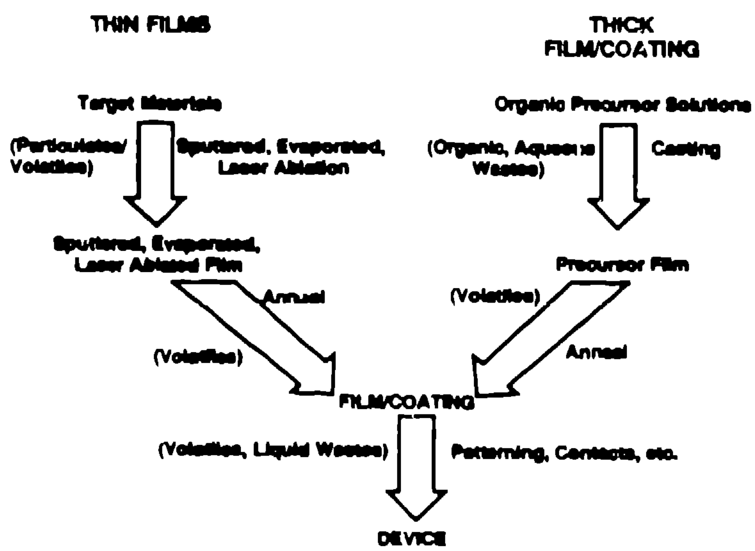

Fig. 2. Thin/thick film processing.

between materials properties and effluent and waste generation may yield alternate processes that could be more acceptable
environmentally. In addition, new synthetic routes using alternate synthetic precursors may yield significant improvements relative to potential environmental constraints. These considerations should be continually evaluated as existing and new synthetic pathways to these materials are proposed and researched.

In the following paragraphs, we will discuss some of our materials synthesis efforts directed at thin films and powders. We will describe our laser-ablation technique for thin film deposition citing examples from our YBCO processing activities. We also will describe some of our powder synthesis efforts focusing on the thallium-based compounds, TBCCO. These descriptions include a summary of what are believed to be the important processing issues.

1. Thin Films/Laser Ablation Deposition. Thin film deposition by laser ablation is accomplished by directing the output of a high-energy pulsed laser (in our case a XeCl excimer laser) at a ceramic precursor target. The resulting plume of vaporized material is then intercepted by a suitable substrate. The process is carried out under medium vacuum, often with a few millitorr of oxygen to allow the film to grow with the proper structure and oxygen stoichiometry. Typically, we get two to ten monolayers per laser pulse ablated from the target surface. The pulse repetition rate and the amount ablated per pulse may also be important parameters to control. The composition and spatial characteristics of the vapor plume depends on other laser characteristics, including fluence and spot size and shape. Without optimization of these parameters the film composition will be different than the target material, usually copper deficient due to selective redeposition. An additional consideration is film homogeneity, which is sensitive to the spatial characteristics of the plume. Without careful control, the films will tend to have compositional and thickness variations across the film surface. In order to avoid post-deposition annealing, it is necessary to oxygenate the film as it is deposited. This requires careful control of the substrate temperature, gas pressure, and gas dynamics at the substrate. In addition a variety of oxygen activation schemes to produce reactive oxygen atoms at the substrate surface have been investigated and need to be optimized. In addition to the process parameters that are already available for optimization and control, we are also planning the development of in situ optical diagnostics for real time mapping of plume composition.

We have used this technique to deposit YBCO and TBCCO films. However, most of our recent work has been with the YBCO materials, because of reluctance to coat the inner surfaces with thallium compounds. Most of our experience with process optimization has been developed in studies of the YBCO materials. Target stoichiometry and chemical purity are known to be important. Other materials properties are also thought to be important. Properties such as chemical homogeneity, density, and pre-deposition conditioning of the target are thought to be important parameters in controlling the properties of the film.

2. Powder Synthesis. The preparation of powders suitable for fabrication of wires and tapes for high-current carrying conductors is key to large scale applications of high temperature superconductivity. The synthesized ceramic powders are used for pressing into monolithic shapes, mixing into pastes for extrusion into wires, packing of tubes for swaging and drawing into wires and tapes, and mixing into inks for screen printing onto substrates. Our powder synthesis efforts are varied, and include classical precipitation methods, classical solid state techniques, and spray drying techniques. One of our large DOE-sponsored programs involves the preparation of monolithic TBCCO superconductors, and we have concentrated on the synthesis of these thallium phases. Because thallium oxides are highly volatile at the temperatures that the phases are formed, maintaining thallium stoichiometry is difficult, and is common to all synthetic techniques currently employed. Time, temperature, and oxygen partial pressure are parameters known to influence thallium loss from the bulk ceramic. Thallium oxide volatility has implications for occupational health, safety, and environmental issues discussed later. To alleviate some of these difficulties, we must develop an understanding of the chemistry and phase relationships in the TBCCO family of

compounds, not only to improve the materials properties but to have better control of process effluents. Correlation of synthetic parameters with phase stability and transitions has not yet been accomplished for these systems.

