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Electrochemical Polishing of Hydrogen Sulfide from Coal Synthesis Gas

Authors:

E. Faith Gleason
Dr. Jack Winnick, P.E.

Contractor:

Georgia Tech Research
Corporation
School of Chemical Engineering
778 Atlantic Drive
Atlanta, GA 30332-0100

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7B.5 Electrochemical Polishing of Hydrogen Sulfide From Coal Synthesis Gas

CONTRACTOR INFORMATION

Contractor No.: DE-FG22-94-PC94207

Contractor: Georgia Tech Research Corporation
School of Chemical Engineering
778 Atlantic Drive
Atlanta, GA 30332-0100
(404) 894-2834 (phone)
(404) 894-2866 (fax)

Contractor Project Manager: E. Faith Gleason

Principle Investigator: Dr. Jack Winnick, P.E.

METC Project Manager: Dr. Kamal Das

Period of Performance: September 1, 1994 to May 31, 1995

OBJECTIVES

An advanced process has been developed for the separation of H_2S from coal gasification product streams through an electrochemical membrane. This technology is developed for use in coal gasification facilities providing fuel for co-generation coal fired electrical power facilities and Molten Carbonate Fuel Cell electrical power facilities.

H_2S is removed from the syn-gas by reduction to the sulfide ion and H_2 at the cathode. The sulfide ion migrates to the anode through a molten salt electrolyte suspended in an inert ceramic matrix. Once at the anode it is oxidized to elemental sulfur and swept away for condensation in an inert gas stream. The syn-gas is enriched with the H_2. Order-of-magnitude reductions in H_2S have been repeatably recorded (100 ppm to 10 ppm H_2S) on a single pass through the cell.

This process allows removal of H_2S without cooling the gas stream and with negligible pressure loss through the separator. Since there are no absorbents used, there is no absorption/regeneration step as with conventional technology. Elemental sulfur is produced as a by-product directly, so there is no need for a Claus process for sulfur recovery. This makes the process economically attractive since it is much less equipment intensive than conventional technology.

BACKGROUND INFORMATION

Use of selective membranes for separating gaseous components from mixtures is a common unit operation. The thermodynamic basis for separation is very simple: a component will only move down a chemical potential gradient, $\Delta\mu$:

$$\Delta \mu_i = \mu_i - \mu_i' = RT \ln(\frac{a_i}{a_i'}) \qquad (1)$$

where the prime ' refers to the extracted phase. Thus, for a separation from a phase with 1% into a pure phase, a minimum pressure ratio of about 100 is needed. In actual practice a higher pressure drop is needed to promote a significant flux. These processes do not produce a high-purity product, nor do they remove one component with perfect selectivity.

The situation is different for a charged species in the presence of an electric potential, $\Delta\Phi$. Here, the electrochemical potential, $\bar{\mu}$, is the driving force:

$$\Delta \bar{\mu} = \bar{\mu}_i - \bar{\mu}_i' = RT \ln(\frac{a_i}{a'_i}) + z_i F \Delta \phi \qquad (2)$$

So, for a species with a charge of +/- 2, a potential difference of 0.06 V can maintain the same concentration difference that requires 100 atm for an uncharged species. The effect is more pronounced as the concentration in the feed drops to levels encountered in contaminant removal, e.g. 10 ppm. Here a pressure driven separation to a pure stream would require more than 10^5 atm while an electrochemical separation requires only 0.15 V [1].

This principle has been applied to high temperature gas mixtures including H_2S in N_2 [2], sour coal gas (H_2S levels greater than 1000 ppm) [3], and natural gas (H_2S levels from 1.3% to 100 ppm) [4]. The primary gaseous pollutant in each of these cases has been H_2S in a fuel gas stream, but removal of SO_2 has also been achieved from flue gas streams [5]. The membrane is exposed to the same pressure on both sides, so there is no theoretical limit to the pressure at which the process can operate. The main thrust of this paper is polishing H_2S from coal synthesis gas (H_2S levels of 100 ppm and less).

PROJECT DESCRIPTION

The major gaseous contaminant in raw coal gas is H_2S. Much of the coal reserves in the United States contain up to 5 wt% sulfur, which is converted to H_2S during gasification. The H_2S concentration (and raw coal gas composition) depends on the type of coal and the gasification conditions, but levels from 0.5 to 1.0 volume percent are typical (see Table I for a listing of some representative compositions [6]). Before this gas can be used for power generation, the H_2S concentration must be reduced to 100 ppm or less (Molten Carbonate Fuel Cell plants require concentrations of no more than 1 ppm H_2S). Conventional processes to remove H_2S rely on low to ambient temperature absorption, followed by sorbent regeneration and Claus treatment for conversion of concentrated H_2S to elemental sulfur [7].

A hot gas electrochemical membrane process for the removal of H_2S is illustrated schematically in Figure 2. The process gas is passed by the cathode. Here, the most easily reduced component, that is, the strongest Lewis acid, will be electronated. In many mixtures of sour gas, this is H_2S:

$$H_2S + 2e^- \rightarrow H_2 + S^{2-} \qquad (3)$$

A membrane which contains sulfide ions in a molten state acts to transport sulfide across to the anode where, in the simplest case, hydrogen can be supplied to form H_2S. If the membrane is capable of preventing the diffusion of hydrogen from the cathode side, an inert sweep gas such as N_2 can be used at the anode to carry away oxidized sulfide ions as vaporous sulfur.

