Successes

High-Temperature Ceramic Microsensor Development for Combustion Boiler Optimization

Advanced Research

To support coal and power systems development, NETL's Advanced Research Program conducts a range of pre-competitive research focused on breakthroughs in materials and processes, coal utilization science, sensors and controls, computational energy science, and bioprocessing—opening new avenues to gains in power plant efficiency, reliability, and environmental quality. NETL also sponsors cooperative educational initiatives in University Coal Research, Historically Black Colleges and Universities, and Other Minority Institutions.

Accomplishments

- ✓ Process improvement
- ✓ Cost reduction
- ✓ Greater efficiency
- ✓ Environmental benefits

Description

The Ohio State University's Center for Industrial Sensors and Measurements (CISM) partnered with GE Reuter Stokes (GERS, a part of GE Power Systems), NASA Glenn, Argonne National Laboratory, Case Western Reserve University, and Makel Engineering in a broad-ranging research effort to develop a ceramic-based microsensor array. The purpose of the array is to monitor total concentrations of gaseous nitrogen oxides (NO_x), carbon monoxide (CO), and oxygen (O_2) within the hot zones of the burner (480–815 °C) of a coal-fired boiler in order to provide feedback for burner balancing and optimization. Development of these award winning sensors has received support from the U.S. Department of Energy's (DOE) Office of Fossil Energy through the National Energy Technology Laboratory's (NETL) Advanced Research Program.

The CO and O_2 concentrations provide a measure of the completeness of combustion, while the NO_x concentration measures the main controllable pollutant from the combustion. Successful development and use of such sensor systems will dramatically alter how boilers are operated, since many emissions creation and boiler problems occur at local zone conditions rather than at the overall boiler level. The real-time profiles of combustion parameters at multiple points across the boiler will provide the operator with knowledge of the boiler's response characteristics to individual burner, air, fuel, and other control settings, ultimately leading to more efficient boiler operation with associated energy savings and minimization of emissions. In addition, sensor systems with subsecond response times should allow integration into neural nets and other controlling algorithms. The concept of zone monitoring is illustrated in Figure 1.

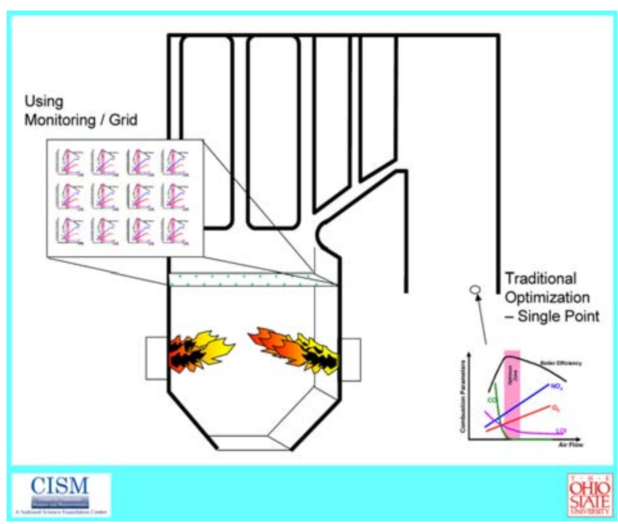

Figure 1. Combustion optimization using zone coverage instead of traditional single-point measurement.

Project Duration

Start Date
07/11/2003

End Date
12/31/2008

Cost

Total Project Value
$948,923

DOE/Non-DOE Share
$723,928 / $224,995

Partners

The Ohio State University
Columbus, OH

GE Reuter Stokes, Inc.
Cleveland, OH

NASA Glenn
Cleveland, OH

Argonne Research Laboratory
Argonne, Illinois

Case Western Reserve
University Cleveland, OH

Makel Engineering
Chico, CA

Technical Approach

The partners adopted a research strategy to assemble highly selective microsensors for each gas using novel materials chemistry and sensing principles that allow for operation at high temperatures in harsh combustion environments. Pattern recognition algorithms also were developed to extract quantitative information about the gas composition from the collective sensor responses. The strategy also includes development of suitable packaging for the units. Evaluation of the sensor arrays took place under laboratory conditions both at Ohio State and GERS, and at other industrial facilities.

The microsensor array comprises a resistive CO sensor and electrochemical potentiometric O_2 and NO_x sensors.

- The CO sensor is based on titanium dioxide (TiO_2) and is designed to monitor concentrations of 0–1,000 ppm. The researchers examined catalysts for improving CO selectivity and composite p-n semiconducting TiO_2 for reducing cross-sensitivity.
- The O_2 sensor can monitor oxygen concentrations from 0.1 percent to 15 percent. It is based on a sealed metal-metal oxide reference electrode with yttria stabilized zirconia (YSZ) as the electrolyte.
- The NO_x sensor also measures concentrations of 0–1,000 ppm and uses YSZ as the electrolyte with metal oxide sensor electrodes. It includes a catalytic filter that is designed to reduce CO, hydrocarbon and ammonia interference as well as allow for measurements of total NO_x.

