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Novel Refractory Materials for High Alkali, High Temperature Environments

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ABBREVIATIONS AND ACRONYMS

$MgO\text{-}Al_2O_3$	Magnesia Aluminate
MINTEQ	MINTEQ International, Inc.
MS&T	Missouri University of Science and Technology
ORNL	Oak Ridge National Laboratory
WFO	Work For Others

NOVEL REFRACTORY MATERIALS FOR HIGH ALKALI, HIGH TEMPERATURE ENVIRONMENTS

J. G. Hemrick

1. ABSTRACT

Refractory materials can be limited in their application by many factors including chemical reactions between the service environment and the refractory material, mechanical degradation of the refractory material by the service environment, temperature limitations on the use of a particular refractory material, and the inability to install or repair the refractory material in a cost effective manner or while the vessel was in service. The objective of this project was to address the need for new innovative refractory compositions by developing a family of novel MgO-Al_2O_3 spinel or other similar magnesia/alumina containing unshaped refractory composition (castables, gunnables, shotcretes, etc) utilizing new aggregate materials, bond systems, protective coatings, and phase formation techniques (in-situ phase formation, altered conversion temperatures, accelerated reactions, etc). This family of refractory compositions would then be tailored for use in high-temperature, high-alkaline industrial environments like those found in the aluminum, chemical, forest products, glass, and steel industries.

A research team was formed to carry out the proposed work led by Oak Ridge National Laboratory (ORNL) and was comprised of the academic institution Missouri University of Science and Technology (MS&T), and the industrial company MINTEQ International, Inc. (MINTEQ), along with representatives from the aluminum, chemical, glass, and forest products industries. The two goals of this project were to produce novel refractory compositions which will allow for improved energy efficiency and to develop new refractory application techniques which would improve the speed of installation. Also methods of hot installation were sought which would allow for hot repairs and on-line maintenance leading to reduced process downtimes and eliminating the need to cool and reheat process vessels.

The newly developed materials were expected to offer alternative material choices for high-temperature, high-alkali environments that may be capable of operating at higher temperatures (goal of increasing operating temperature by 100-200^{o}C depending on process) or for longer periods of time (goal of twice the life span of current materials or next process determined service increment). This would lead to less process down time, greater energy efficiency for associated manufacturing processes (more heat kept in process), and materials that can be installed/repaired in a more efficient manner. The overall project goal was a 5% improvement in energy efficiency (brought about through a 20% improvement in thermal efficiency) resulting in a savings of 3.7 TBtu/yr (7.2 billion ft^3 natural gas) by the year 2030. Additionally, new application techniques and systems were developed as part of this project to optimize the installation of this new family of refractory materials to maximize the properties of installed linings and to facilitate nuances such as hot installation and repair.

Under this project, seven new shotcrete materials were developed for both primary and repair applications in aluminum, black liquor, coal gasification, and lime kiln environments. Developed materials were based on alumino-silicate, magnesia, and spinel forming systems. One of the developed materials was an insulating shotcrete to be used behind the high conductivity spinel linings developed under this project.

Fundamental research work was carried out at MS&T throughout the life of the project to provide support for the development and production of the experimental refractory materials being developed. Additionally, energy savings estimates based on measured properties of the experimentally developed refractory systems from this project were made at MINTEQ to validate the energy savings estimates originally proposed for the project.

It was determined that although repair materials were developed under this project for aluminum, black liquor, and coal gasification systems which enable hot repair, there is only minor interest from industry in implementing these materials. On-line inspection techniques were also identified under this project which are currently used in the steel industry, but implementation of these techniques in applications such as black liquor and coal gasification where higher temperatures and tighter access clearances exist proved difficult due to cost considerations. Therefore, on-line inspection was not further pursued under this project.

Information from data collected during this and previous DOE projects was inputted into a refractory database housed at a public site (http://extwebapps.ornl.gov/crpd/Default.aspx). Industrial trials of the insulating shotcrete (INSULSHOT™ FH) and the material for use in aluminum rotary furnaces (ROTOSHOT™ AL) developed under this project were performed validating the commercial potential of these materials. Additionally, the magnesia-rich spinel formulation (FAST FIRE® MG-SP SHOT) for use in black liquor and lime kiln/cement applications was commercially released by MINTEQ. Ten presentations were given, eight papers were published, and one poster and one R&D 100 Award application were composed regarding this project. Further collaboration is currently being sought between MINTEQ and ORNL to further develop and deploy these materials in lime and cement kiln applications, coal gasfication environments and to extend the use of spinel-based materials into other applications beyond the scope of this work.

2. STATEMENT OF OJECTIVES

Refractory materials available when this project was proposed (bricks, castables, gunnables, etc.) were found to be limited in their application by many factors. These included chemical reactions between the service environment and the refractory material, mechanical degradation of the refractory material by the service environment, temperature limitations on the use of a particular refractory material, and the inability to install or repair the refractory material in a cost effective manner or while the vessel was in service. Therefore, there was an identified need to develop new innovative refractory compositions utilizing novel aggregates, binder systems (bonds), methods of phase formation, and refractory application systems.

The objective of this project was to address the need for new innovative refractory compositions by developing a family of novel $MgO-Al_2O_3$ spinel or other similar magnesia/alumina containing unshaped refractory composition (castables, gunnables, shotcretes, etc) utilizing new aggregate materials, bond systems, protective coatings, and phase formation techniques (in-situ phase formation, altered conversion temperatures, accelerated reactions, etc). This family of refractory compositions would then be tailored for use in high-temperature, high-alkaline industrial environments like those found in the aluminum, chemical, forest products, glass, and steel industries. Both practical refractory development experience and computer modeling techniques would be used to aid in the design of this new family of materials. Additionally, new application techniques and systems were to be developed as part of this project to optimize the installation of this new family of refractory materials to maximize the properties of installed linings and to facilitate nuances such as hot installation and repair.

The project was also to address the applicability and limitations of currently available materials and the improvements possible through the use of the newly developed family of materials, by measuring and comparing key properties of refractory materials. This was to include the determination of properties such as thermal conductivity, corrosion, abrasion and wear, creep, modulus of rupture, thermal expansion, thermal shock, toughness, elastic modulus, strength, and density. These property measurements were also to be used to initiate the formation of an un-biased, comprehensive database concerning currently used and newly developed refractory materials, a needed but unavailable resource highly desired by the refractory user community.