The situation can become complicated when coal gas mixtures are processed. Carbon dioxide and water compete in the reduction reaction by:

$$CO_2 + H_2O + 2e^- \rightarrow CO_3^{2-} + H_2 \qquad (4)$$

The ionic flux through the membrane depends upon the relative mobilities of carbonate and sulfide as well as their concentrations.

From the equilibrium constant for reaction (5) below, it is possible to know the electrolyte composition which would be in equilibrium with a given process gas at a given process temperature. Theoretical membrane electrolyte compositions are calculated by thermodynamic analysis of equilibrium reaction (5). Since membranes similar to those used in the Molten Carbonate Fuel Cell were used in these studies, the cations present were K and Li in a ratio corresponding to the low melting carbonate eutectic ($Li_{0.62}K_{0.38}$):

$$(Li_{0.62}K_{0.38})_2CO_3 + H_2S \rightleftharpoons (Li_{0.62}K_{0.38})_2S + CO_2 + H_2O \qquad (5)$$

This analysis was performed by finding the Gibbs energy change of reaction (5) at the process temperature and relating this to the equilibrium constant, K_a,
with K_a defined as:

$$K_a = \frac{(P_{CO_2}P_{H_2O}a_{M_2S})}{(P_{H_2S}a_{M_2CO_3})} \qquad (6)$$

If the activity coefficients, γ, of the molten phase constituents (namely the sulfide and carbonate in the electrolyte) are assumed to be equal, then the activities of the molten phase constituents can be replaced by mole fractions (X_i):

$$K_a = \frac{(P_{CO_2}P_{H_2O}X_{M_2S})}{(P_{H_2S}X_{M_2CO_3})} \qquad (7)$$

with

$$X_{M_2S} + X_{M_2CO_3} = 1 \qquad (8)$$

By this analysis, a process gas with a composition of 14.4% CO_2, 6.2% H_2O, and 100 ppm H_2S with a run temperature of 973 K will correspond to an electrolyte composition of 0.6% sulfide and 99.4% carbonate. Post-run quantitative chemical analysis of membranes used in these experiments has shown good agreement with predicted electrolyte sulfide levels. Figure 1 shows a comparison of calculated equilibrium sulfide levels and the corresponding experimentally determined sulfide compositions.

The direct oxidation of carbonate:

$$CO_3^{2-} \rightarrow CO_2 + \frac{1}{2}O_2 + 2e^- \qquad (9)$$

occurs at a standard potential some 0.70 V more positive than that for sulfide:

$$S^{2-} \rightarrow \frac{1}{2}S_2 + 2e^- \qquad (10)$$

When the half-cell reactions (3) and (10) are summed, the resulting cell reaction and standard potential at 900 K is:

$$H_2S \rightarrow H_2 + \frac{1}{2}S_2 \quad E^o = -0.239\,V \qquad (11)$$

and when the half-cell reactions (4) and (9) are summed, the resulting cell reaction and standard potential are:

$$H_2O \rightarrow H_2 + \frac{1}{2}O_2 \quad E^o = -1.030\,V \qquad (12)$$

This shows an electrochemical potential 'window of operation' between the two cross cell reactions. If the cross-cell potential (cathode to anode) with current applied to the cell is kept below the level required for the sulfide transport reaction (11) yet above the level required for the carbonate transport reaction (12), then sulfide is preferentially transported across the cell and H_2S is preferentially removed from the process gas stream.

Theoretical Potentials and Kinetics

The equilibrium potential for combined reactions (3) and (10) is:

$$E = E^o - \frac{RT}{nF}\ln\left(\frac{P_{H_{2\,cathode}}P_{S_2}{}^{\frac{1}{2}}{}_{anode}\,a_{S^{2-}}{}_{cathode}}{P_{H_2S_{cathode}}\,a_{S^{2-}}{}_{anode}}\right) \qquad (13)$$

Additional voltage is required to run the separation cell due to irreversibilities. These losses originate primarily from three sources: ohmic polarization (η_{ohm}), concentration polarization (η_{conc}), and activation polarization (η_{act}) [8].

Ohmic polarization can be described by using Ohm's Law:

$$\eta_{ohm} = IR \tag{14}$$

where I is the current flowing through the cell and R is the total cell resistance which includes electronic, ionic and contact resistances.

Several processes contribute to concentration polarization: slow diffusion in the gas phase through the electrode pores, solution/dissolution of reactants/products into/out of the electrolyte, and diffusion of reactants/products through the electrolyte to/from the electrochemical reaction site. For the purposes of our analysis, concentration polarization was estimated by the following equation:

$$\eta_{conc} = \frac{RT}{nF} \ln\left(1 - \frac{i}{i_L}\right) \tag{15}$$

where i is the current density applied to the cell and i_L is the limiting current density dictated by the rate at which reagent can be transported to the electrode surface. The derivation of this equation is beyond the scope of this paper, but the reader is referred to reference [8] for a complete derivation.

