TARGETING CARBON CAPTURE IN FUTURE POWER GENERATION SYSTEMS

The U.S. Department of Energy’s vision for future clean coal power generation systems assumes the availability of cost effective techniques to separate carbon dioxide (CO₂) from mixtures of gases. Once captured or separated, the CO₂ might be used to achieve enhanced recovery of oil from underground oil reservoirs or it might be sequestered in an underground geologic formation or at the bottom of the ocean.

Carbon dioxide capture processes are needed for a range of power generation systems. For example, a cost effective CO₂ separation method would make it possible to produce relatively pure and low cost hydrogen for use in fuel cells and other applications, it would make it possible to gasify coal for use in a combined cycle power plant while capturing the CO₂ produced in the gasifier, and it would make it possible to burn coal in a boiler and capture the CO₂ from the flue gas.

Process and materials research being carried out by Drs. Hugo S. Caram and Shivaji Sircar of the Chemical Engineering Department of Lehigh University on a novel CO₂ separation technology shows promise for meeting these various needs. One of their processes is referred to as the “Thermal Swing Sorption Enhanced Reaction (TSSER)” concept.

Sircar explains, “One of the important applications of the TSSER concept involves a power generation system which contains...”

NEW ALLOY VERIFIED FOR SAFER DISPOSAL OF SPENT NUCLEAR FUEL

A new alloy developed and patented by researchers at Lehigh University and two U.S. Department of Energy National Laboratories could help the U.S. dispose of highly enriched spent nuclear fuel.

Dr. John DuPont, the principal Lehigh investigator on the project, said that a nickel-based alloy containing gadolinium (Gd) showed far greater ability than other alloys to maintain criticality controls by absorbing thermal neutrons over thousands of years. The researchers found that the nickel-gadolinium alloy passed an important test—it can be fabricated in small-scale quantities using conventional ingot metallurgy and has been welded by fusion welding techniques.

The research group included Drs. DuPont, David Williams, and Zhen Liu from Lehigh University; Drs. Charles Robino and Joseph Michael from Sandia National Laboratories; and Mr. Ronald Mizia from the Idaho National Laboratory. The project is supported by the National Spent Nuclear Fuel Program under the technical direction of Mr. William Hurt at the Idaho National Laboratory. The National Program had identified Gd as the preferred neutron absorber, and it was up to the research group to determine what structural alloy would best accommodate alloying with Gd.

Gadolinium, a silvery-white metal, is found in several different minerals. The research conducted by the group demonstrated that Gd could be added to specific nickel alloys that would retain their malleability and ductility as well as their ability to be heat-treated, shaped and fabricated into desired shapes.

Mr. Hurt explains, “Safe disposition of Department of Energy (DOE) highly...”
an oxygen and steam fired coal gasifier. This type of gasifier converts coal into a mixture of carbon monoxide (CO), carbon dioxide (CO₂), water vapor (H₂O), and hydrogen (H₂) gases. The gas mixture from the gasifier would be fed into a TSSER system where the CO and H₂O would be catalytically converted to H₂ and CO₂ by a process referred to as the water gas shift reaction. The CO₂ would simultaneously be adsorbed from the reaction zone by a special chemisorbent material, resulting in a relatively pure product stream of CO₂-free H₂ gas. Removal of CO₂ from the reaction zone will drive the equilibrium controlled reaction to completion. This will result in extremely high conversion of CO and H₂O to H₂ in the sorber-reactor. The catalyst and the chemisorbent will be contained as an admixture in the same reactor vessel and the reaction temperature will be in the range of 300 – 400°C. Once the sorbent material has become saturated with CO₂, the chemisorbed CO₂ will be desorbed by counter-currently purging the reactor with superheated steam at ~500 – 550°C and at feed gas pressure. The effluent steam will then be condensed, resulting in a flow of mostly CO₂ at feed gas pressure, suitable for sequestration (after necessary compression). At the conclusion of the purge process, the gasifier effluent would be reintroduced into the reactor, and the cyclic process would be resumed. To permit continuous operation, the TSSER system would need to contain two reactors so that one is in the sorption mode while the other one is undergoing regeneration.

Sircar adds, “There are many competing process concepts for separating CO₂ from mixtures with H₂. These include physical adsorption of CO₂ on a zeolite or an activated carbon and physico-chemical adsorption of CO₂ by a liquid solvent. A variety of Pressure Swing Adsorption (PSA) and Gas Absorption schemes are commercially used. While these methods can produce high purity H₂, many of these processes do not recover CO₂. PSA processes have also been designed to produce separate streams of high purity H₂ and CO₂, but the CO₂ product is produced at near atmospheric pressure. Physical adsorbents also require the H₂O to be removed from the feed gas prior to CO₂ adsorption, which is a disadvantage.

