ADMINISTRATIVE INFORMATION

1. **Project Name:** Thermochemical Models and Databases For High-Temperature Materials Processing and Corrosion

2. **Lead Organization:**

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4. **Project Partners:** Advisory Board:
Dr. David Russo, Atofina
Dr. Randy John, Shell Oil
Ms. Jill Troup, PPG Industries
W. B. A. Sharp, MeadWestvaco Corporation
Dr. David Strickler, Pilkington-LOF
Dr. Amul Gupta, Monafrax
Dr. Dilip Patel, RHI Refractories
Dr. Angel Sanjurjo, SRI International
Dr. Ellen Meeks, Reaction Design

5. **Date Project Initiated:** Initiated 10/1/2001; currently in Project Year 3

6. **Expected Completion Date:** 9/30/2006

PROJECT RATIONALE AND STRATEGY

7. **Project Objective:** The objective of this project is to develop computational approaches and models for the generation of thermodynamic data required to simulate high-temperature industrial processes, and to make these data widely available to industry users through a convenient, no-cost web-accessible database. Data relevant to the manufacturing, use, and stability of refractory materials are of particular interest.

8. **Technical Barrier(s) Being Addressed:** Efficient use of energy and raw materials at high temperatures, minimization of waste, and elimination of corrosion are intimately linked to process thermodynamics. Unfortunately, thermodynamic data for gas- and condensed-phase species needed to develop even rudimentary models of industrial processes such as glass manufacturing, metals processing, catalysis, refractory corrosion, and coating formation are often unavailable or inaccurate. Experimental efforts worldwide to generate needed data are at an all-time low due to lack of funding and the time- and cost-intensive nature of such efforts.

9. **Project Pathway**: The approach employed in this project is to use computational methods to predict thermodynamic data and then to make these available in a user-friendly format via a web-based database. Computational methods developed over the past 20 years for predicting thermodynamic properties have demonstrated their ability to generate data sufficiently accurate for process modeling efforts. In particular, quantum-chemistry methods can now provide heats of formation for gas-phase species that are typically accurate to 2 – 3 kcal mol^{-1}. Similarly, methods for modeling condensed-phase systems, in particular amorphous and glassy phases/melts allow accurate reproduction phase diagrams and activities. Amorphous and crystalline phases formed when high-temperature water and/or oxygen react with refractories and metals them become predictable. We are using these methods, which have been under development in our laboratories prior to this project, to obtain data for chemical systems of particular relevance to industrial processes and the use of refractories in those processes. Initial efforts focused on chemistries containing main-group elements such as boron, aluminum, silicon, and tin, since these are the most-common components of refractory materials. Current efforts are focused on systems containing transition metals such as iron, chromium, and manganese, all of which are routinely used in high-temperature manufacturing, and are developing theoretical approaches capable of accurately modeling these systems. All data are provided via the web to users free of charge. Data are provided in formats compatible with standard software used to model high-temperature reacting systems, such as CHEMKIN and FactSage. The site also provides detailed information concerning the calculations and useful references.

10. Critical Technical Metrics:

- Generation of thermodynamic models capable of simulating the thermochemistry of all major refractory systems and their typical corrosion modes by oxygen, steam, and halogens.
- Generation of gas- and condensed-phase data for main-group and transition-metal species relevant to refractory corrosion, including oxides and halides of the elements B, C, Ca, Al, Si, Sn, Ti, Fe, Cr, and Mn.
- Production of an on-line database that presents all of the data generated within the project.