A research team was formed to carry out the proposed work led by Oak Ridge National Laboratory (ORNL) and was comprised of the academic institution Missouri University of Science and Technology (MS&T), and the industrial company MINTEQ International, Inc. (MINTEQ), along with representatives from the aluminum, chemical, glass, and forest products industries.

The overall goal of this project was two-fold. The first goal was to produce novel refractory compositions which will allow for improved energy efficiency through better insulation, decreased deterioration (corrosion and wear), and reduced process down-time for repair or replacement of refractory linings. Additionally, improved refractories could lead to increased process operating temperatures which will lead to more energy and cost efficient operations. The second goal was to develop new refractory application techniques which would improve the speed of an installation, thereby reducing the down time of the process. Also methods of hot installation were sought which would allow for hot repairs and on-line maintenance leading to reduced process downtimes and eliminating the need to cool and reheat process vessels.

The tasks in the originally proposed work included the following:

Task 1: Development and production of a family of novel magnesia and/or alumina containing unshaped refractory materials.
(Task duration – first year, with production of refractories extending through life of project)
New aggregate materials, bond systems and protective coatings will be identified and investigated for use in our target applications. These refractory components will consist of both naturally occurring materials and new synthetic materials that may or may not currently be used in refractory production. ORNL will lead this effort with significant support from MS&T and MINTEQ drawing on their extensive refractory research history and current refractory production technology. MINTEQ will then use the findings from this task to identify and evaluate application (installation) and processing (production) techniques (such as in-situ phase formation, altered conversion temperatures, accelerated reactions, etc.). These efforts will also be supported at ORNL and MS&T through more fundamental work to provide insight into these new refractory systems through thermodynamic, microstructural, or mechanical modeling.

Once candidate refractory systems have been identified and validated for application and production, MINTEQ will produce small batches of these new refractories. New refractories will be screened for corrosion resistance and strength as they are produced to insure their applicability to the end uses defined by the industrial partners. Refractory systems meeting these qualifications will meet the first milestone of the project and will be investigated for use in the remainder of the project. Such materials will be tailored in the remainder of the project to meet the energy goals through extended lifetimes (2X goal) and improved thermal efficiency (20% improvement) over currently used materials.

Task 2: Measurement of key properties of current and newly developed refractory materials.
(Task duration – second year)
The project will address the applicability and limitations of currently used materials from the aluminum, chemical, forest products, and glass industries and newly developed materials from this project by measuring and comparing key properties of the materials. The best currently performing refractory materials from each industry will be supplied by the four industrial participants for characterization as in-kind cost share. MINTEQ will also supply samples of the new refractory systems from Task 1 for analysis. All materials will be evaluated for properties such as thermal conductivity, creep, thermal expansion/shock, abrasion/wear, corrosion, and strength/modulus. Samples will also be characterized by various physical and microstructural means both before and after testing. These properties will be the basis for evaluating the improved performance of the new materials as compared to existing materials and for predicting the meeting of the energy goals of the project.

Task 3: Development of new refractory application techniques.
(Task duration – second year)
For success in this project, it will be necessary to develop entirely new application techniques and systems to optimize material installation and maximize the installed material's properties of the newly developed refractory materials. For this task, MINTEQ will draw on its extensive prior art and experience in this area to identify and develop suitable application techniques and equipment for installation of the refractory materials developed in Task 1. MINTEQ will then perform testing of these techniques and equipment, along with the effect on physical and mechanical properties of the installed refractory at their facility. Such measured quantities will include application rate, % rebound, density, porosity, and strength. In addition, samples of the installed material will be supplied to ORNL and MS&T for more extensive testing and evaluation through corrosion and wear testing, strength testing, and microstructural evaluation. These properties will directly impact the performance of the newly developed refractories in their end use and therefore are crucial to meeting the energy goals of the project. Successful development and validation of suitable application techniques and equipment will meet the second milestone of the project.

Task 4: Development of on-line inspection methods and hot-repair techniques.
(Task duration – third year)
To further reduce the energy used by industrial refractory consumers, as part of the project, improved methods of performing hot refractory maintenance will be sought and methods of on-line inspection will be developed or modified from existing technologies. This effort will be led by MINTEQ, drawing on its extensive prior experience in this area. ORNL and MS&T will support this effort by providing efforts into the reviewing of current on-line maintenance methods and modeling support to predict how methods could be improved or modified to lead to better heat retention or lower energy demands for installing repair materials. MINTEQ will develop applicable on-line inspection methods, hot-repair techniques, and equipment along with adapting the newly developed refractory systems and application methods from Task 1 and 3 for on-line repair. This task should lead to additional energy savings through reducing the need to shut down or fully cool refractory lined vessels in order to repair failed or deteriorating refractory. On-line monitoring and maintenance will also allow for identification of refractory deterioration in real time allowing for immediate repair of areas where heat is being lost and will allow for repair of only needed areas instead of having to replace entire linings resulting in not only energy savings for the process but energy savings through not having to produce the extra refractory materials. Hard numbers for these energy savings are not known at this time and would vary by process, but effects could be large considering the gross amount of energy lost in cooling and then reheating a typical glass melter, aluminum furnace, or industrial gasifier. The completion of the development of hot-repair techniques will meet the third milestone of this project.

Task 5: Formation of a comprehensive database concerning currently used and newly developed refractory materials.
(Task duration – middle of third year to middle of fourth year)
The property measurements made on currently used materials and newly developed materials in Task 2 will be used to initiate the formation of an un-biased, comprehensive

database concerning refractory materials. This has been identified as a needed but unavailable resource, highly desired by the refractory user community which will lead to better refractory selection for industrial processes resulting in more energy efficient furnaces throughout American industry. A server location for such a database will be created at ORNL and arrangements for its upkeep will be put in place. ORNL and MS&T will organize the data collected from this project and other previous refractory projects for input into the database. Additional data for the database will be provided by industrial partners and MINTEQ as in-kind support.