Precipitation of precursor powders from solution has been investigated as a method of generating chemically homogeneous, fine partical size powders suitable for use in the operations described above. Typically, the metal cations are dissolved in a suitable solvent, and then the cations are precipitated from solution simultaneously (to allow a high degree of chemical homogeneity) with an appropriate precipitating agent that renders the metal cations mostly insoluble in the solvent. The resulting powders are then washed to remove unwanted contaminants, dried, and then calcined to decompose the precursor powder to a powder containing the metal oxides. This step may involve the evolution of carbon and nitrogen oxides resulting from the decomposition of the original cation counterions, in addition to some volatilization of thallium oxides. The metal oxide powder may then be formed into shapes, and sintered to final form at higher temperatures. In this process, it is necessary to consider not only the thallium oxide effluent from the high temperature calcining and sintering steps, but also the solvent effluent that is contaminated with the constituent metal cations.

Classical solid state techniques involve the milling of metal oxides, or metal oxide precursors such as metal carbonates, nitrates, etc., into an intimate mixture. This mixture is then calcined to decompose any metal oxide precursors, and then shaped into the desired form for final sintering, or casting into tapes, etc. The formed material is then sintered at elevated temperature to yield the superconductor in final form. In this process, the milling operation may generate fine particulates that should be accounted for in the overall processing and waste minimization strategy.

Spray drying of metal oxide precursor solutions to generate fine particles suitable for subsequent ceramic processing is another viable method that has been applied to powder generation. Again, fine particulates represent a handling problem, as does the generation of carbon and nitrogen oxides from the decomposition of the counterions, and the generation of vapor phase thallium oxides.

It is clear that our efforts in thin film deposition and powder processing are giving us insights into the types of effluents and waste that will be generated during manufacturing. Examination of the health, safety, and environmental issues associated with the synthetic routes to these materials will lead to rational choices between synthetic pathways or synthetic alternatives may be developed. As mentioned elsewhere, early identification of potential problems or advantages in the process development stage will lead to minimization of process development costs.

3.) Transitioning to Processing Technology. Scale up of processes from a research scale to larger scales will introduce effects that will influence the identity and behavior of products, wastes, and effluents. Heat and mass transfer effects, solid-gas equilibria, and solid-phase stoichiometries will all influence the chemical kinetics of high temperature processes at larger scales. These effects will potentially alter reaction pathways because of the kinetics effects, and must be carefully studied. These investigations provide the opportunity to understand scaling effects in the context of effluents and wastes, as well as product composition and properties. Similar problems will be encountered with solution chemical reactions during scale-up of solution processing procedures, and these studies will provide the opportunity to optimize solution processes by changes in synthetic precursors, changes in solution properties, and changes in final processing to the desired materials. Both high temperature solids processing and lower temperature solution processing can be studied for tradeoffs between product and waste properties and can be optimized for both economic and environmental benefit. These scale-up studies are an excellent opportunity to influence effluent and waste compositions before the process development activities are too far along to be changed.

B. Materials Characterization.

1. Chemical Properties. An important set of critical parameters is the atomic ratios of elements in the various samples prepared by very diverse methods by a very diverse group of researchers. Methods currently exist to do metal assays and impurity concentrations in these materials. All experiments designed to do structural studies or investigations of materials properties should include analytical results on a routine basis. Our experience suggests that some very interesting physics and chemistry can be postulated on poorly characterized systems. This physics and chemistry is usually associated with those species in the materials that were not supposed to be there. These situations can be avoided by utilizing the appropriate types of characterization as part of the research program. Characterization schemes for thin films and bulk powders are similar in some respects, but often the characterization strategy varies markedly due to the grossly different morphology and quantity of the material available for characterization. Techniques, such as inductively coupled plasma (ICP) emission spectroscopy, ICP-mass spectrometry, and x-ray fluorescence, and Rutherford back scattering (RBS) are suitable techniques for determination of major, minor, and trace elements in these materials.