Use of equation (15) requires an estimation of the limiting current, i_L. Since i is linked to the rate of transport of H_2S to the electrode surface it can be described by Fick's first law of diffusion:

$$i = \frac{nFD(C_{H_2S_B} - C_{H_2S_S})}{\delta} \tag{16}$$

where D is the diffusion coefficient of the reacting species, $C_{H2S\ B}$ is the concentration of H_2S in the bulk, $C_{H2S\ S}$ is the concentration of H_2S at the electrode surface, and δ is the thickness of the diffusion layer. The limiting current, i_L is the maximum rate at which H_2S can be supplied to the electrode and occurs when $C_{H2S\ S} = 0$:

$$i_L = \frac{nFDC_{H_2S_B}}{\delta} \tag{17}$$

The thickness of the diffusion layer above the electrode surface, δ, is not well defined in this system. However, the limiting current density can be estimated using the average mass transfer coefficient, k_m, for the geometry involved. Thus, the estimation of the limiting current density becomes:

$$i_L = nFk_m\rho \frac{(y_{inlet} - y_{exit})}{\ln\left(\frac{y_{inlet}}{y_{exit}}\right)} \tag{18}$$

where ρ is the molar density of the gas phase, y_{inlet} is the mole fraction of H_2S entering the removal cell, and y_{exit} is the mole fraction of H_2S exiting the cell. The average mass transfer coefficient, k_m, is given by the Sherwood number defined as:

$$N_{Sh} = \frac{k_m D_{eq}}{D} \tag{19}$$

where D_{eq} is defined as the equivalent channel diameter above the electrode surface:

$$D_{eq} = 4r_H = \frac{4(\mathit{cross\ sectional\ area})}{(\mathit{wetted\ perimeter})} \tag{20}$$

The Sherwood number is an empirical term and has been tabulated for a variety of flow channel geometries and physical characteristics of the gas phase [22].

The activation polarization at the cathode and the anode of the cell is tied to the rates of the electrochemical reactions occurring at these electrodes. There is a close similarity between electrochemical and chemical reactions in that both involve an activation barrier that must be overcome. The standard model to describe the current-overpotential relationship behind these electrochemical kinetics is the Butler-Volmer equation [23]:

$$i = i_o[\exp\left(\frac{\alpha_a F \eta_{act,electrode}}{RT}\right) - \exp\left(\frac{-\alpha_c F \eta_{act,electrode}}{RT}\right)] \qquad (21)$$

For specified electrochemical parameters α_a , α_c, and i_o which must be determined experimentally, the activation overpotential $\eta_{act,\ electrode}$ can be solved for at a specified applied current, i.

The total polarization at each electrode is the sum of activation polarization ($\eta_{act,\ electrode}$) and the concentration polarization ($\eta_{conc,\ electrode}$):

$$\eta_{electrode} = \eta_{act,electrode} + \eta_{conc,electrode} \qquad (22)$$

The effect of polarization is to shift the Nernstian potential of the electrode ($E_{electrode}$) to a new value ($V_{electrode}$):

$$V_{electrode} = E_{electrode} \pm |\eta_{electrode}| \qquad (23)$$

The cross cell voltage includes ohmic polarization and is defined as:

$$V_{cell} = V_{cathode} - V_{anode} - IR \qquad (24)$$

The lines presented in Figure 3 were generated analytically using this approach. Figure 3 is presented to demonstrate the relative magnitudes of the different components of the cell potential and is not intended as anything other than an illustration of the expected cell polarizations in a hypothetical laboratory scale removal cell with a perfectly manufactured membrane. The conditions assumed consisted of a cathodic flow rate of a coal synthesis gas equal to the anodic flow rate of N_2 sweep gas (0.0002 m^3/min), a system pressure of 1 atmosphere, a run temperature of 898 K, and the polishing of H_2S from 100 ppm down to 10 ppm. The cathodic and anodic exchange current densities were estimated at 400 Amp/m^2 from the results of the free electrolyte studies performed by Banks [9] and White [10]. The exchange coefficients, α_a and α_c, were assumed to each be unity. Ohmic resistance across the cell was estimated to be 1Ω [11]; and the superficial surface area of both the cathode and the anode was 0.00079 m^2 (7.9 cm^2).

Examination of Figure 3 shows that the calculated activation polarization at both the cathode and the anode is negligible. This shows extremely rapid electrochemical kinetics when compared to diffusion effects in the gas phase and in the electrolyte. All cross-cell potentials are shown to be due primarily to concentration polarization effects. Examination of this illustration shows that at 90% removal (100 ppm H_2S going to 10 ppm H_2S), a total cross- cell potential of only about -0.660 V (cathode to anode) is expected.

Since the carbonate transport reaction (12) is parallel to the sulfide transport reaction (11), some current to the cell will also act to transport CO_2 across the cell. The minimum required potential for this reaction is predicted by the Nernst equation for reaction (12):

$$E = E^o - \frac{RT}{nF}\ln\left[\frac{P_{CO_{2anode}} P_{O_2}{}^{\frac{1}{2}}{}_{anode} P_{H_{2cathode}} a_{CO_3^{2-}}{}_{cathode}}{P_{CO_{2cathode}} P_{H_2O}{}_{cathode} a_{CO_3^{2-}}{}_{anode}}\right] \qquad (25)$$

This means that there is a maximum current efficiency with respect to H_2S removal for any given H_2S removal, depending on gas composition and the cross-cell potential required for the desired separation of H_2S. By solving the carbonate transport Nernst equation, (25), at a given cross-cell potential for the CO_2, H_2, and H_2O levels in the cathode gas and CO_2 and O_2 levels in the anode gas, the extent of this parallel carbonate transport reaction can be determined. This assumes that the electrode kinetics for sulfide and carbonate transport contribute negligible activation overpotential and that concentration overpotential for CO_2 removal is also negligible (a reasonable assumption since in this case the concentration is some three orders-of-magnitude higher for CO_2 and H_2O than for H_2S, with approximately 13% CO_2 and 3.3% H_2O in the cathode gas).

The extent of the anode CO_2 production with % H_2S removal is presented in Figure 4. Current efficiency is expected to drop to 35% at 90% H_2S removal. This means that, theoretically, applied current to the cell must be increased by a factor of about 3 over stoichiometric current to achieve this removal level. The excess current goes to reduction of CO_2 and H_2O at the cathode and production of anodic CO_2. Even with a current efficiency of only 35%, power costs to perform this removal are negligible, as shown later.