Task 6: Performance of in-plant trials and commercialization.
(Task duration – fourth year)
Based on the results obtained in Tasks 2-4, the project research team will work with the industrial partners to select processes in which to test the newly developed materials. Industrial facilities from the aluminum, chemical, forest products, and glass industries will be used for in-plant trials and access and testing done in these facilities will be counted toward each company's in-kind contribution to the project. The research team will closely work with the industrial partners in setting up the testing facilities and testing conditions. The specimens obtained in industrial testing will be characterized by the research team and the results obtained in the industrial testing will be documented as special reports for the industrial organizations which will be distributed to the project members. Commercialization efforts will be led by MINTEQ following their standard methods. Successful in-plant trials will validate the energy savings goals set forth and predicted by the various tasks of the project and will meet the final milestone of the project.

Task 7: Reporting and Administration.
(Task duration – entire project)
This task will be led by ORNL, with participation from MS&T and MINTEQ. Quarterly review meetings will be held and required reports will be sent to DOE quarterly and annually. Reports will be composed and submitted to the industrial partners upon completion of industrial trials. Costs will cover personnel time for report writing and some travel costs for meetings. A final report will be prepared as soon as the work is complete and within the CRADA period of performance. Additionally, the final report will be finished and distributed before the CRADA is officially complete. The final report will be jointly written following the guidance set forth in Guidance Document Number ORNL-TT-G1: Guidance For Preparing CRADA Final Reports.

Milestones:

Year One: (1) Demonstrate capability of producing a family of new materials with twice the life span of current materials and which have 20% better thermal efficiency than current materials. (09/30/07)

Year Two: (2) Validate that new materials possess twice the life span of current materials and 20% better thermal efficiency than current materials. (9/30/08). (3) Demonstrate ability to install the family of new materials produced in year one. New applications techniques and systems will be tailored for the newly developed materials to optimize installed material properties. Installed materials will preserve the 2X improvement in life span and 20% improvement in thermal efficiency over current materials. (09/30/08)

Year Three: (4) Demonstrate ability to perform on-line inspection and feasibility of hot-repair techniques. These methods are expected to increase lining lifetimes by at least 2X and to decrease the number of needed maintenance shut-downs by half. (09/30/09)

Year Four: (5) Obtain six months of in-plant operating experience at industrial partner locations. This will provide a validation of refractory performance on an industrial scale, as compared to lab scale results previously obtained during the project. By comparing performance of new materials to that of currently used materials under identical service conditions, the goals of 2X improvement in life span and 20% improvement in thermal efficiency will be validated. (09/30/10)

3. BENEFITS OF THE FUNDING DOE OFFICE'S MISSION

The objective of this project was to address the need for new innovative refractory compositions by developing a family of novel $MgO-Al_2O_3$ or other similar spinel structured or alumina-based unshaped refractory compositions (castables, gunnables, shotcretes, etc.) utilizing new aggregate materials, bond systems, protective coatings, and phase formation techniques. The newly developed materials were expected to offer alternative material choices for high-temperature, high-alkali environments that may be capable of operating at higher temperatures (goal of increasing operating temperature by 100-200^{o}C depending on process) or for longer periods of time (goal of twice the life span of current materials or next process determined service increment). This would lead to less process down time, greater energy efficiency for associated manufacturing processes (more heat kept in process), and materials that can be installed/repaired in a more efficient manner. The overall project goal was a 5% improvement in energy efficiency (brought about through a 20% improvement in thermal efficiency) resulting in a savings of 3.7 TBtu/yr (7.2 billion ft^3 natural gas) by the year 2030. Additionally, new application techniques and systems were developed as part of this project to optimize the installation of this new family of refractory materials to maximize the properties of installed linings and to facilitate nuances such as hot installation and repair.

When implemented, the materials developed under this project directly lead to the improved energy efficiency of American industry through increased thermal efficiency and longer refractory lining lifetimes for high temperature furnaces and process vessels. Specifically, the newly developed materials are expected to offer alternative choices for high-temperature, high-alkali environments that may be capable of operating at higher temperatures or for longer periods of time. This will lead to less process down time, greater energy efficiency as more heat kept in associated manufacturing processes, and materials that can be installed/repaired in a more efficient manner. By decreasing the amount of waste heat and extending furnace life times, the materials developed in this project could help increase the overall efficiency of furnaces and process vessels used in the aluminum, chemical, forest products, glass, and steel industries.

4. TECHNICAL DISCUSSION OF WORK PERFORMED

In the final execution of this project, Task 1 defined in Section 2 was further differentiated by dividing it into three separate tasks. "Task 1. Development of Refractory Materials" dealt specifically with the original development of candidate materials under this project during year one of the project. "Task 2. Identification of new materials and fundamental understanding of materials" was a more fundamental task largely carried out at MS&T throughout the duration of the project in support of the material development and deployment efforts. "Task 3. Production of Refractory Materials" encompassed the original production of experimentally developed materials and the subsequent continued production of materials during the duration of the project for both laboratory and industrial testing as needed. Table 1 shows the new task structure, subtasks, and the planned and actual completion dates of each task.

Table 1. Task Schedule

Task/ Subtask Number	Title or Brief Description	Task Completion Date				Comments
		Original Planned	Revised Planned	Actual	% Complete	
1	**Development of refractory materials**	9/28/07		9/28/07	100	
1.1	Identification of refractory components	1/31/07	2/28/07	2/28/07	100	Refractory families and candidate materials defined.
1.2	Evaluation of application techniques	2/28/07	3/30/07	3/30/07	100	Candidate application techniques defined.
1.3	Identification of processing techniques	3/30/07		3/30/07	100	Candidate processing techniques defined.
1.4	Microstructural, mechanical, and thermodynamic modeling	6/29/07	9/28/07	9/28/07	100	Modeling of initial materials completed.
1.5	Wear and strength testing standardization	9/28/07		9/28/07	100	Methods have been selected, but will be revisited throughout the project.
1.6	Initial production of refractory materials	9/28/07		9/28/07	100	Initial materials produced and validated.
2	**Identification of new materials and fundamental understanding of materials**	3/31/10		3/31/10	100	Refractory development will continue through the entire life of the project.
2.1	Study of spinel solid solutions and thermal conductivity effects	9/28/07	3/31/08	3/31/08	100	
2.2	Fundamental understanding of spinel (microstructure/formation)	12/31/09	3/31/10	3/31/10	100	