PROJECT PLANS AND PROGRESS

11. Past Accomplishments:

Task 1 Thermodynamic modeling of condensed-phase systems

- A subcontract with Prof. Karl Spear (Penn State University) to supply thermochemical data for the Si-Ca-(Na or K)-O condensed-phase, which are important for predicting corrosion of ceramics in black-liquor gasification facilities and glass furnaces, is nearly complete. Data are undergoing analysis and are expected to be submitted for publication and upload to the web by fall 2004.
- A global model of a base glass system has been completed that now includes CaO: Na_2O-CaO-Al_2O_3-B_2O_3-SiO_2.
- The spinel phase model containing Mn, Fe, Cr, and Al has been developed using the two-sublattice approach. Attendant models of the sesquioxide solution of the Fe, Cr, and Al have also been included.
- The binary ZrO_2-containing systems that include CaO, Al_2O_3, and SiO_2 have been completed based on existing phase equilibria. Models for ZrO_2-(Cr_2O_3, B_2O_3, Na_2O, K_2O) were prepared, however the lack of phase equilibria for those systems make them speculative.

Task 2 Prediction of high-temperature thermochemistry of gas-phase species

- New computational methods needed to predict thermochemistry for transition-metal compounds were developed, using coupled cluster techniques. Data for the following systems were calculated: hydrides, chlorides, and fluorides of titanium; chlorides and fluorides of, chromium, manganese, and iron; oxyhydrides of chromium. The accuracy of "standard"

computational methods was also evaluated, since these methods are relatively fast and can be applied to larger molecules. They are also more straightforward to use than customized (but more accurate). A paper describing the titanium results was submitted to *J. Phys. Chem. A.*

- A subcontract with Drs. Nathan Jacobson and Elizabeth Opila at NASA/Glenn Research Center was placed to obtain experimental measurements of thermodynamic data needed to validate computational methods for chromium. Preliminary results will be reported at the June 2004 program review meeting.

Task 3 Database development

Rapid and accurate dissemination of the data produced by this project requires electronic means of communication. Building a database on a web site is clearly the method of choice today. A major portion of the activities in this project to date involved the design and launching of a new web site tailored to provide a clear and useful display of the data in a format that is readily accessed by potential users in industry.

- The database was given a new, more compact name: *Thermodynamics Resource*. A brochure describing the site was prepared and distributed at major scientific/engineering conferences. Broad mailings in the coming months are also planned. The database now contains properties for approximately 850 gas-phase species and condensed-phase models for the Na_2O-Al_2O_3-Cr_2O_3-MnO-NiO-B_2O_3-SiO_2, Si-Na-O, Si-K-O, Al-Na-O, and Al-K-O systems.
- The database now has 78 "subscribers," including personnel at DuPont, Corning, GE, PPG, Shell, and SRI International, as well as major research institutions (MIT, Stanford, University of Chicago, Penn State, and Univ. California, Davis). Subscribers were contacted by email in Jan. 2004 with an update on the site's capabilities and new data.
- The following new data were uploaded to the web site: 120 compounds in the B-H-C-N-O-Cl system; 47 compounds in the Si-B-H-Cl system; and 60 compounds in the Sn-H-C-Cl system.
- New models for the Si-Na-O, Si-K-O, Al-Na-O, and Al-K-O condensed-phase systems were uploaded onto the database.
- The site capabilities were upgraded with the following features: A molecule index was added to the site to make it easier for users to get an overview of the available data. Multiple file formats added to download the capability. A "recent news" feature was also added to provide updates to users.
- An on-line equilibrium calculator is undergoing testing and should be fully operational by 9/04. Software and programming assistance for this effort is provided by Reaction Design, a member of the project advisory board.
- Results of a survey sent to the members of our industry advisory group were received. Suggestions for improving the web site were implemented.

12. Future Plans: The major milestones to be accomplished are to:

Task 1 Thermodynamic modeling of condensed-phase systems

- Complete the condensed phase models for the Si-Na-Ca-O and Si-K-Na-Ca-O systems.
- Integrate models Na_2O-CaO-Al_2O_3-B_2O_3-SiO_2, spinel and sesquioxide phases, and zirconia
- Upload the data to the web and publish the results in a reviewed technical journal.
- Complete models for remaining, relevant components.