While the above analysis suggested that electrochemical polishing of H_2S from coal gas was possible, experiments were needed to verify that removal of H_2S from very low inlet levels could be attained in the presence of high concentrations of CO_2 and H_2O. The following is a description of those experiments and a discussion of the results.

Experimental Methods

Cell Geometry. The cell housings were machined from MACOR (machinable ceramic) blocks. The housings were 0.076 m diameter and 0.025 m deep cylinders. Gas flow channels were machined into the large surface faces and gas flow tubes were connected to supply process and sweep gases to the cell (see Figure 5). Once the electrodes and membrane materials were ready for testing, the electrodes were set onto platinum current collectors placed on top of the gas flow channels on one side and contacting the membrane on the other (see Figure 6). The active superficial electrode area was 0.00079 m^2 (7.9 cm^2), of which 0.00064 m^2 (6.4 cm^2) was exposed to the process gas, the remainder occluded by the flow guides. The full cell was then assembled by placing the membrane between the MACOR blocks and connecting the gas supply lines to the assembly within a custom designed oven (see Figure 7).

Electrode Preparation. Weaver surveyed several possible electrode materials for this system [3,12,13]. Of these, lithiated Ni and NiO electrodes were used for this study. Ni electrodes were donated to this research by the Energy Research Corp. (ERC) as 0.20 m by 0.28 m sheets; average porosity was between 75 and 80%. A die was used to cut 0.032 m diameter electrodes from this sheet. These electrodes were then soaked in 1 M LiOH and then dried. When the Ni electrodes were used, the electrodes were then loaded into the cell and the run was started. If NiO electrodes were to be used, the electrodes were placed between two sintered Al_2O_3 sheets and loaded into an oven at 923 K under atmospheric air for at least six hours. Gravimetric analysis of these oxidized electrodes showed that the Ni was at least 96% converted to NiO.

Membrane Preparation. The membrane between the two electrodes serves two purposes. First it holds the electrolyte in place between the cathode and the anode by capillary action and prevents the molten salts from completely flooding the porous electrodes; second, the membrane acts to prevent the bulk diffusion of gases between the cathode and the anode side of the cell.

Manufacture of the membrane involved making a composite structure consisting of woven zirconia cloth which was densified with MgO powder. The structure consisted of a single mat of ZYW-30A zirconia cloth (purchased from ZIRCAR Inc.) layered with two tapes of MgO ceramic powder suspended within acrylic binder K565-4 (purchased from Metoramic Sciences, Inc.). An oxygen sweep was applied to both sides of the cell and the cell was loaded into the furnace for heat-up. The binder from the MgO tapes was burned out at 648 K overnight. The temperature was then ramped up to run temperature and the electrolyte was wicked into the MgO powders and zirconia cloth. Process gas was then supplied to the cell and the electrolyte was allowed to reach the equilibrium described by reaction (5).

Pre-Run and Analysis. Once assembled, the cell was loaded into a custom-made furnace and connected to the process and sweep gas supply lines. The exit gas from the cathode was routed to a Beckman IR scanner for reading CO_2 levels and a Teledyne UV scanner for reading H_2S levels. A Hewlett/Packard gas chromatograph fitted with a flame photometric detector was also used for reading H_2S levels exiting the cell. A gold reference electrode was placed on the surface of the membrane away from either process electrode and supplied with a flow of 15% CO_2 / 3% O_2 / balance N_2 mixture to maintain a stable thermodynamic reference potential by reaction (26):

$$CO_2 + \frac{1}{2}O_2 + 2e^- \rightleftharpoons CO_3^{2-} \qquad (26)$$

Melting of the electrolyte was verified by a sudden improvement in the seals formed by contact of the membrane with the MACOR surfaces along with observed electrical conductivity through the cell. Process gas, consisting of specified levels of CO_2, CO, H_2, H_2O, and H_2S was then supplied through the cell via a stainless steel shift reactor which allowed the water/gas shift reaction, (27), to go to equilibrium at the process temperature before the gases entered the cell.

$$CO_2 + H_2 \rightleftharpoons CO + H_2 \qquad (27)$$

Test Procedure. Once the cell had reached run temperature, conductivity across the cell was estimated by current interrupt. The equilibrium potentials at the cathode and anode were measured with respect to the reference electrode. Base-line exit cathode gas compositions were also measured at this point. Current was then applied to the cell in a step-wise fashion and the cell was allowed to equilibrate for at least 15 minutes after each current step. Once stabilized, potentials with respect to the reference electrode and exit gas compositions were measured.

EXPERIMENTAL RUN RESULTS

This study was primarily concerned with improving H_2S selectivity and removal efficiency through the development of a gas-impermeable membrane. Removal of H_2S and CO_2 from the process gas stream at the cathode and evolution of products at the anode was measured over a range of gas compositions representing sour coal gas which had been cleaned of H_2S to a level of 100 ppm to 10 ppm H_2S. Process temperature and gas flow-rates were also varied to be representative of conditions likely to be of industrial interest.