2.3	Study of polycrystalline diffusion couples	6/30/09	3/31/10	3/31/10	100	
2.4	Study of refractory mix components and roles	6/30/09	9/30/09	9/30/09	100	
3	**Production of refractory materials**	3/31/10	9/30/11	9/30/11	100	
3.1	Production of refractories	3/31/10	9/30/11	9/30/11	100	Refractory production continued through the entire life of the project.
3.2	Microstructural, mechanical, and thermodynamic modeling	9/30/09		6/30/09	100	
4	**Measurement of key refractory properties**	9/30/08	12/31/08	12/31/08	100	
4.1	Thermal conductivity and creep	3/31/08	9/30/08	9/30/08	100	
4.2	Abrasion, wear, and thermal expansion	3/31/08	9/30/08	11/30/08	100	
4.3	Corrosion, strength, and thermal shock	6/30/08	9/30/08	9/30/08	100	Thermal shock testing not needed.
4.4	Physical characterization	9/30/08		9/30/08	100	
4.5	Microstructural evaluation	9/30/08		9/30/08	100	
5	**Development of new refractory application techniques**	9/30/08	12/31/08	12/31/08	100	
5.1	Development of techniques	7/31/08		7/31/08	100	
5.2	Development of equipment	8/29/08		8/29/08	100	
5.3	Initial application and property evaluation	9/30/08		9/30/08	100	
5.4	Wear testing	9/30/08	12/31/08	12/31/08	100	
5.5	Strength testing	9/30/08		9/30/08	100	
5.6	Microstructural evaluation	9/30/08	12/31/08	12/31/08	100	
6	**Development of on-line inspection and hot-repair techniques**	9/30/09		9/30/09	100	Hot repair materials developed, on-line inspection not feasible

6.1	Review of current methods	3/31/09		3/31/09	100	
6.2	Microstructural, mechanical, and thermodynamic modeling	6/30/09		6/30/09	100	
6.3	Development of new methods and techniques for new materials	3/31/09	6/30/09	6/30/09	100	
6.4	Adaptation of newly developed technology to developed materials	9/30/09		9/30/09	100	On-line inspection found to be cost prohibitive
7	**Formation of database**	3/31/10	12/31/10	12/31/10	100	
7.1	Creation of server	7/31/09	7/31/10	9/30/10	100	
7.2	Organization and input of data	3/31/10	6/30/11	6/30/11	100	
7.3	Distribution of information	3/31/10	6/30/11	6/30/11	100	
8	**In-plant trials and commercialization**	9/30/10	9/30/11	9/30/11	100	
8.1	Performance of in-plant trials	9/30/10	9/30/11	9/30/11	100	Monitoring of sites continued into FY12 on project no-cost extension
8.2	Commercialization efforts	9/30/10	12/31/10	12/31/10	100	Plan put together and implemented by MINTEQ
8.3	Training efforts	6/30/10	9/30/11	9/30/11	100	
9	**Reporting and administration**	9/30/10	9/30/11	9/30/11	100	Reporting continued through the entire life of the project.

The original project milestones and their completion dates are shown in Table 2. More in depth discussion of key results from each task are also given below.

Table 2. Milestone Schedule

Milestones Go-No Go's	Title or Brief Description	Milestone Completion Date				Comments
		Original Planned	Revised Planned	Actual	% Complete	
1	Get CRADA with MINTEQ in place	12/29/06	1/31/07	1/23/07	100	
2	Demonstrate production of new family of refractory materials	9/28/07		9/28/07	100	
3	Validate properties of new materials will lead to improved life span and thermal efficiency	9/30/08	12/31/08	12/31/08	100	
4	Demonstrate ability to install new family of materials	9/30/08		9/30/08	100	
5	Demonstrate ability to perform on-line inspection and feasibility of hot-repair	9/30/09		9/30/09	100	Hot repair materials developed, on-line inspection found to be cost prohibitive
6	Obtain six months of in-plant operating experience at industrial locations	9/30/10	9/30/11	9/30/11	100	Goal met. Monitoring of sites continued into FY12 on project no-cost extension

Task 1 Development of refractory materials

This task was completed at the end of the first year of the project (9/07).

- Refractory families and candidate materials were defined:
  - alumino-silicate, magnesia, and spinel forming systems
  - family of light weight refractory back-up materials

Table 3. Summary of Materials Developed Under Project

Industry	**Material**	**Application**
Aluminum	Alumino-Silicate (A) Alumino-Silicate (B) Spinel Former (A)	Primary lining Repair material Repair material (alumina rich)
Black Liquor	Spinel Former (B) Phosphate Bonded Castable (A)	Repair material (magnesia rich) Repair material (magnesia rich)
Coal Gasification	Spinel Former (C)	Repair material (alumina rich)
Insulating Back-up	Light Weight Castable (A)	Secondary lining for spinel material applications
Lime Kiln	Spinel Former (B)	Primary lining (magnesia rich)

(note: letters A, B, C designate materials of same family, but different compositions)

- Candidate application and processing techniques were defined – shotcreting
- Modeling of initial materials was completed
- Standardized methods for wear and strength testing of existing and developed materials were selected (see Task 4)
- Experimental materials were produced and validated meeting Milestone/Go-No Go Decision Point 2.

Refractory development efforts were based on characterization of failed materials from industrial partners and analysis utilizing a tool known as "Quality Function Deployment" (QFD). This tool, brought to the project by MINTEQ, was used for capturing, prioritizing and translating the needs of our four originally targeted markets into a single development program and to guide the initial research direction and efforts of the project. This tool was being used to aid in project direction and maximizing the chance of project success by targeting areas where there is 1) commonality between processes/furnaces from various industries, 2) significant chance of meaningful energy savings, and 3) likelihood of achieving success using the approaches proposed for this project. Spreadhseets were developed for Aleris rotary and reverberatory furnaces, a PPG melting furnace and regenerator, the Eastman coal gasifier, and the Weyerhaeuser gasfier and lime kiln based on visits to industrial partner sites.

