ABSTRACT

Coal Gasification in tandem with electric power generation provides a potentially large market for Illinois coal. At maximum efficiency, these so-called Integrated Gasification Combined Cycle Systems (IGCC) remove sulfur and other noxious species from the coal gasification product gas while it is hot. Until recently, plans were made to clean the gas at a temperature of approximately 1200°F, and regenerable sorbents were being developed for that temperature. Now systems architects are asking that sorbents be developed for an operating temperature of 1000°F or less. It has been found to be difficult to stretch the capabilities of previously developed sorbents down to the temperatures of current interest, so a new approach is being taken. The sorbent being developed is zinc-based, as in much of the prior work. In the project just completed, innovations were made in the overall composition and method of preparation, which are proprietary. Through a screening study, a formulation with an excellent combination of mechanical properties and sulfur sorption characteristics was identified. The sulfur sorption rate and sulfur capacity were very high at 1000°F. The same properties were reasonably good at 800°F after activating the material at a higher temperature. A method was developed to activate the sorbent without using H₂S as a source of sulfur. The sorbent just described was prepared from reagent-grade raw materials. When commercially available raw materials were used, a sintering aid was found to make it possible to obtain similar properties. One technical problem remains. A method must be developed to carry out the regeneration reaction at 1000°F. Ideas were formulated to solve the problem.

Pages 2-23 contain proprietary information.
EXECUTIVE SUMMARY

Integrated Gasification Combined Cycle Systems (IGCC) are in the early stages of commercialization in the United States and abroad. These systems are ideal for expanding the use of Illinois coal because of the incorporation of desulfurization methods. There are now two IGCC plants operating in the United States. A third plant has been built and is completing check-out testing. For IGCC plants to operate at full potential, the product gas from the coal gasifier must incorporate hot gas clean-up, which removes both sulfur-bearing gases and particulate matter. The development of regenerable sulfur sorbents is a critical part of the effort to improve system efficiency through hot gas clean-up.

E&A Associates, collaborating organizations, and competitors have been working for many years to develop sulfur sorbents with acceptable properties, but there is still doubt concerning satisfactory performance over hundreds or even thousands of sulfidation-regeneration cycles. Filling this need was made more difficult recently because most of the development work was undertaken with the understanding that the service temperature would be in the neighborhood of 1200°F. Now sorbent developers are being asked to focus on operating temperatures of 1000°F and below. One reason is the temperature limitations of valves and particle filters used in the same systems. Another is that most of the gain in system efficiency occurs when the clean-up temperature is raised from ambient to roughly 600°F, and there may be diminishing returns when the temperature is raised further. There is still debate among analysts on the latter argument.

This lowering of the operating temperature has stimulated a considerable amount of new work. Some developers modified their sorbents on a crash basis to try to solve the problem. This approach is very risky because improving low temperature reactivity probably causes a penalty to be paid in mechanical properties and service life. A better approach and the one taken here is to develop a new sorbent specifically for the lower temperature range of current interest. One need not abandon the use of zinc oxide as the desulfurizing agent because it is currently being used commercially as a once-through sorbent for desulfurizing natural gas at temperatures below 600°F. The main problem then is to find a new way to incorporate zinc oxide in a matrix that offers regenerability and durability over hundreds of sulfidation-regeneration cycles. The addition of titanium dioxide to form zinc titanate is not an attractive option because it has been used in the past to reduce the vapor pressure of zinc, thereby improving high temperature performance. At lower temperatures, vaporization loss is not a problem, and the compounding of the zinc oxide reduces chemical reactivity.

An idea was conceived to incorporate zinc oxide in a matrix that, in theory, should result in good low temperature reactivity, together with good mechanical properties and durability. Because the idea is believed to be unique, the chemical compositions, preparation procedures, and properties are considered proprietary. The bench-scale work done this year was a collaborative effort between E&A Associates and the Illinois State Geological Survey. The investigation started with a screening study to characterize the properties of dozens of sorbent formulations. Property measurements made included pellet
density, from which %porosity is calculated, crush strength, and single-cycle chemical reactivity. The latter was measured in a thermogravimetric analysis (TGA) apparatus. These results were supplemented in a few cases with BET surface area measurements, powder particle size measurements, and scanning electron microscopy. The parameters that were varied in sorbent preparation were raw materials, chemical composition, and sintering or calcining temperature.

Success was achieved in obtaining a good combination of properties in one of the sorbents at a sulfiding temperature of 1000°F. To obtain good reaction kinetics at 800°F, it was necessary to activate the material at a higher temperature first, then sulfide at the lower temperature. This behavior is not surprising because it was observed before by the Principal Investigator with both dispersed nickel and zinc titanate sorbents. The sorbent just described was made from reagent-grade raw materials. Initial attempts to obtain comparable properties with commercial grades of raw materials were unsuccessful. With the help of consultations with industry personnel, a sintering aid was found to solve the problem. While sorbent properties are presently not quite as good as with the use of reagent-grade raw materials, further improvement does not appear to be difficult. Single-cycle fluidized bed tests were carried out on both types of sorbents. The H₂S breakthrough times and bed efficiencies were quite good.

Potential users of the sorbent would like to have sorbent manufacturers take responsibility for activation treatments so that they do not have to be carried out on-line at a commercial IGCC plant. Therefore, a feasibility study was done to try to achieve activation without using H₂S as a sulfur source. A liquid chemical was found that accomplished this purpose. In the TGA, the chemical was used to presulfide twice at 1150°F for achieving good reactivity in H₂S at 800°F.

While the mechanical properties and sulfur sorption characteristics of the new sorbent appear to exceed requirements for the Sierra Pacific IGCC plant, so far it has not been possible to regenerate the sorbent at the required temperature of 1000°F. Modifying the sorbent composition is not believed to be a good approach. Instead, it is recommended that a separate ignitor material be used with the sorbent. Another investigator has claimed success with such an ignitor.

The remainder of this report contains proprietary information and is not available for distribution except to the sponsor(s) of this project.