The maximum removals reported below are removals of H_2S and CO_2 on a zero current basis to compensate for the chemical scrubbing effect of the non-equilibrium composition electrolyte in the membrane. H_2S removal is therefore defined as:

$$\%\,Removal = \left[\frac{Exit\ Conc._{No\ Current} - Exit\ Conc._{With\ Current}}{Exit\ Conc._{No\ Current}}\right] X\ 100 \qquad (28)$$

Selectivity is defined by the following equation:

$$Selectivity = \left[\frac{\%\ Removal_{H_2S}}{\%\ Removal_{CO_2}}\right]\left[\frac{\%\ CO_{2_{Inlet}}}{\%\ H_2S_{Inlet}}\right] \qquad (29)$$

If selectivity is equal to one, removals of H_2S and CO_2 are equivalent. If the selectivity is greater than one, H_2S is preferentially removed.

A total of nine successful experiments were performed. Two of these are presented here. Reproducibility of removal trends was observed in all of these runs.

Polishing Application with 100 ppm H_2S in Coal Gas. This experimental run used a simulated coal gas with a composition of 14.3% CO_2, 50.8% CO, 4.8% H_2O, 30.1% H_2, and 100 ppm H_2S after shift reaction. It used two tapes of MgO and one mat of 0.00076 m thick zirconia cloth as the membrane matrix material. The electrodes were both lithiated NiO. The acrylic binders used in the MgO tapes (Metoramics K565-4 binder system) were burned out under an O_2 atmosphere at 623 K and the Li/K eutectic-composition electrolyte was added with the cell at run temperature. The inlet gases were passed through a stainless steel shift reactor to allow them to come to their equilibrium composition before passing through the cell.

The cell temperature was 973 K; at this temperature, analysis of the limiting current densities within the system, as outlined earlier, shows that the gas phase limiting current density was 11.5 Amp/m^2 while the membrane limiting current density was 32.9 Amp/m^2. This shows that the maximum flux of material through the membrane is three time greater that the maximum flux of material through the gas phase to the membrane surface. H_2S removal at a variety of flow-rates was observed and is presented here in Figure 8 through Figure 11. Cell polarization is presented in Figure 12. Parametric numbers on this graph are cathodic flowrates in $m^3 \times 10^{-6}$. The measured cross-cell resistance was measured by current-interrupt and was found to be about 1Ω. With the maximum current applied to the cell of 0.02 Amp, this corresponds to 0.02 V of ohmic loss. This is slight compared to the overall cross-cell potential, which includes concentration effects and other overpotentials.

An H_2S removal level of 89.2% (exit H_2S level brought from 89.5 ppm to 9.7 ppm with applied current) was achieved. Cell current efficiency and species removal for this run are presented in Figure 11. At only slightly above stoichiometric current, H_2S current efficiency is 40%. The remaining 60% of the 0.0012 Amp applied to the cell at this point would remove only 62.9 ppm CO_2 from the process gas stream with 19.1% CO_2 entering the cell; such transport of CO_2 is completely negligible. Even at the highest applied current to the cell the cell at the cathode flow-rate of 0.000088 m^3/min, an H_2S current efficiency of only 4.6% (see Figure 11). This H_2S current efficiency would correspond to a drop in CO_2 of only 0.17%. The theoretical maximum current efficiency for this system at 89% removal of H_2S would be approximately 35%.

Polishing Application to 19 ppm H_2S in Coal Gas. Several experimental runs using 1 mat of 0.00076 m thick zirconia cloth which was rigidized to 60.8% voids using sub-micron particles of ZrO_2 within an aqueous slurry (44 wt%) were performed. These were accomplished by cutting a 0.076 m diameter mat of zirconia cloth and soaking it in Zircar brand Rigidizer. The mat soaked the aqueous slurry into its voids and left the ZrO_2 particles behind after the H_2O was dried out. Two tapes of MgO/ZrO_2 (4 micron particle size, Aesar) in vinyl binder (B73305 Metoramics binder system) were layered on each side of the rigidized mat to further densify the structure. The electrolyte was eutectic Li/K carbonate and was added to the cell as a pressed disk before heat-up. The electrodes were lithiated Ni. The housings were MACOR with Al foil gaskets. The run temperature was 923 K. After binder burnout and electrolyte melting, fuel gas of composition 15.2% CO_2, 44.2% CO, 5.4% H_2O, 35.0% H_2, (after shift reaction) with 18.8 ppm H_2S was put through the cell. This gas composition and temperature gives an estimated equilibrium-membrane-sulfide level of 0.06 mole% sulfide. The gas-phase limiting-current density was estimated to be 1.8 Amp/m^2 and the membrane limiting current density was 3.4 Amp/m^2.

H_2S removal data was taken at a variety of cathodic flow-rates. Current efficiency and species removal for this run are presented in Figure 13. H_2S levels were brought from 15.8 ppm exiting the cell with no current applied, to 4 ppm H_2S with 0.2 Amp applied. The selectivity of this membrane was high (selectivity of 2×10^4), but some CO_2 transport was observed. H_2S current efficiency was low (no higher than 1.2%) because of H_2 cross-over.

ECONOMIC PROJECTION

Accurate cost figures for processes early in development are impossible to project. However, it is possible to roughly estimate the power and capital requirements to assess viability. The power consumption has been shown to be overwhelmingly due to cell current, which is near stoichiometric. Cell voltage, as shown earlier, can be estimated with reasonable accuracy. Capital costs can be estimated by analogy with Molten Carbonate Fuel Cell (MCFC) stacks, whose design these cells will mimic.