Task 2 Identification of new materials and fundamental understanding of materials
Work on this task continued at MS&T throughout the life of the project to provide support for the development and production of the experimental refractory materials being developed. Work was focused on extending the fundamental understanding of the spinel microstructure and of spinel formation, along with the effects of microstructure and degree of formation on properties such as thermal expansion and refractoriness, density/porosity, thermal conductivity, and penetration/corrosion resistance. This work directly fed into the spinel forming refractory development which was on-going though out the duration of the project at MINTEQ.

Task 3 Production of refractory materials
Work on this task continued through the life of the project as materials were optimized for performance and individual applications. Materials were produced by MINTEQ for laboratory testing during development efforts, for laboratory validation trials, and for full industrial trials as needed.

Task 4 Measurement of key refractory properties
Original work on this task was completed in 12/08 to meet Milestone/Go-No Go Decision Point 3. Testing was continued though throughout the life of the project as information was required periodically when materials were modified or new materials were identified.

Work was ongoing at ORNL and MS&T through the duration of the project on the measurement and characterization of key refractory properties as identified during year one of the project. Both materials currently being used in the industrial processes as identified and supplied by the industrial partners of this project and new materials being provided and developed by MINTEQ will be evaluated as necessary.

Additionally, a rotary furnace simulation test system was commissioned by MINTEQ for evaluation of material performance in the aluminum and lime kiln environments. The furnace was capable of being lined with test samples of both currently used and new materials developed under this project for a side by side comparison of materials on a scale between lab-scale and actual industrial implementation.

Energy savings estimates based on measured properties of the experimentally developed refractory systems from this project were made at MINTEQ to validate the energy savings estimates originally proposed for the project. One such analysis for lime kilns is shown below in Table 4

Table 4. Lime Kiln Energy Analysis

Refractory Configuration	60 % Al2O3 Brick & Insul. Tiles	Spinel Material With New Insulation
Estimated Shell Temp	446 F	383 F * *2 in eff insulation K=1.5BTUin/DegFhrft2
Estimated Heat Loss/sqft	1378 BTU	1022 BTU
Estimated Heat Loss per kiln per year	43.6 B BTU	32.4 B BTU

This analysis assumes a traditional lime kiln refractory lining consisting of 60% alumina brick backed by insulating refractory tiles as found in the current configuration used by industrial partner Weyerhaeuser. The performance of this lining system is compared to a refractory system composed of the experimental spinel forming and back-up materials developed under this project. For identical service conditions (based on those observed at Weyerhaeuser) a reduction in shell temperature of 63^oF is realized using the new lining system which results in a reduction of estimated heat loss through the shell of 356 Btu/ft.^{2} or 11.2 billion Btu per kiln per year. At an estimated cost of $12/MMBtu for natural gas (average spot price), this results in an annual savings of $134,400/year per kiln.

Task 5 Development of new refractory application techniques

Work on this task was completed during year two of the project (meeting Milestone #4). Initial property evaluation of installed materials was also completed in year two, with wear testing and microstructural evaluation being competed in the first part of year three.

Task 6 Development of on-line inspection and hot-repair techniques

This task was completed during year three of the project. Efforts were completed to evaluate current methods, along with applicable new systems and techniques for targeted applications. Additionally, discussions were held with various partners about interest in on-line inspection and hot-repair techniques being developed with MINTEQ and their possible participation in the final year of the project as an industrial test site.

It was determined that although repair materials have been developed for aluminum, black liquor, and coal gasification systems which enable hot repair, there is only minor interest from the industrial partners in implanting these materials. The best opportunities for hot repair are still felt to currently exist in the aluminum industry and discussions were continued throughout the life of the project with industrial aluminum partners. Discussions were also held with the developers of black liquor gasification systems (Chemrec who oversaw the New Bern Weyerhaeuser gasifier) about implementation of materials in a repair capacity in their high pressure unit located in Sweden.

On-line inspection techniques were identified which are currently used in the steel industry, but implantation of these techniques in applications such as black liquor and coal gasification where higher temperatures and tighter access clearances exist proved difficult due to cost considerations. Therefore, on-line inspection was not further pursued under this project.

Milestone 5 was completed in the third quarter of year three with the completion of the development of hot repair materials for aluminum, black liquor, and coal gasification systems and the determination of on-line inspection techniques being cost prohibitive for implementation.

Task 7 Formation of database

This task was scheduled to be completed during year four of the project based on data collected in Task 5. Actual completion of this task took place in 12/10 during a no-cost extension of the project. Information was entered from data collected during this and previous DOE projects. Over twenty five separate materials were initially included in the database at a publically available site (http://extwebapps.ornl.gov/crpd/Default.aspx). A sample of the database site is shown in Figure 1.