In addition to the assay techniques described above, electron microprobe analysis of these materials can provide approximate stoichiometries on volume elements of approximately 1 cubic micron. This information can be correlated with the bulk and thin film characterization methods, and can also be used to probe phase segregation and grain boundaries in these materials. Our electron microprobe analysis capability differs from scanning electron microscopic (SEM) analysis by virtue of using both wave-length dispersive and energy dispersive spectroscopies. This feature allows more accurate determinations of elemental compositions that are required to determine accurate stoichiometries. This has been very useful for the characterization of single crystals and also can be applied to thin films. It also can be used for characterization of powders and other bulk materials by doing statistical analyses of elemental determinations over many samples (i.e., spots). Rutherford back scattering spectroscopy complements microprobe analysis in adding information concerning the thickness and morphology of thin films.

Structural analysis using x-ray crystallography and neutron scattering as complementary techniques also has become commonplace. These materials have also been characterized by a variety of spectroscopic tools, including various vibrational spectroscopies, solid-state nuclear magnetic resonance spectroscopy, and x-ray absorption spectroscopy.

2. Electronic and Magnetic Properties. Because the electrical and magnetic properties of superconductors are extremely sensitive to composition, phase purity, and the presence of impurities, it is important to build the correlation of the chemical and structural techniques mentioned above with the electronic and magnetic properties exhibited by the various families of HTS materials. Bulk materials are routinely screened using magnetic susceptibility measurements as a function of temperature and magnetic field using a SQUID magnetometer. Because the figure of merit for bulk materials is the current density, the electrical resistivity and also the critical current density, Jc, is measured routinely as a function of magnetic field up to 8 tesla. For the latter two measurements, it is necessary to provide leads to form electrical contact to the superconductor. This is generally performed by applying a silver contact pad to the surface of the superconductor. The pad is formed from silver epoxy, or plasma spraying or evaporation of a silver film onto the surface of the superconductor. The characterization of thin films varies in that magnetic susceptibility is not routinely measured, bu rather the eddy current inductance is measured instead. Thin films are also subjected to microwave measurements that yield a measure of the surface resistivity, the figure of merit for many of our programmatic thin film RF and microwave applications.

3. Materials Characterization for Process Evaluation. As we apply our analytical tools to materials characterization, we continually evaluate the efficacy of these techniques for process evaluation and diagnostics. For example, our experimental need to characterize plume composition

in laser ablation experiments, can lead to an important process diagnostic that could be used in manufacturing operations for process control. As we continue our research, we will be investigating real-time or near real-time techniques to determine stoichiometries, oxygen contents, morphologies, structural information, and superconducting properties. For example, we are investigating the possibility of in-situ eddy current measurements for determination of qualitative superconducting properties of thin films. Concepts for in situ x-ray fluorescence and Auger spectroscopies also are being considered for quantitative determination of cation stoichiometries. In summary, our materials characterization efforts support our materials synthesis research, but we continually evaluate the possible use of these approaches for process evaluation and materials characterization in processing environments.

C. Effluent and Waste Characterization. In parallel with on-going materials processing research, it will be necessary to characterize processes regarding the effluents and waste materials that will be generated. Two examples of generic processes, and the potential wastes and effluents generated by these processes, are shown schematically in Figures 1 and 2. This activity requires extensive chemical characterization of gaseous emissions, liquids, and solids that are generated during processing and are not associated with the desired products. The approach is to use a combination of classical analytical procedures and real-time chemical diagnostics to characterize the composition of these waste and effluents and to develop an understanding of the reaction mechanisms responsible for their generation. In many instances, the physical and biological properties of these waste materials also require characterization, in addition to the chemical properties. After characterization of the fundamental properties of the effluents and wastes are completed, preliminary studies to assess their potential environmental behavior are necessary. These studies can be used to make early estimates of the possible environmental consequences that may be faced without proper control strategies and waste disposal technologies. If the environmental behavior of these materials suggest potential negative consequences, further assessment of ecosystem and human health impacts is warranted. These waste and effluent characterization activities at the early stages of process development efforts provide useful input regarding process modifications that lead to reduced environmental constraints on the ultimate processing technology.

D. Health Hazard Identification and Characterization. Identification and characterization of potential health hazards associated with HTS material processing are also conducted in parallel with materials processing research. Proposed processing operations and activities are systematically evaluated to identify potential health hazards from the HTS materials, associated materials used in processing, and from the operations or activities themselves. These potential health hazards are then characterized to determine the real potential for exposure of employees working with the process or to the public if released from the facility. Toxicity of the materials is an important characteristic of the potential hazard, but not the only one of concern. Limited toxicological data are presently available, and this is limited primarily to data on pure metals. Thallium is of greatest concern, currently. Additional toxicological evaluations are needed for specific formulations of the HTS materials, to evaluate the effect of long-term exposure limits. Quantities of materials, chemical and physical properties, duration of exposure, and routes of exposure are other important factors that will determine the types and degree of control needed for the process operations.