The process we’ve developed simultaneously converts CO and H₂O to CO₂ and H₂ and also separates the H₂ and CO₂ with high recovery of both products in a single unit operation. A novel chemisorbent, which selectively and reversibly adsorbs CO₂ at an elevated temperature of 300 – 400°C in presence of excess steam, is used for this purpose. We use the temperature swing mode instead of a pressure swing for sorbent regeneration. This can be highly beneficial because it avoids or substantially lowers the need to recompress the CO₂ stream, which results in energy and cost savings.

We are also developing several variations of the basic TSSER concept for other applications such as steam reforming of natural gas (CH₄) to directly produce fuel-cell grade H₂ and a CO₂ by-product. The reforming reaction, in this case, can be carried out at a substantially reduced temperature of ~400°C instead of the conventional ~850°C without sacrificing conversion of CH₄ to H₂ and this saves energy.

Another application of the novel chemisorbent will be to capture and recover low concentration CO₂ from a hot and wet flue gas without pre-cooling and pre-drying the gas.”

Caram continues, “With financial support from the Pennsylvania Infrastructure Technology Alliance (PITA) and a donation from the Air Products and Chemicals, Inc., we have constructed a single-column laboratory scale TSSER system to study the production of H₂ and CO₂ by steam reforming of natural gas. We are currently in the process of testing CO₂ chemisorbents, by measuring the CO₂ adsorption and desorption characteristics under various conditions by determining the sorption column dynamics for various steps of the TSSER concept and by determining the thermal stability of the chemisorbent. We are also simulating various steps of the cyclic process. Our project team includes Michael Beaver, a graduate student from Chemical Engineering, Jennifer Purcell and Jonathan McMullen, undergraduate students from Chemical Engineering, and Dr. Alex Verdooren, a Postdoctoral Researcher.

We’ve also received funding from DOE for a project scheduled to start up in January 2006, to investigate the application of this technology to generate H₂ and CO₂ streams from syngas produced by a coal-fired gasifier. That project will focus on the design and operation of a research scale system to characterize the performance of a TSSER system for the gasifier application. It will also develop a mathematical process design model needed for scale up and optimization studies.”
Gadolinite-enriched spent nuclear fuel requires the availability of thermal neutron absorbing properties to be maintained for extended periods of time. Ideally, the Gd would be deployed in a structural material fabricated for use as the internal canister baskets. These baskets separate spent fuel assemblies providing structural support during storage, transportation and disposal. In the disposal setting, the Gd is an essential factor in maintaining nuclear criticality safety. Given the large quantity of material required for this application, the material must be producible using conventional large-scale production methods such as ingot casting and hot working. Because the material will be formed and welded into internal structures that will cradle the fuel to maintain a specified geometry, the material must also exhibit good weldability.”

Mr. Mizia further explains, “Previous research on selection of candidate alloys, which could meet these requirements, focused on stainless steels containing boron. While alloys with boron are available as American Society of Mechanical Engineers (ASME) code-approved materials, Gd has received considerable attention in recent years. Gd has a much higher thermal neutron absorption cross section than boron, and thus, Gd additions could potentially provide a better means for safely storing highly enriched fuels in a disposal setting. The higher thermal neutron absorption capacity may also allow thinner sections of this material to be used, which would help ensure the total weight of the canister stays within prescribed limits. In addition, there are also long-term corrosion issues with nuclear fuel and Gd, containing constituents in the alloy that should not dissolve as quickly as chromium borides in the presence of water. Therefore, there is interest in the use of Gd-containing alloys for storage, transportation and disposal of DOE spent nuclear fuel. However, prior to our study, there had been very little research on production and welding of Gd-containing alloys.”

The research group conducted laboratory tests to determine the optimal chemical composition of the nickel-based alloy. The tests involved mixing the constituent elements of the alloy, heating and melting the mixture, and allowing it to cool and solidify. The alloy was then heated and rolled into half-inch-thick sheets and subjected to strength and ductility tests.

“We designed and developed various alloys to determine the quantity of gadolinium that could be added while still maintaining the desired properties,” says DuPont. “We needed to be able to heat-treat the final material, weld it and fabricate it.”

“Although we have demonstrated the ability of the alloy to achieve these goals,” Robino adds, “there is still a lot of development work to do to make the alloy feasible on a commercial scale.