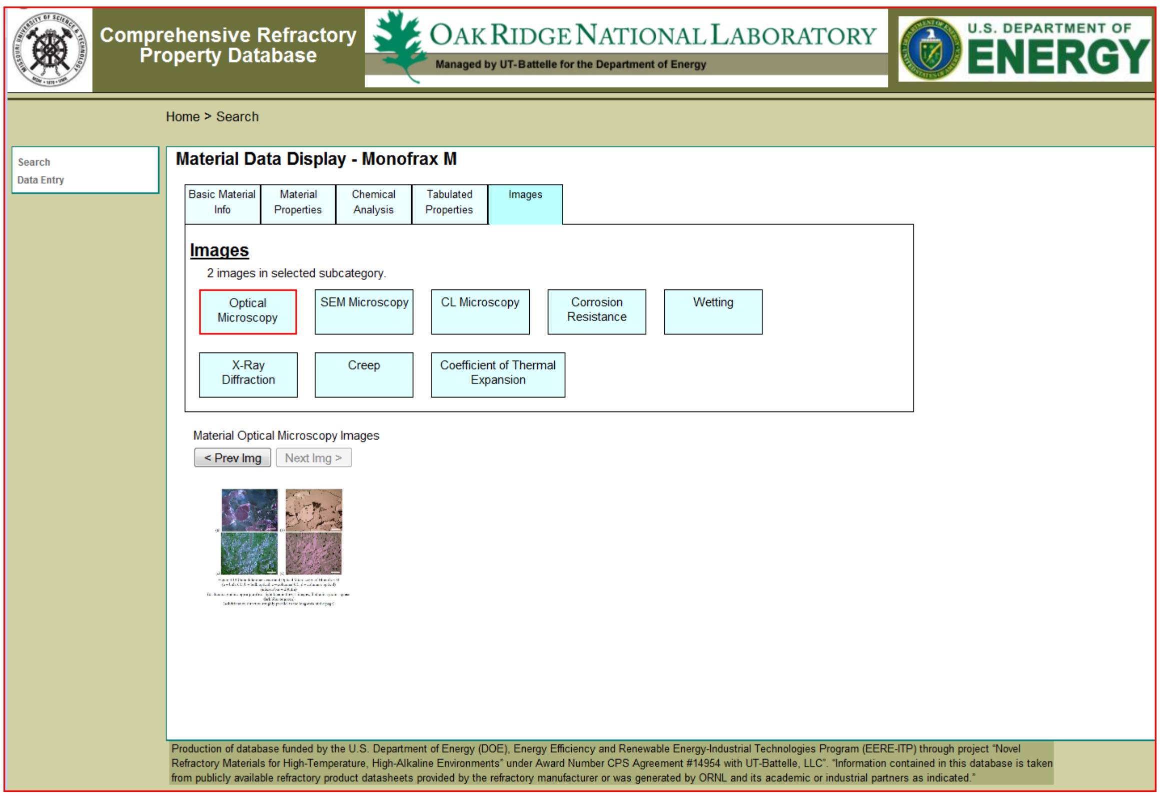

Figure 1. Example of Page from Comprehensive Refractory Property Database

Task 8 In-plant trials and commercialization

Work on this task took place during the final planned year of the project (Year 4) and has continued during a no cost extension of the project. The focus of the work was identifying and securing industrial trial sites for validation of the materials developed during the first three years of the project.

A plant trial of the insulating shotcrete product developed under this project was conducted at a MinTeq plant in Portage, IN to demonstrate industrial scale production of this material.

An industrial scale shotcrete demonstration of the insulating shotcrete product developed under this project was also conducted at a MinTeq facility in Steubenville, OH.

An industrial trial was held at Newco Metals (Bedford, IN) through a field installation of 14 tons of material developed for aluminum rotary dross furnace applications. The same customer placed a second order based on the easy/rapid installation of this product. It was noted by the customer during the second order that the durability of the product had already met the customer's expectation. These trials were monitored in excess of six months (linings actually monitored in excess of nine months and still installed at the time of the writing of this report) meeting Milestone Go/No Go Decision Point #6. This trial is still on-going.

The field installation of three tons of light weight insulating back-up material developed under this project was carried out at Tate & Lyle in Lafayette, IN. This material was used behind a hot face lining to improve the thermal efficiency of the combustion chamber for a drying system. The installation was still being monitored at the time of the writing of this report, but had been operating successfully for over six months. This trial is still on-going.
The field installation of 70 tons of material developed for aluminum rotary dross furnace applications was performed in collaboration with Refractory Engineers Inc./Ceramic Technology Inc. and MinTeq at Alcoa Warrick Operations. This installation was performed near the end of FY11 and will be monitored into FY12 as part of a no-cost extension to this project.

Discussions with Houghton Cascade Holdings, LLC (formerly employees of original industrial partner Weyerhaeuser) about possible trial sites for the lime kiln materials developed under this project resulted in determination that many lime kiln operators are hesitant to install shotcrete materials and multi-layer linings. Single component, traditional brick linings were found to be preferred, as opposed to multi-component systems consisting of a corrosion resistant hot-face material backed by a more insulating material, as was pursued under this project. Therefore, a different approach would have to be taken to implement materials from this project in this application.

Original discussions were held with Eastman regarding industrial trials of materials developed for coal gasification, but an actual trial could never be agreed on. Subsequent discussions were held with the Energy and Power Research Institute (EPRI) regarding possible coal gasification test sites and materials developed under this project.

Discussions were held with Chemrec, the company who designed and aided in the operation of the black liquor gasifier at the Weyerhaeuser New Bern, NC facility, concerning the installation of trial refractories at the Chemrec experimental high pressure unit running in Sweden or in other units being constructed by Chemrec. No trials resulted from these discussions.

Plans for commercialization were developed and implemented by MINTEQ.

Publications, and Presentations Resulting From This Project:

A presentation was given to the Chattanooga Tennessee Engineers Club (January 2009) entitled "Refractory Ceramics, An Opportunity for Improved Energy Efficiency" which contained information from this project.

A presentation was given and a proceedings paper was published – J.G Hemrick, K.M. Peters, and J. Damiano, "Energy Saving Strategies for the Use of Refractory Materials in Molten Material Contact", Energy Technology Perspectives: Conservation, Carbon Dioxide Reduction and Production from Alternative Sources, TMS, February (2009).

Two presentations with accompanying proceedings papers (one by ORNL entitled "Novel Spinel-Family Refractories for High-Temperature, High-Alkaline Environments" and one by MS&T entitled "Solid Solution Effects on the $MgAl_2O_4$ System") were presented at the Unified International Technical Conference on Refractories (UNITECR 2009) meeting in Salvador Brazil (October 2009).

A poster was prepared by SULI summer student Kyle Anderson from Missouri University of Science and Technology regarding the analysis of salvaged aluminum metal contact refractories from the first year of this project. This poster was displayed at a student poster competition for the SULI participants where their research work was showcased and at a SERCH poster competition for outstanding work from the previous competition (November 2009).

A presentation was given at the University of Tennessee entitled "Refractory Ceramics: An Opportunity for Improved Energy Efficiency" which contained information from this project (March 2010).

A paper regarding this project entitled "Solid Solution Effects on the $MgAl_2O_4$ System" with accompanying proceedings paper was presented by Kelley O'Hara (MS&T) at the Forty-sixth Symposium on Refractories sponsored by The Saint Louis Section and Refractory Ceramics Division of the American Society in Saint Louis, MO (March 2010).

A presentation was given at the Oak Ridge Chapter of ASM International May Technical Meeting and Awards Night entitled "Refractory Ceramics, An Opportunity for Improved Energy Efficiency" which discussed concepts and materials from this project, Knoxville, TN, May 20, 2010.

