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Quarterly Progress Report:
High Temperature Electrochemical Separation
Of H₂S from Coal Gasification
Process Streams

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by

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Objective

A method of polishing coal synthesis by an electrochemical operation is being perfected. The operation which takes advantage of an electrochemical potential gradient rather than conventional techniques, removes H_2S from the coal gas stream leaving only H_2 to enrich the exiting polished gases. Sulfur is the by-product which is swept away by an inert sweep gas and condensed downstream. The technology is attractive due to aesthetics as well as economics when compared to other alternatives.

Current experiments are based on improving selective removal from low initial H_2S concentrations (10 ppm) and developing a consistent method of sealing the cell housings. The best option uses the Zircar manufactured membranes, or a lab replication of the Zircar manufactured membranes. Both result in similar removals, over 80% with applied current.

Another membrane, an electrolyte filled rigid tile, was examined this quarter. Elimination of prepressing and addition of the electrolyte into the cell housing relieves calculation errors, dealing with electrolyte content, needed to fill the voids of the membrane and to react with the alumina for seal formation.

Introduction

A schematic of the technology being used is presented in Figure 1. The process gas, cleansed of particulates, is passed by the cathode. Here the best Lewis acid (electron acceptor), will be reduced. In this case H_2S is favored, resulting in the following:

The sulfide ions are transported, by current through the membrane. Once the sulfide ion reaches the anode side, oxidization to elemental sulfur occurs.

The sulfur vapor is then carried away by an inert gas, preferable N_2 due to low cost. The vaporous sulfur is condensed downstream.

Experimental Results

Experimental results presented are based on five experiments with initial H_2S concentrations of ~100 ppm. In order to represent probable industrial conditions, variables such as flow rates, selectivity of the membranes, and cell housing seals, were of primary concern in these experiments. Over 90% Removal of H_2S with applied current has been recorded with similar conditions.

Cell housing materials used for runs 6 - 9 were made of machineable ceramic (MACOR), while stainless steel housings were used in run 10. Cathode and anode electrodes consisted of Ni which oxidized in-situ to form NiO. All runs were unsuccessful in removing H_2S due predominantly to H_2 cross-over, caused by cracking

of the membranes. A summary of these experiments is presented in following paragraphs.

Run #6

This experimental run used a rigidized, electrolyte filled membrane, which becomes molten around 550° C. Flow tubes into the cell housings were changed from conventional high temperature, high density ceramic to Silicon Nitride tubing. The purpose being to find a more convenient material to repair if a flow tube was broken. This created leakage problems due to lack of bonding between the tubes and bonding material (adhesive cement). Reversion back to the original ceramic tubing should cure the problem. Aluminum foil gaskets, coupled with an electrolyte-water solution, were used on both housings for a sealant. Initial seals never developed creating deficiencies in fuel gas residence time and interaction at the electrode-electrolyte interface.

The membrane was advantageous in the initial stages because of its pre-electrolyzed make-up, eliminating conventional steps of pre-pressing and infiltration of the electrolyte. However, the tile performed inadequately in the experimental environment. Once molten, the stability of the tile seemed to weaken. The tile transformed into a limp paste, lacking the qualities necessary for electrolyte support or protection from gas cross-over. The cell was shut-down after 166 hours, mainly because of H₂ cross-over due to cracks in the tile.

Run #7

Use of another rigid electrolyte tile failed to provide adequate selectivity from H₂ cross-over. Thermal stress caused by thermocouple damage, lead to severe cracks in the membrane. The thermal stress developed once the thermocouple malfunctioned, causing the temperature in the oven to reach 900° C. When repairing the thermocouple, the temperature plummeted to 400° C. At 400° C the electrolyte solidifies, causing cracks due to expansion. Shut-down occurred 15 hours after start-up.

Run #8

Another run using an electrolyte filled tile failed. Aluminum paint, cooked onto the cell housings, was to provide gas seals. The seals never developed and cross-over progressively worsened with time. Once again the stability of the tile was evidenced due to continual cross-over. The run was shut-down after 24 hours.

Run #9

A laboratory replication of the Zirconia membrane was utilized in this experiment. A combination of two thin weaved Zirconia mats were hardened using the rigidizer supplied by Zircar. The mats were combined and air dried on a strip of Teflon to prevent surface bonding. An iron mesh atop weighing paper covered the mats to prevent warping. After drying, the membrane was baked in a high temperature oven to burn off the weighing paper, then autoclaved to insure uniformity. The porosity was estimated at 80% which indicates not enough rigidizer absorbed in the initial step of

rigidization. In the past, similar experiments were successful with membrane porosities around 65%. Similar porosities must be met in the future before the run is started. 80% porous membranes do not provide enough stability to protect against gas cross-over. Therefore, cross-over resulted in cell shut-down after 24 hrs.

Run #10

A Zircar manufactured membrane provided the electrolyte support in this experiment. Seals developed by reaction of cooked aluminum paint with lithium in the molten electrolyte. The initial problem was not effected by lack of seals or cross-over, but by carbon formation caused by insufficient H_2O concentration in the water-gas shift reactor. The build-up of carbon formed a barrier to entering gases, leaving the cell inactive. Cell repair, while keeping the electrolyte molten, initially saved the experiment. Once seals redeveloped with no evident cross-over, H_2S (140 ppm) was sent to the cell. Sulfide equilibrium never occurred due to a consistent lack of electrolyte. Continuous addition of electrolyte should have caused flooding of the electrodes but reaction with the aluminum paint exceeded the small estimates of required electrolyte. Future experiments must contend with reactions dealing with seal formation. Also the water-gas shift reaction must be strictly adhered to, due to the consequences of carbon build-up. Shut-down occurred after 140 hours.

Summary

Experimentation with a rigidized, electrolyte filled tile, left much to be desired. The instability of the tiles at molten conditions ($> 550^{\circ} \text{C}$), provided the necessary mechanism for H_2 to penetrate the membrane. Once H_2 cross-over occurs the entire objective of electrochemical separation becomes nullified. The Zircar membranes used last quarter provided excellent protection against H_2 , prompting a reversion back to them. If porosities are strictly adhered to and the water-gas shift is properly handled, the membranes should provide an adequate mechanism for selective H_2S removal.

Work for Next Quarter

Work for next quarter will deal with improving seals on the MACOR housings. Also the rigidized mats produced in our lab will be emphasized due to the economic advantage over the manufactured membranes or electrolyte filled tiles. If a porosity of approximately 66% is achieved, removal seems almost assured, with proper seals.

References

1. Weaver, D., Electrochemical Removal of Hydrogen Sulfide From Multi-Component Gas Streams, PhD Thesis, Georgia Institute of Technology, 1988.
2. Alexander, S., Electrochemical Removal of H₂S from Fuel Gas Streams, PhD Thesis, Georgia Institute of Technology, 1992.

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