Evaluation of these factors concurrent with HTS materials process development will allow consideration of design changes or process modifications at an early period in the process development. Work practices and procedures needed for specific process operations should also be developed. Other issues to be addressed for quick technology transfer include recommended health and environmental programs for industrial hygiene/environmental monitoring, training of workers in health hazards and controls, selection of personal protective equipment, and employee health surveillance through medical evaluations and bioassays.

E. Process Diagnostics and Control. Process diagnostics and control are the keys to development of a fundamental understanding of reaction pathways and chemical kinetics that contribute to the design of efficient processes. Most physical parameters, such as temperature, pressures, flow rates, etc., can be adequately monitored in real-time with commercial sensor technology. The ability to make real-time *in situ* chemical measurements is a much less mature technology. Analytical chemical characterization of process streams will have its foundation in classical analytical chemistry measurements, including spectroscopy, chromatography, electrochemistry, and flow injection analysis. However, continued development of advanced chemical diagnostics for real-time measurements will be essential. One primary focus is the development of practical prototype instruments for on-line analysis. This capability will require expertise in the design of instruments that will function in the process plant environment. A second focus is the development of in-line chemical sensors and probes. These efforts will need to combine expertise in analytical chemistry with materials chemistry to develop rugged sensors that will have selective chemical responses. Technology transfer of advanced instrumentation into industrial environments and applications will be extremely important.

Data acquisition and analysis of these process parameters is essential for development of feedback loops and process control strategies. The incorporation of multivariate statistical techniques to obtain the maximum amount of information from chemical measurements is allowing the analysis of sample matrices that could not be handled with classical data analysis methods. Pattern recognition and multivariate statistics also will assist in understanding the chemistry of processes and in providing new methods for process modeling and control. The ultimate goal of this process understanding and advanced diagnostics is to provide real-... e chemical monitoring for improved process control, leading to safer, environmentally acceptable, and more efficient processes. Research in this field should go beyond the traditional control strategies to include control systems based on artificial intelligence and pattern recognition.

Our current efforts involve the coupling of the ASPEN process modeling code with PC based expert systems to allow users to make more efficient use of ASPEN. This is important so that chemical engineers and materials scientists can collaborate on aspects of process optimization, as various materials processing routes are explored. This work is continuing.

We also are continuing the evaluation of the expert system G2, that has been developed by Gynsum Corporation. Many of the process control tasks that will be required in the initial stages of our process development activities may be accomplished with this software. We have had extensive discussions with both Gynsum Corporation and the ASPEN people and both are enthusiastic concerning our plans for coupling these packages through a software interface. Both organizations have offered assistance in accomplishing this task. In this fashion, G2 can take advantage of the powerful plant simulation capabilities of ASPEN. Our concept is to use ASPEN offline (on a separate computer) to understand various processing scenarios and provide input back to G2 concerning process simulations, without interfering with the real-time control potential of G2. We also have identified a hardware interface for linkage of the process control software with process diagnostic instrumentation. Discussion with the vendor have indicated that some software development will be required.

Working with new technologies invariably means dealing with processes that are not entirely understood. Observations of input versus output can lead to rules that are very reliable for controlling processes. An expert system built on such rules makes the technology transfer possible without transferring the expert, who has been involved in developing the process operation expertise. This approach is an excellent way to exert process control before the process is understood to an extent that it can be modeled mathematically. This approach facilitates technology implementation. In addition, environmental regulations and constraints, that cannot be described algorithmically, can be added to the process control expert system. In this fashion, the process can be optimized and operated for both product quality and health and environmental acceptability. Another positive aspect of expert system process control, is the ability to incorporate change. This change can result from a more thorough understanding of the process that can develop after the initial technology implementation. A future possibility is that the expert system can be designed to learn in a fashion similar to the process engineer. This emerging process control concept is based on neural networks, where the expert system is allowed to adapt as the process changes. This could be a great advantage for processes that become more sophisticated as they change over the years, but also would be quite important for dealing with small perturbations that occur more frequently (*e.g.*, process upsets). The approach when dealing with emerging technologies is to develop design rules and process control rules in parallel. In the early stages this will be a data base, then a knowledge base, and then a fully capable expert system. If the technology development continues in this manner, there will be synergism between the various process development dimensions, and ultimately a much more powerful process control system. It is much better than designing process control strategies after the product development stage is completed.