A presentation entitled "Novel Spinel-Family Refractories for High-Temperature, High-Alkaline Environments" with associated proceedings paper was given at the 2010 Advances in Refractories V, 5^{th} International Symposium, The Michel Rigaud Symposium, Vancouver, British Columbia, Canada, October (2010).

A presentation entitled "IMPROVED FURNACE EFFICIENCY THROUGH THE USE OF REFRACTORY MATERIALS" with associated proceedings paper was given at the TMS 2011 Meeting in San Diego, CA, February (2011).

An R&D 100 Award application was completed and submitted by MinTeq regarding the refractory materials for aluminum applications developed under this project.

A presentation entitled "Development of Novel Spinel Refractories For Use in Coal Gasification Environments" with associated proceedings paper was prepared by James Hemrick (ORNL) for the 28^{th} Annual International Pittsburgh Coal Conference, Pittsburgh, Pennsylvania, September (2011).

A presentation entitled "Solid Solution Effects on the MgAl2O4-MgGa2O4 System" with associated proceedings paper was prepared by Kelley O'Hara (MS&T) for the UNITECR 2011 Meeting in Kyoto, Japan, October (2011).

5. SUBJECT INVENTIONS

None.

6. COMMERCIALIZATION POSSIBILITIES

The back-up material formulation developed under this project for use as a shotcretable thermal insulation layer useable with the high conductivity spinel shotcretes developed under this project was finalized and a technical data sheet was issued by MINTEQ as shown in document attached in Appendix A at end of this report ("INSULSHOT™ FH Technical Data Sheet").

The material formulation developed under this project for use in the aluminum industry was finalized and a technical data sheet was issued by MINTEQ as shown in document attached in Appendix B at end of this report ("ROTOSHOT™ AL Technical Data Sheet").

The magnesia-rich spinel formulation developed under this project for use in black liquor and lime kiln/cement applications was finalized and a technical data sheet was issued by MINTEQ as shown in document attached in Appendix C at end of this report ("FAST FIRE® MG-SP SHOT Technical Data Sheet").

Industrial trials of the insulating shotcrete (INSULSHOT™ FH) and the material for use in aluminum rotary furnaces (ROTOSHOT™ AL) were performed validating the commercial potential of these materials. Additionally, the magnesia-rich spinel formulation (FAST FIRE® MG-SP SHOT) for use in black liquor and lime kiln/cement applications was commercially released by MINTEQ.

7. PLANS FOR FUTURE COLLABORATION

Further collaboration is currently being sought between MINTEQ and ORNL to further develop and deploy these materials in lime and cement kiln applications (2011 DOE/ITP Innovative Manufacturing Call). Additionally, the extension of spinel-based materials into other applications beyond the scope of this work is being investigated. Work is also on-going under "Work For Others" (ORNL WFO) funding to further explore the use of materials developed under this project in coal gasification environments.

8. CONCLUSIONS

- Seven new materials were developed under this project for both primary and repair applications in aluminum, black liquor, coal gasification, and lime kiln environments. Developed materials were based on alumino-silicate, magnesia, and spinel forming systems. One of the developed materials was an insulating shotcrete to be used behind the high conductivity spinel linings developed under this project. Shotcreting was selected as the preferred application method for materials developed under this project.
- Fundamental research work was continued at MS&T throughout the life of the project to provide support for the development and production of the experimental refractory materials being developed. Work was focused on extending the fundamental understanding of the spinel microstructure and of spinel formation, along with the effects of microstructure and degree of formation on properties such as thermal expansion and refractoriness, density/porosity, thermal conductivity, and penetration/corrosion resistance. This work directly fed into the spinel forming refractory development which was on-going though out the duration of the project at MINTEQ.
- Energy savings estimates based on measured properties of the experimentally developed refractory systems from this project were made at MINTEQ to validate the energy savings estimates originally proposed for the project.
- It was determined that although repair materials were developed under this project for aluminum, black liquor, and coal gasification systems which enable hot repair, there is only minor interest from industry in implementing these materials. On-line inspection techniques were also identified under this project, which are currently used in the steel industry, but implementation of these techniques in applications such as black liquor and coal gasification where higher temperatures and tighter access clearances exist proved difficult due to cost considerations. Therefore, on-line inspection was not further pursued under this project.
- Information from data collected during this and previous DOE projects was inputted into a refractory database housed at a publically available site (http://extwebapps.ornl.gov/crpd/Default.aspx). Over twenty five separate materials have been initially included in the database.
- Industrial trials of the insulating shotcrete (INSULSHOT™ FH) and the material for use in aluminum rotary furnaces (ROTOSHOT™ AL) developed under this project were performed validating the commercial potential of these materials. Additionally, the magnesia-rich spinel formulation (FAST FIRE® MG-SP SHOT) for use in black liquor and lime kiln/cement applications was commercially released by MINTEQ.
- Ten presentations were given, eight papers were published, and one poster and one R&D 100 Award application were composed regarding this project.
- Further collaboration is currently being sought between MINTEQ and ORNL to further develop and deploy these materials in lime and cement kiln applications, coal gasfication environments and to extend the use of spinel-based materials into other applications beyond the scope of this work.

Appendix A. INSULSHOT™ FH Technical Data Sheet

MINERALS TECHNOLOGIES

MINTEQ®

TECHNICAL DATA

INSULSHOT™ FH

Shotcrete Material

Ref: F-1376
Issued: 26-Mar-10

DESCRIPTION:

INSULSHOT™ FH refractory material is a 2300°F INSULATING SHOTCRETE castable that exhibits low densities, low thermal conductivity, excellent strengths, and energy saving characteristics. *INSULSHOT FH* refractory material is ideal for use as a working and/or back up lining. Applications include: Fireproofing, Coking Systems, Catalytic Cracking Systems and back up linings for industrial furnaces and process vessels.

Packaging:

500 lb. bags	2 or 3 per pallet

CHEMICAL COMPOSITION:

	Typical (Ignited Basis)
Al_2O_3	37.3%
SiO_2	54.6
CaO	4.5
Fe_2O_3	1.3
TiO_2	0.9
Others	1.4

PHYSICAL PROPERTIES:

Typical, as determined on shotcreted specimens, ASTM firing and methods where applicable.