Resistance-based detectors measure change in resistance of the material with a multimeter in the presence of gases. Potentiometric sensors use the potential difference between a reference electrode and a sensing electrode as a signal to measure gas concentration. Microsensors of both types may be made small enough (match head-sized or less) with fast response times.

Accomplishments

Fabrication of the CO sensor was the first task. Research centered on the use of dopants that alter the electrical and chemical characteristics of titania. To achieve better stability and reproducibility for CO sensing at high temperatures above 600 °C, TiO_2 (anatase) was doped with lanthanum oxide (La_2O_3), providing microstructural, crystallographic, and electrical stability during long-term, high-temperature operation, thereby minimizing drift. Improved selectivity was achieved by adding cupric oxide (CuO) to the La-stabilized anatase. This sensor was used by NASA for fire detection and *R&D Magazine* in 2005 recognized the fire detection sensors as one of the 100 most technologically significant products introduced into the marketplace over the previous year.

Figure 2. Ohio State's reference-free potentiometric oxygen sensor is capable of withstanding temperatures of 1,600 °C.

The second task was fabrication of the O_2 sensor. With collaborators from Argonne National Laboratory, the researchers succeeded in developing a high-temperature air-reference free oxygen sensor that was also selected by *R&D Magazine* in 2005 as one of the top 100 products for the previous year. This sensor is readily miniaturizable and does not require an external oxygen reference, relying instead on an internal metal/metal oxide to generate a fixed partial pressure of oxygen. A unique deformation bonding method was developed to provide the sealing that contains the metal/metal oxide reference. It is fabricated from relatively common and inexpensive ceramic materials that can withstand the environment inside a combustion chamber. These features enable multiple oxygen sensors to be placed throughout a combustor, allowing the operator to map the combustion process and control it more tightly, leading to higher efficiency and lower emissions.

The third task was fabrication of the NO_x sensor. Again, researchers succeeded in developing a high-temperature total NO_x sensor whose central feature is a platinum-based porous catalyst filter that provides total NO_x readings and removes interference from CO, hydrocarbons, and ammonia. An active reference electrode also eliminates the need for air reference. Integrating this filter with a platinum-based sensing element provides the opportunity for miniaturization. Connecting several sensors in series amplifies the signal and makes it possible to push detection limits to parts-per-billion NO_x, enabling use of these sensors in low-NO_x combustion processes such as in power generation with turbines, in diesel engines for trucks and passenger vehicles, and most recently in breath analysis for asthma patients. Successful development of this total NO_x sensor was recognized with another "R&D 100" award in 2007.

EmiSense has licensed exclusive patents from Ohio State for the sensor, which is being marketed as NO_xTrac™. EmiSense is a spin-off company from Ceramatec Inc. Ceramatec is a 30-year old technology incubator whose business strategy involves spinning off successful new companies, such as EmiSense, when high-potential technologies become commercially ready.

The National Science Foundation (NSF) and the Glenn Research Center of the National Aeronautics and Space Administration (NASA) have provided additional funding for aspects of Ohio State's microsensor research.

Benefits

The performance of today's advanced power systems is limited by the lack of sensors and controls capable of withstanding high temperature and pressure conditions. Harsh environments are inherent to new systems that aim to achieve high efficiency with low emissions. In addition, these systems are complex, with operational constraints and system integration challenges that push the limits of traditional process controls. As R&D enhances the understanding of these evolving advanced power systems, it is clear that new, robust sensing approaches, including durable materials and highly automated process controls, are needed to optimize their operation and performance. Through cooperative R&D with academia, government, and industry, NETL's Advanced Research Program leads in the effort to develop sensing and control technologies and methods to achieve seamless, integrated, automated, optimized, and intelligent power systems.

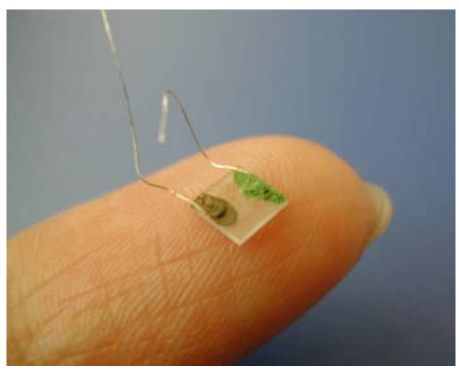

Figure 3. High-temperature total NO_x sensor is highly miniaturized.

Further Reading

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