Task 2 Prediction of high-temperature thermochemistry of gas-phase species

- Complete computational method for predicting thermochemistry for titanium, chromium, manganese, and iron compounds. Obtain properties for hydrides, halides, and hydroxides. Upload data to web and publish results in reviewed scientific journals.
- Obtain experimental data for chromium compounds to validate computational methods.

- Publish results of calculations indium, tin, and antimony compounds.
- Begin method development for second-row transition-metal compounds.

Task 3 Database development

- Add the ability to obtain temperature-dependent fits in forms useful for modeling programs other than CHEMKIN, such as FACTSage.
- Complete testing of on-line equilibrium calculator and implement on public web site.
- Supplement current database for hydrocarbons with data for higher hydrocarbon species (> C_6).

13. Project Changes: N/A

14. Commercialization Potential, Plans, and Activities:

Thermochemical data for gas-phase and condensed compounds are essential for predicting the thermal and chemical stability of materials used in high-temperature and/or corrosive industrial environments. Thus, such data are expected to be of wide interest to companies involved in glass melting, chemicals production, metals refining, and pulp/paper processing. The product of this research is the data obtained from high-level computations, which is the only practical means today of obtaining this information. These data are being made freely available through an interactive web site. To alert potential users to this resource, we are widely advertising it through both electronic and print-media, and by linking where possible to related web site. We also developed a brochure to distribute at conferences attended by potential users. This document will also be distributed by mail.

15. Patents, Publications, Presentations:

M. D. Allendorf, I.M.B Nielsen, M. L. Medlin, T.M. Besmann, C. F. Melius "*ThermoResource*: A Database for Industrial High-Temperature Applications," presented at the spring meeting of the American Chemical Society, Annaheim, CA, March 2004.

M. D. Allendorf, I.M.B Nielsen, M. L. Medlin, T.M. Besmann, C. F. Melius "A Practical Database of Gas-Phase Thermochemistry Obtained from *Ab Initio* Electronic Structure Calculations," presented at the fall meeting of the American Institute of Chemical Engineers, November 2003.

M. D. Allendorf, C. F. Melius "BAC-MP4 Predictions of Thermochemistry for Gas-Phase Tin Compounds in the Sn-H-C-Cl System," submitted to *J. Phys. Chem. A.*, 2004.

M. D. Allendorf, A. M. B. van Mol, "Gas-Phase Thermochemistry and Mechanism of Organometallic Tin Oxide Precursors," book chapter accepted for publication in *Topics in Organometallic Chem*, 2004.

I. M. B. Nielsen, C. L. Janssen, M. D. Allendorf "Ab initio predictions for thermochemical parameters for tin-oxygen compounds," *J. Phys. Chem. A.*, **107**, 5122 (2003).

M. D. Allendorf, R. H. Nilson, B. Bugeat, U. Ghani, O Marin, K. E. Spear, P. M. Walsh, A. Gupta, H. E. Wolfe, G. A. Pecoraro "Analytical Models For High-Temperature Corrosion Of Silica Refractories In Glass-Melting Furnaces," accepted for publication in *Proc. 7th Int. Conf. Adv. Fusion and Processing of Glass*, 2003.

T. M. Besmann, N. S. Kulkarni, and K. E. Spear, "Thermochemical And Phase Equilibria Property Prediction For Oxide Glass Systems Based On The Modified Associate Species Approach," *High Temperature Corrosion and Materials Technology IV,* The Electrochemical Society, Pennington, NJ 2003, in press.

T. M. Besmann, K. E. Spear, and J. D. Vienna, "Extension of the Modified Associate Species Thermochemical Model for High-Level Nuclear Waste: Inclusion of Chromia," II5.12.1, *Scientific Basis for Nuclear Waste Management XXVI,* R. Finch and D. Bullen, eds., MRS Proc. Vol. 757, Materials Research Society, Warrendale, PA (2003).