Fired to °F	Bulk Density (pcf)	Linear Change (%)	Modulus of Rupture (psi)	Cold Crushing Strength (psi)	Apparent Porosity (%)
230	72	-	440	1000	37
1500	68	-0.5	210	1100	45
2000	69	-0.8	330	1100	48
2300	69	-1.1	450	900	55

Thermal Conductivity: Mean Temperature, °F	Typical "K" (BTU•in/hr•ft²•°F)
500	2.8
1000	2.8
1500	3.2

SERVICE LIMIT: 2300°F

For more information please call the Customer Service Department at 1-800-390-9393.

APPLICATION METHOD:

The recommended water addition to an intensive concrete mixer is 34 - 38% by weight to achieve a 20-40% static flow (cone test). The typical air pressure requirement for INSULSHOT™ FH installations is 12-15 psi at the nozzle. A hose lubricant is not necessary during pumping for hose length shorter than 75 ft. INSULSHOT™ FH requires its unique accelerator. Dry out schedule is dependent upon its application. Consult your MINTEQ representative for selecting the accelerator and the dry out schedule.

Appendix B. ROTOSHOT™ AL Technical Data Sheet

MINERALS TECHNOLOGIES

MINTEQ®

TECHNICAL DATA

ROTOSHOT™ AL

Shotcrete Material

Ref: F-1377
Issued: 05-Mar-10

DESCRIPTION: ROTOSHOT™ **AL** refractory material is a low cement, abrasion resistant, shotcrete material designed for molten aluminum contact. The hot strengths and non-wetting characteristics provide exceptional performance when exposed to temperatures up to 2300 °F. Typical applications include working linings for aluminum rotary dross furnaces and high wear of aluminum reverb furnaces.

Packaging:
2000 lb. bulk bags 2 bags/ pallet

Shelf Life:
6 months

CHEMICAL COMPOSITION:

	Typical (Ignited Basis)
Al_2O_3	73.4%
SiO_2	19.6
CaO	1.5
TiO_2	1.5
Fe_2O_3	0.4
Others	3.6

PHYSICAL PROPERTIES: Typical, as determined on shotcreted specimens, ASTM methods where applicable.

Fired to °F	Bulk Density (lbs/ft³)	Linear Change (%)	Modulus of Rupture (psi)	Hot Modulus of Rupture (psi)	Cold Crushing Strength (psi)	Apparent Porosity (%)	Abrasion Volume Loss (cc)
230	172	-	2150	—	7100	11.7	-
1500	173	-0.3	1600	3000	11100	18.9	5.9
1850	170	-0.3	1650	3500	15000	19.5	7.5
2200	167	-0.4	2000	2500	11150	20.5	6.5
2300	169	-0.4	1900	1650	13550	20.4	7.6
2500	171	-0.6	2150		16500	18.9	6.8

ALCOA Aluminum cup penetration (72 hr. @ 1500 °F)

	After firing @ 1600 °F for 10 hrs.	After firing @ 2300 °F for 10 hrs.	ALCOA standard
Si pick up (%)	0.21	0.24	0.5 max
Fe pick up (%)	0.03	0.03	0.1 max
Rated	Excellent *	Excellent *	

** No visual reaction, discoloration or metal penetration as rated by an independent lab.*

SERVICE LIMIT: 2300 °F for aluminum contact and 2800 °F for non-aluminum contact

APPLICATION METHOD: The recommended water addition to an intensive concrete mixer is 5.4-6.2 % by weight to achieve 40-60% static flow (cone test). The material must be applied through a high-pressure concrete pump. OPTISHOT™ *Installation Procedures* (MII-INST-021) should be followed when mixing, placing, using and storing this product.

Appendix C. FASTFIRE® MG-SP SHOT Technical Data Sheet

MINERALS TECHNOLOGIES

MINTEQ®

TECHNICAL DATA

FASTFIRE® MG-SP SHOT

Shotcrete Material

Ref: F-1382
Issued: 04-Jan-11

DESCRIPTION:

FASTFIRE® MG-SP SHOT refractory material is a magnesia-rich spinel forming, shotcrete castable. It provides all of the physical properties and performance of a traditional cast in place refractory lining with the added benefit of reduced installation time and reduced heat-up time required during initial start-up of the unit. Typical applications for **FASTFIRE® MG-SP SHOT** refractory material include refractory working linings in lime kilns, cement kilns, and other metallurgical processing vessels.

Packaging:

2000 lb. bags — 2 per pallet

CHEMICAL COMPOSITION:

	Typical (Ignited Basis)
MgO	79.8%
Al_2O_3	14.3
SiO_2	3.2
CaO	1.7
Others	1.0

PHYSICAL PROPERTIES:

Typical, as determined on shotcreted specimens, including specimens fast fired at 2000°F (*). ASTM methods where applicable.

Fired to °F	Bulk Density (lbs/ft³)	Linear Change (%)	Modulus of Rupture (psi)	Hot Modulus of Rupture (psi)	Cold Crushing Strength (psi)	Apparent Porosity (%)	Abrasion Volume Lost (cc)
230	171	-	1020		6800	16	9.8
1500	167	-0.1	1320		7500	21	11.3
2000	164	0.5	720	1000	6500	22	13.6
FF2000(*)	168	0.4	710		7300	22	12.8
2500	172	-0.3	1300	860	8400	20	10.2
2750	176	-0.9	1500		8500	18	9.9
2850	178	-1.3	1300		9000	17	9.6

Material Required to install one cubic foot (without waste):

(lbs) 171

SERVICE LIMIT: 3000 °F

APPLICATION METHOD:

The recommended water addition to an intensive concrete mixer is 5.0-6.0% by weight to achieve 40 - 60% static flow (cone test). The material must be applied through a high-pressure concrete pump. **OPTISHOT®** Refractory Installation Procedures (MII-INST-021) should be followed when mixing, placing, using and storing this product. Dry Out Schedule for **FASTFIRE®** Refractory Procedure (MII-INST-039) or for **OPTISHOT®** Products (MII-INST-046) could be followed when drying this product.

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