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 the poisonous 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 later condensed. 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). High flow rate data is also being investigated along with developing a consistent method of sealing the cell housings. The latest option for consistent removal and seals is the Zircar manufactured membranes, which have shown promise prompting further testing.

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

Five experimental runs using simulated coal gas were attempted this quarter. Runs 1-5 varied in the membranes used as well as the technique to seal the housings. Runs 4 & 5 were successful in removing H_2S with applied current. Run 1 was successful in maintaining seals but not in removal. Runs 2 & 3 were not successful. A summary of these experiments follows.

Figure 1. Schematic of H_2S Removal Cell.

Successful Runs

Run #4

This experimental run used a combination of two thin Zirconia weave mats. These mats were hardened using the zirconia rigidizer supplied by Zircar. The mats were then combined and air dried on a strip of Teflon to prevent surface bonding. The mats were covered with weight paper and an iron mesh atop to prevent warping of the membrane. After drying, the membrane was baked in a high temperature oven to burn off the weight paper. The membrane was then autoclaved to insure uniformity. The porosity of the membrane was estimated at 68%. Both cathode and anode electrodes were lithiated Ni, which was converted in-situ to a mixture of NiO and Ni on the cathode side. The anode was converted completely to NiO due to the oxidizing nature of the anode. Li/K eutectic carbonate electrolyte was prepressed and inserted between the cathode housing and the rigidized Zirconia membrane. The housings were made of MACOR, which is a machineable ceramic. The inlet synthesis gases were allowed to go to their equilibrium concentrations (6.0% CO₂, 25.9% CO, 6.4% H₂O, 61.6% H₂, and 14 ppm H₂S) via a stainless steel water-gas shift reactor, before entering the cathode housing. The electrolyte was allowed to go its equilibrium sulfide concentration (0.1 mole%). Aluminum foil gaskets, coupled with an electrolyte-water solution, were used on both housings for a sealant.

The temperature and flow rate were maintained at 650°C and 215 cc/min respectively. Inlet concentration was held between 6 and 20 ppm H₂S. As much as 94%

removal with applied current was seen in this experiment as shown in figure 2. The results of both run 4 & 5 are tabulated in table 1. The experiment was shut down due to hydrogen cross-over. Run #4 lasted 163 hours.

Figure 2

Run #5

This experiment used the Zircar manufactured membranes. The advantages of this membrane are uniform porosity and no warping. Wicking electrolyte into the cell, via the Zircar membrane, rather than using an electrolyte well atop the cathode housing aids in stabilizing the membrane. The Li/K electrolyte was prepressed and placed

between the cathode housing and the manufactured membrane, in the amount corresponding to a 66% membrane porosity. Aluminum foil gaskets, were used on both housings to aid the sealing process. Lithiated Ni electrodes were used allowing them to convert to NiO in-situ. The inlet gas where allowed to reach equilibrium (5.8% CO₂, 25.6% CO, 6.7% H₂O, 65.3% H₂) after the water-gas shift reaction. The equilibrium sulfide concentration in the electrolyte (0.11 mole%) was reached in-situ.

Temperature in this experiment was maintained at 650°C, flow rate was varied from 170 to 814 cc/min. The results are shown in table 1 along with these from run #4. Removal at all flow rates exceeded 90% with applied current as shown in figure 3. The cell was shut down due to an increasing membrane thickness (δ). This was caused by excess addition of electrolyte, resulting in increased resistance to diffusional transport of sulfide:

$$i_d = n F \rho (x_{\text{cath}} - x_{\text{an}}) / \delta$$

$$IR = n F \ln (i / i_d)$$

Table I. Experimental Results for Runs #4 & #5

Temp. (°C)	Flow-Rate (cc/min)	Residence Time (sec.)	Inlet H ₂ S (ppm)	Exit H ₂ S (@ I _{app})	I _{app} (mA)	E _{ca} (Volts)
650	170	0.197	25	1	1	-0.190
	225	0.146	8.5	1	2	-0.013
	375	0.089	22	1	2	-0.003
	580	0.058	20	1	5	-0.047
	814	0.041	22	1	5	-0.199

Figure 3

as δ increases, diffusional current decreases; therefore, the resistance to ionic transport increases, reducing sulfide migration across the cell. The cell was shut down after 208 hrs.

Unsuccessful Performance

Run #1

This experiment utilized stainless steel housings, the purpose of which is longevity. The housings were initially painted with aluminum paint (29 wt% Al), once the paint dried, the housings were placed in an oven and baked at 500°C for 3 hrs. This converted the Al to alumina which can aid in sealing by reacting with the Li in the Li/K eutectic carbonate electrolyte to form LiAlO_2 . A manufactured Zircar membrane was

used along with a pressed disk of the aforementioned electrolyte. The electrodes were lithiated Ni and allowed to convert to NiO in-situ. The success of this experiment came from the development of strong seals that withheld back pressures as high as 30 mm H₂O. No effective removal data was taken during this run , but the experiment lasted for 453 hours, which is the longest to date.

Run #2 - #3

These experiments are combined due to the usage of the same type Zircar manufactured membrane for both. Lithiated Ni were used as electrodes and aluminum paint was applied to the MACOR housings for sealant. The electrolyte, sized to fill the 66% voids in the membrane, was prepressed and placed between the cathode and Zircar membrane.

Run #2 lasted only 48 hrs due to carbon build up between the cathode electrode and the membrane. This was caused by the Bourdouart reaction, avoidable by increasing hydration of the fuel gas:

Run #3 lasted only 24 hrs due to cracks in the membrane, causing diffusion of hydrogen, and lack of seals. There was no outflow of gas on either side of the cell.

Summary

The manufactured Zircar membranes have shown promise obtaining removals of over 90% with applied current. The rigidized mat produced in our laboratory produced excellent removal. The most exciting aspect of the quarter was the removal at high flow rates. Although seals were a problem, run #1 showed promise in that aspect.

Work for Next Quarter

Work for next quarter will deal with improving seals by using the method suggested in run #1. Also the rigidized mats produced in our lab will be further investigated due to the economic advantage over the manufactured membranes. Once the cell is running removal seems almost assured.

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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