The proposed Electrochemical Membrane Separator (EMS) design is compared to a Sulfinol process with a Claus plant for sulfur recovery. The base case is provided in a discussion of coal gas processing economics by Oak Ridge National Laboratory (ORNL-5425)[14]. The medium-Btu gas treating facility discussed here treats 590 million kg/hr of coal synthesis gas with composition outlined in Table II. The capital cost for a Sulfinol plant consisting of two parallel units was estimated at 39.4 MM$ in the first quarter of 1978. This scales to 145 MM$ in mid-1987 dollars using Marshall-Swift cost indexes[15]. This does not include costs for cooling the gas stream from gasification temperatures (approx. 1023 K) to Sulfinol process temperature (311 K) or the cost of reheating the gas for feed to the turbines of a cogeneration power plant or an MCFC power plant.

The acid gas stream generated by the Sulfinol plant as an H_2S level of 28.5 vol%. This is fed to a Claus plant capable of handling a load of 247 metric tons/day of sulfur production. The Claus plant for treating this acid gas had an estimated capital cost of 8 MM$ in 1978 dollars. This scales to 29.4 MM$ in 1987 dollars by Marshall-Swift indexes. The combined Sulfinol/Claus plant capital cost for treating this coal synthesis gas is therefore 174 MM$ in 1987 dollars (not including gas cooling and reheating costs).

The capital cost of the EMS is more difficult to estimate than the power consumption. In the MCFC, current densities greater than 1600 Amp/m^2 are routinely achieved. There are, however, two major differences between the MCFC and the EMS. In the MCFC the gases are relatively rich, as compared with the dilute reactants treated in the EMS. Further, there is no competing reaction to dilute the current carrying anion. Thus, gas-phase diffusion of H_2S or sulfide migration in the membrane may limit the current density and define the needed active membrane area for a given duty.

Gas-phase transport can be controlled through proper design of the gas channels [16]; pore diffusion in the electrodes has been found not limiting in similar designs for CO_2 removal to very low levels [17]. The limiting step for removal in this analysis is gas diffusion of H_2S to the cathode of the cell. This was found by comparison of species diffusion through the gas phase to species diffusion through the molten salt electrolyte. The capital cost estimation assumes that the membranes are available as 1.2 m by 1.2 m squares (as used in MCFC units) and are arranged in 'stacks' of parallel removal cells with the process gas equally divided to each cell. Each 'stack' removes approximately 90% of the H_2S fed to it. There is also assumed to be series of parallel 0.003 m by 0.003 m flow channels directing gas flow across the surface of each electrode. A break-down of the costs associated with the EMS stacks is provided in Table III [18]. For an EMS system operating at a pressure of 42.7 atm at gasification temperatures of 1023 K, the limiting current density for the first stack (which removes H_2S from 0.9% to 900 ppm) is 1133 Amp/m^2. The second stack (900 ppm to 90 ppm H_2S) has a limiting current density of 113.2 Amp/m^2. The third stack (90 ppm to the final H_2S level of 6 ppm) has a limiting current density of 9.986 Amp/m^2.

Once the limiting current density of the stack is known, the total stack area (or number of cells in the stack) can be calculated by dividing the required stack current by the stack limiting current density. The H_2S stack current is assumed to be stoichiometric for the moles of H_2S

removed. The total molar flow-rate to be treated by the EMS system is 18.8 kgmole/sec. Thus, the H_2S current applied to the first stack (0.9% to 900 ppm H_2S) is 2.82×10^7 Amps, the second stack (900 ppm to 90 ppm H_2S) requires 2.94×10^6 Amps, and the third stack (90 ppm to 6 ppm H_2S) requires 3.05×10^5 Amps. For the first stack, with $I_{H2S} = 2.82 \times 10^7$ Amps and $i_{d,H2S} = 1133$ Amps/m^2, the total active membrane area is 24889 m^2. If 1.2 m^2 by 1.2 m^2 membranes are used in this application, this comes to 17284 electrochemical cells in the first stack. The active membrane area of the second stack is 25971 m^2 (18036 cells), and the active membrane area for the third stack is 30543 m^2 (21210 cells).

Stack power requirements depend on the total current driving the H_2S removal and the cross-cell potential of the removal cell. Because of parallel CO_3^{2-} transport, current levels greater than stoichiometric H_2S removal current are required. By the analysis presented earlier in this paper, current efficiency at 90% H_2S removal was found to be 89.1% in the first stack with a cross cell potential of 0.764 Volts. At this current efficiency, the first stack requires 24180 kW. The second stack has a current efficiency of 81.6% with a cross cell potential of 0.665 Volts; at these conditions this translates to 2396 kW required by the stack. The third stack has a current efficiency of 51.6% and a cross cell potential of 0.611 Volts; at these conditions the third stack requires 361 kW. This sums to 26937 kW for the entire system. In these calculations, cell resistivity was estimated to be $2.5\times10^{-5}\ \Omega\ m^2$ after MCFC results for tape-cast electrolyte membranes of 5.0×10^{-4} m thickness and containing 40 wt% electrolyte [19].

The system costs for the EMS plant are listed in Table III. Note in Figure 14 that there is no need for heating the coal synthesis gas stream since the coal gasification EMS plant operates at gasification temperatures. There is, therefore, no need for a regenerative heat exchanger system to cool for H_2S removal and reheat the gas for use in a cogeneration power plant or MCFC. Since sulfur condenser costs are negligible compared to electrochemical cell stack costs, there are effectively no heat exchanger costs for this plant. An overall operation cost comparison is shown in Table IV. Note that even with the lower current efficiencies in the polishing steps of the process, the treating cost per 1000 SCM of gas treated are still competitive (in fact, even if the power requirements were doubled, the comparatively low capital investment of the proposed technology compared to the conventional technology still provides favorable economics). The overall operation cost of the two facilities was estimated after the method reported by Maddox in Gas and Liquid Sweetening [20]. The utilities cost and sulfur credit used in this comparison are the same used in a previous natural gas treating plant analysis by Fluor Technology, Inc. [21].