F. Process Optimization and Engineering/Integrated Processes. During the course of the ERDC's research efforts and collaborations with industry, various processes will move from a research stage to a development stage, an understanding the effluents and wastes from these processes will evolve, and better process diagnostics will become available for monitoring. As progress is made in these areas, process optimization and engineering to develop integrated processes will become an important activity. These efforts will involve sub-unit design and process integration, with optimization using economics and product quality as important variables. At this stage of technology development, it also will be important to consider the information generated by the health and environmental dimension of the program, and optimize processes in the multidimensional variable space defined by economics, product quality, and environmental acceptability. Collaborations with the industrial partners to develop and exercise process models is an efficient way to pursue these investigations. Of course, these modeling studies and optimization efforts will require experimental validation, presumably at development or pilot plant scales. Because the industrial partners presumably have extensive experience with these latter stages of process design and engineering (at least regarding economics and product quality), these investigations will require the closest collaboration between the Laboratory and the industrial partners.

IV. SUMMARY

A. Industrial Perceptions. Extensive interactions with industrial representatives that visit the ERDC will be required to determine the recognition of and the support for a health and environmental dimension in the Los Alamos program. There are a number of possible responses that can be anticipated from industry. There may not be an appreciation of the need for this kind of research to complement the materials processing research and development. A second possibility may be that larger industrial participants have in-house programs to address these concerns, while smaller industrial concerns do not have resources to independently address these issues. A third possibility may be that most industrial partners recognize the importance of these issues, but would prefer that Los Alamos address these concerns in the context of their overall program. We should anticipate a wide range of responses to the importance of a health and environmental dimension, and we should design a flexible program that can interface with industrial partners at any stage of research and development. We believe that this will be an area of research for Los Alamos, that will lead to unique contributions in the area of HTS materials processing.

It also will be necessary to interact with industrial visitors to determine the state of technology in a number of important areas. Most importantly, it is essential to establish a dialogue with industry representatives concerning current assessments of the health and environmental acceptability of existing process technologies and envisioned processes. This will be required to define the current occupational health and environmental control technology issues that must be resolved. It also will be necessary to probe industry perceptions concerning the current effectiveness of existing control technologies and the need for new strategies. Another important issue is the current state of process diagnostics and control, as well as monitors for occupational health requirements. Requirements for real-time *in situ* measurements for process monitoring, data acquisition and analysis for process control, and process optimization issues will be defined through continuing dialogue between Laboratory researchers and industrial partners. Monitoring needs for occupational health concerns also will be defined by these discussions. It is through interaction process with industrial partners that future research directions in the program's health and environmental dimension will be determined.

Lastly, it will be important to continue interactions with the industrial partners to define future processing technologies that should be subjected to critical health and environmental assessments. In addition, new materials with desirable properties that may enter into a process development phase also should be evaluated regarding the health and environmental issues to be considered during development. It is through this continuing dialogue with industry that the Los Alamos health and environmental dimension of the ERDC will remain productive and effective.

B. Industrial Collaborations. The main goal of these industrial interactions will be to develop an industrial market and resource base for the health and environmental dimension of the ERDC. The first step in this process will be to establish the importance of this approach, and the research that is required to develop economic and environmentally acceptable processes for HTS materials. At this stage it is difficult to predict industry response to these concepts. However, many of the inquiries to the Laboratory since the formation of the ERDC have dealt with some aspect of the safety and health issues associated with handling of these materials, for example the concerns and difficulties with processing of Tl-based materials.

Another aspect of these interactions will be to establish our interests and capabilities that can contribute to the health and environmental dimension of the program. It will be necessary to educate our industrial partners concerning Los Alamos interests in health and environmental issues, and our desire to develop basic research and programmatic efforts that address this important national issue. It also is important to showcase Los Alamos expertise and capabilities that are available for excellent research and technology development in these areas. Obvious strengths that are applicable to the health and environmental dimension include: (1) our extensive capabilities in effluent and waste characterization and our evolving experience in waste minimization through process innovation; (2) our excellent capabilities in physical and chemical diagnostics, data acquisition and analysis, and process control; (3) our process optimization and engineering expertise; and (4) our established expertise in effluent control and waste disposal technology development. The combination of our interests and expertise place us in a competitive position to address aspects of health and environmental issues of HTS materials processing through an integrated research and technology development approach.