A specification has been issued for the alloy by the ASTM (American Society of Testing Materials), which sets technical standards for materials, products, systems and services. The alloy is being reviewed by the ASME, which also sets design standards for the use of new products. Neutron-absorption tests on the alloy were performed at Los Alamos National Laboratory in New Mexico.

Prior to its work with the gadolinium-nickel alloy, the researchers spent a year investigating gadolinium-enriched stainless-steel alloys for spent nuclear fuel storage applications before coming up against major obstacles to the production of those alloys using conventional hot working techniques.

The group’s research results, described in an article in the December 2004 issue of the American Welding Society’s Welding Journal, cap a 4-year study funded by the U.S. Department of Energy’s National Spent Nuclear Fuel Program. The article, titled “Physical and Welding Metallurgy of Gadolinium-enriched Austenitic Alloys for Spent Nuclear Fuel Applications - Part II,”” won the welding society’s Warren F. Savage Award for advancing the understanding of welding metallurgy.

Schematic illustration of standardized canister assembly for transportation and long term storage of spent nuclear fuel owned by Department of Energy.
OPPORTUNITIES FOR SPONSORSHIP OF MERCURY RESEARCH PROJECTS

MODIFICATION OF BOILER OPERATIONS FOR MERCURY EMISSIONS CONTROL

On March 15, 2005, EPA issued the Clean Air Mercury Rules, which mandate nationwide mercury reductions. As a consequence of these new regulations, research and development of cost-effective techniques for control of Hg emissions from coal-fired boilers has become an urgent issue for the U.S. power generation industry. Research has shown that boiler operating settings which affect flue gas conditions and fly ash characteristics have an impact on mercury oxidation and its “naturally occurring” adsorption in the boiler. The Energy Research Center is seeking utility sponsors for a project to determine the feasibility of using modified boiler control settings for mercury emissions reductions for power plants firing Western coals and coal blends.

Testing performed by the Energy Research Center at three units firing bituminous coals demonstrated that boiler operating condition modifications can reduce stack emissions of mercury. Emissions reductions as high as 80 percent were achieved in those tests. It is expected that this technique, used in combination with other technologies such as injection of activated carbon, would reduce the overall cost of Hg emissions compliance.

The proposed project will focus on a unit which fires Western coals and coal blends. Through field tests, the project will demonstrate and quantify the range of mercury reduction by optimization of boiler operations. It will also determine the tradeoffs between Hg capture, NOx emissions, unit heat rate, and other parameters of interest.

The Energy Research Center expects to fund this project by forming a consortium of sponsors. The total budget for this project is estimated to be $242,500, with $35,000 requested from each utility sponsor. For more information, please contact John Sale at jws3@lehigh.edu or (610) 758-4545.

EVALUATION AND COMPARISON OF U.S. AND EUROPEAN UNION REFERENCE METHODS FOR MEASUREMENT OF MERCURY, HEAVY METALS, AND PM EMISSIONS FROM POWER PLANTS

Compliance with regulations which limit emissions of mercury will require use of a continuous emissions monitoring system (CEMS) for mercury and a reference method for calibrating the CEMS. As of today, the only reference approved by EPA for mercury is the Ontario Hydro Method. Ontario Hydro is time-consuming, manpower intensive and expensive. There is a need for a quicker, less manpower-intensive, more automated and less expensive reference method for Hg measurement.

The Energy Research Center is seeking sponsors for a project in which reference methods for Hg, heavy metals and PM, developed in the U.S. and European Union will be compared. The objective of the project is to evaluate alternate measurement techniques with the goal of convincing EPA to consider other reference methods, especially for mercury. Field testing will be performed by a joint U.S. and EU team. The results will be compared and analyzed to explain any potential differences. The ease of use, degree of automation, susceptibility to errors and required effort will also be compared. The EU reference methods will include a method for Hg measurement developed by the Italians, methods for PM2.5 and PM10 measurement developed by the Germans, and flux-derived methods for heavy metals, developed by the French. The Italians have developed an automated measurement system for performing mercury measurements that requires very little training, no human presence during sampling which is only one hour long compared to the two hours that are required for OHM.

The project budget of $78,000 will cover sample analysis and the expenses of the U.S. test team. EU team expenses will be paid by the Italian government. The ERC is planning to assemble a consortium of electric utilities to share the cost of the project. With four sponsors, the cost per sponsor will be less than $19,500.

Please let us know if you are interested in participating in this project. For more information, please contact John W. Sale at jws3@lehigh.edu or (610) 758-4545.