The net treating costs presented in Table IV ($5.644 / 1000 SCM for conventional technology compared to $2.192 / 1000 SCM for the proposed EMS technology) refers to the cost associated with sweetening the gas and producing sulfur. The addition of several plant areas would be required to develop a total cost-of-gas-treating. That is, the Net Treating Cost presented here relates only to the systems described and should be used only to establish the relative economic merits of the proposed EMS technology for selective H_2S removal. Once again, the conventional cost of gas treating presented here does not include the cost of cooling the gas for removal of H_2S and reheating the gas to gasification temperatures after treatment. A step which would not be necessary with the proposed EMS technology.

CONCLUSIONS

Selective removal of H_2S has been demonstrated for polishing application to a coal synthesis gas (100 ppm H_2S) and for a purification application to coal synthesis gas (10 ppm H_2S). Electrochemical scrubbing of H_2S from coal synthesis gas at levels higher than 100 ppm has already been shown by Weaver [3,12,13].

The economic study presented in the previous section shows that the proposed technology is economically favorable as a method of coal gas sweetening. The results of the coal gas analysis shows that a 36.4×10^6 SCMD coal gas sweetening plant can be operated for \$2.192/1000 SCM using proposed technology, as compared to \$5.644/1000 SCM using conventional technology. The removal results reported here support the design specifications for the last two removal cell stacks in the coal gas plant (more concentrated H_2S coal gas streams were studied previously by Weaver).

With the development of even more bulk gas-impermeable membranes and the perfection of cell housing passivating techniques, scale up to a pilot facility is imminent.

ACKNOWLEDGEMENTS

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Table I. Representative Coal Gas Composition

CO:	15 - 30%
CO_2:	4 - 25%
H_2:	12 - 59%
N_2:	0 - 59%
CH_4:	2 - 19%
H_2S:	0.5 - 1.5% (Dry Basis)

Table II. Medium Heating Value Coal Synthesis Gas Composition

Gas	Flow/10^{-3}kg-hr^{-1}	Flow/kmole-s^{-1}	Vol%
H_2	92.33	12.9	68.6
N_2	14.83	0.147	0.781
CO	97.71	0.971	5.16
CO_2	64.48	0.407	2.16
H_2O	3.06	0.047	0.250
H_2S	19.97	0.163	0.866
CH_4	178.50	3.10	16.5
C_2	80.21	0.743	3.95
C_3	36.25	0.230	1.22
C_4	12.39	0.059	0.313
C_5	1.60	0.049	0.260
Total	601.33 (36.4×10^6 SCMD)	18.82	100.0

Pressure, 43.2 bar
Temp., 311 K
Heating Value: 19.1×10^6 J-m^{-3}

Table III. Break-Down of Capital Investment for CG EMS (1987 US dollars)

Electrochemical Membrane Separator Cell Stacks/ $\$ \times 10^6$

Items:	Stack 1	Stack 2	Stack 3
Ion Exchange Area ($m^2 \times 10^3$):	24.9	26.0	30.5
Membranes in Stack:	17284	18036	21210
Anodes:	2.299	2.402	2.824
Cathodes:	0.948	0.991	1.164
Bipolar Hardware:	1.733	1.811	2.129
Membranes:	0.107	0.112	0.131
Auxiliaries:	0.542	0.566	0.666
Assembly:	2.083	2.176	2.558
Stack Cost:	7.712	8.058	9.472
Rectifier:	4.195	4.383	5.153
Controls & Misc.:	5.845	6.107	7.180
Assembly:	4.600	4.807	5.651
Total Stack Cost:	22.35	23.36	27.46

Total EMS Cost:	73.17
Blowers:	0.101
Heat Exchangers:	negligible
Plant Cost:	73.27
Project Contingency (15%):	10.99
Fixed Capital Investment:	84.26

Table IV. Operation Cost Comparison, CG EMS to Sulfinol (1987 US dollars)

	Sulfinol	EMS
Fixed Capital Investment (US $ x 10^6)	174.4	84.26
Direct Operations Costs:		
Utilities ($ x 10^6)		
Steam (@ $5.38/1000 kg):	7.379	0.000
Electricity (@ $0.0524/kW-hr):	2.076	12.20
Raw H_2O (@ $0.198/$m^3$):	8.456	0.610
Gas Losses (@ $77.1/1000 SCM):	0.000	0.000
Chemical Losses	1.307	0.000
	19.22	12.81
Operating Labor (@ $10.30/hr):	0.180	0.089
Maintenance (@ 4% FCI):	6.976	3.370
Plant General (@ 40% Labor):	0.072	0.036
	7.228	3.495
Total Operating Costs:	26.45	16.31
Indirect Operating Costs:		
Depreciation (@ 10% FCI):	17.44	8.426
Tax & Insurance (@ 2.5% FCI):	4.360	2.107
Total Indirect Cost	21.80	10.53
Cost of Profit (@ 25% FCI) (Includes income tax, interest on investment, and reasonable profit)	43.60	21.07
Grand Total Treating Cost:	91.85	47.91
Sulfur Credit (@ $98/metric ton)	-17.89	-17.89
Net Treating Cost (Grand Total - Credit)	73.96	30.03
Treating Cost ($/1000 SCM)	**$5.644**	**$2.292**

