Overview of NETL Supported Research and Development on Novel Sensors for Monitoring Gaseous Emissions

Robert R. Romanosky, PhD, Technology Manager for Advanced Research
National Energy Technology Laboratory, PO Box 880, Morgantown, WV, 26507-0880
Email: Robert.romanosky@netl.doe.gov; Phone (304)-285-4721; Fax (304) 285-xxxx

Susan M. Maley, Project Manager
National Energy Technology Laboratory, PO Box 880, Morgantown, WV, 26507-0880
Email: susan.maley@netl.doe.gov; Phone (304)-285-4721; Fax (304) 285-4403

As regulations create new challenges for controlling and reducing gaseous emission from coal fired power plants, other challenges are created for the measurement and verification of these control technologies. The National Energy Technology Laboratory (NETL) Advanced Research (AR) Program has a focused effort on instrumentation, sensors and controls for power plants and includes work on high temperature gas sensors and gaseous emission sensors. Research is being conducted on micro sensors and novel techniques to monitor trace level contaminants at various locations throughout a power plant to enable the optimization of environmental control technologies. These sensor technologies may also serve as viable options for regulatory emission monitoring and reporting. As emission limits are lowered, existing continuous emission monitoring systems are challenged to accurately detect at these lower levels. In addition, these technologies may not work appropriately at points upstream in the process where measurements are needed for optimization of the environmental control processes. This overview is a summary of the NETL supported research to develop high temperature gas sensors for use in optimization of boilers and environmental control technologies as well as those technologies which may be viable for continuous emissions monitoring.

NETL's AR program supports the development of novel sensor and control technology for advanced power systems. Current efforts are focused on the development of sensors for high temperature (>500 ^oC) fossil energy environments. Fundamental research within this area of interest has centered around sensor materials, design, and packaging that can function in high temperature environments. Important developments have been made in both micro gas sensors as well as laser and optically based measurements that will enable these technologies to be transitioned from the laboratory for full scale evaluation and potential commercialization.

For micro sensors, key developments have been in the identification of materials that enable selective gas detection at high temperatures (200-600 ^oC) and designs that enable continuous operation but easy replacement of sensor elements. Low replacement costs for these sensors are also important if sensor lifetime is limited.

Many micro sensors are based on simple designs of layering materials on top of conductive substrate materials. Suitable substrate materials include yttria stabilized zirconia, semiconductor silicon carbide, alimunia, silicon nitride, and silicon carbide nitride. The primary challenge for micro sensors is to select materials that interact with gases of interest such as NO, NO_2, SO_2, H_2S, CO, CO_2, H_2S, CH_4, HCl, etc. and provide a reasonable, timely, and selective response that can be used to quantitatively identify gases. In many cases, a sensor array is used in combination with algorithms to elicit individual gas identification and quantification. In addition to sensor arrays, individual sensor elements may use combinations of materials to enhance selectivity. Metal oxide based sensor arrays may use mixed metal oxides, bimetal oxides, catalysts, filtration, and material layers to improve selectivity of the sensor element to a single gas. The ability to tailor these sensors for a range of gases and concentrations is great and offers viable opportunities to detect gases (e.g. NOx) at all concentration ranges including low ppm levels. Despite recent developments, improvements, and perceived advantages, few micro sensors have been commercialized for fossil energy applications. DOE is supporting testing of these sensors at various stages including full scale to assist in technology transfer. At present, the performance of these sensors has not been assessed for regulatory emissions monitoring and it is unclear if the sensors can be designed and managed in an appropriate way that is acceptable under EPA regulations.

Alternative approaches that lend themselves more readily to regulatory emission monitoring are laser based measurements in which select wavelengths of light are used excite molecules. The detection of the gases can be done using several methods with absorption being the simplest. Existing emission monitoring equipment use light based methods to detect gases, however limitations exist for certain instrumentation including generation of specific wavelengths of light, laser power, interferences, and overall cost of individual systems. NETL has funded projects to address some these limitations and have realized advancements in techniques to generate specific wavelengths of light, significant size reductions in light sources, and integration of systems to enable detection of multiple gases. Embedded in these efforts are approaches to minimize interferents. Remaining challenges with these systems include viable and practical methods to maintain line of sight and window/site glass cleanliness as well as engineering of robust equipment for long term industrial use. Supported work this area has focused on the detection of NO, NO_2, NH3, CO, CO_2, SO_2, Hg and particulate. New classes of diode lasers for the detection of NO, CO, NH3, and mercury have been developed and select systems have undergone successful testing on pilot scale combustion facilities as well as turbine test stands. Other approaches include the use of quantum cascade lasers to create specific wavelengths of light for the detection of CO2, CO, NO, and NO_2. Combining these laser based techniques with cavity ringdown spectroscopy for mercury and SO2 detection, an integrated system for exhaust gas monitoring is under development. Work is also underway to develop fiber pumped laser light deliver systems which could greatly reduce size of the overall light source, maintain sufficient power, and create new opportunities for sensing in harsh environments.

NETL will continue to support novel developments in the gas measurement area including technology transfer of those technologies which show viability for full scale application.