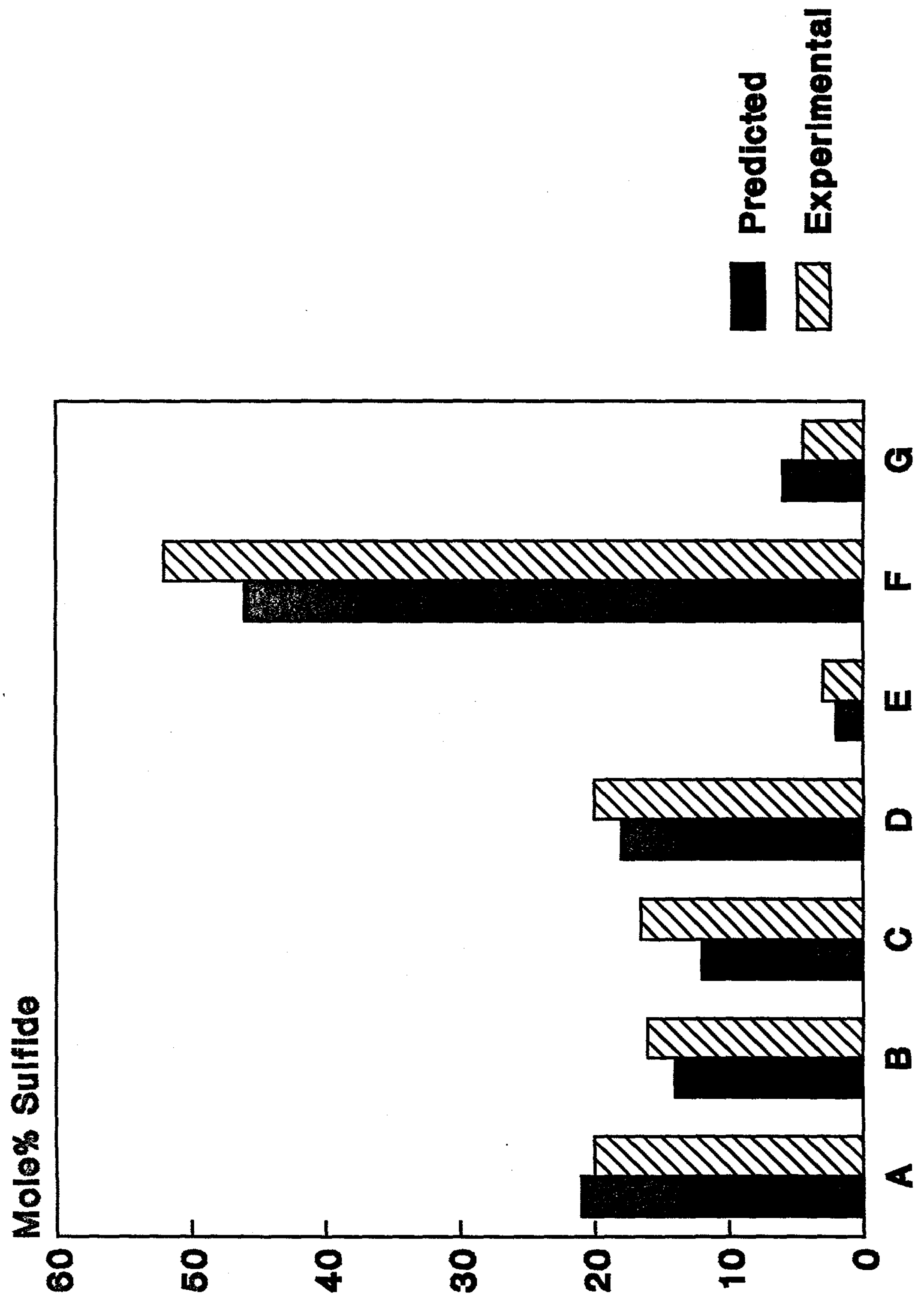

Figure 1. Comparison of Actual Sulfide Levels to Calculated Sulfide Levels in Electrolyte

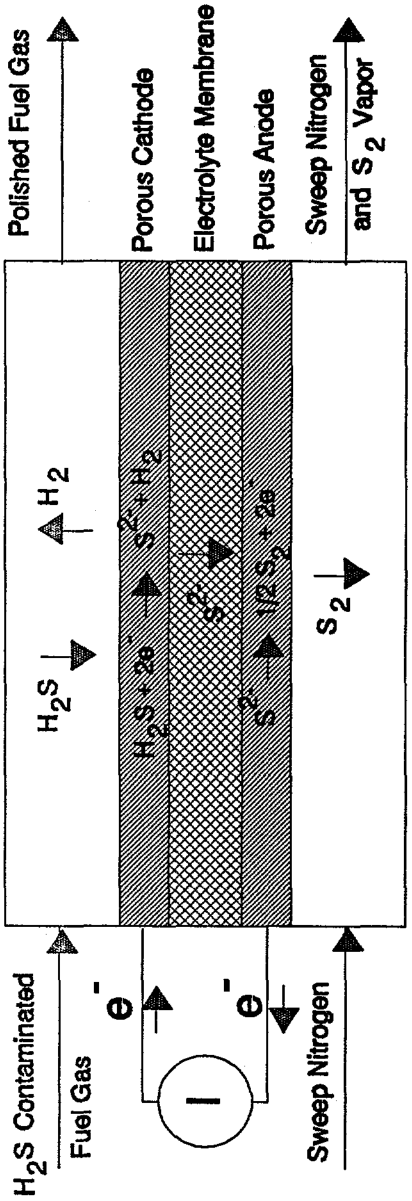

Figure 2. Electrochemical Coal Gas Desulfurization Cell

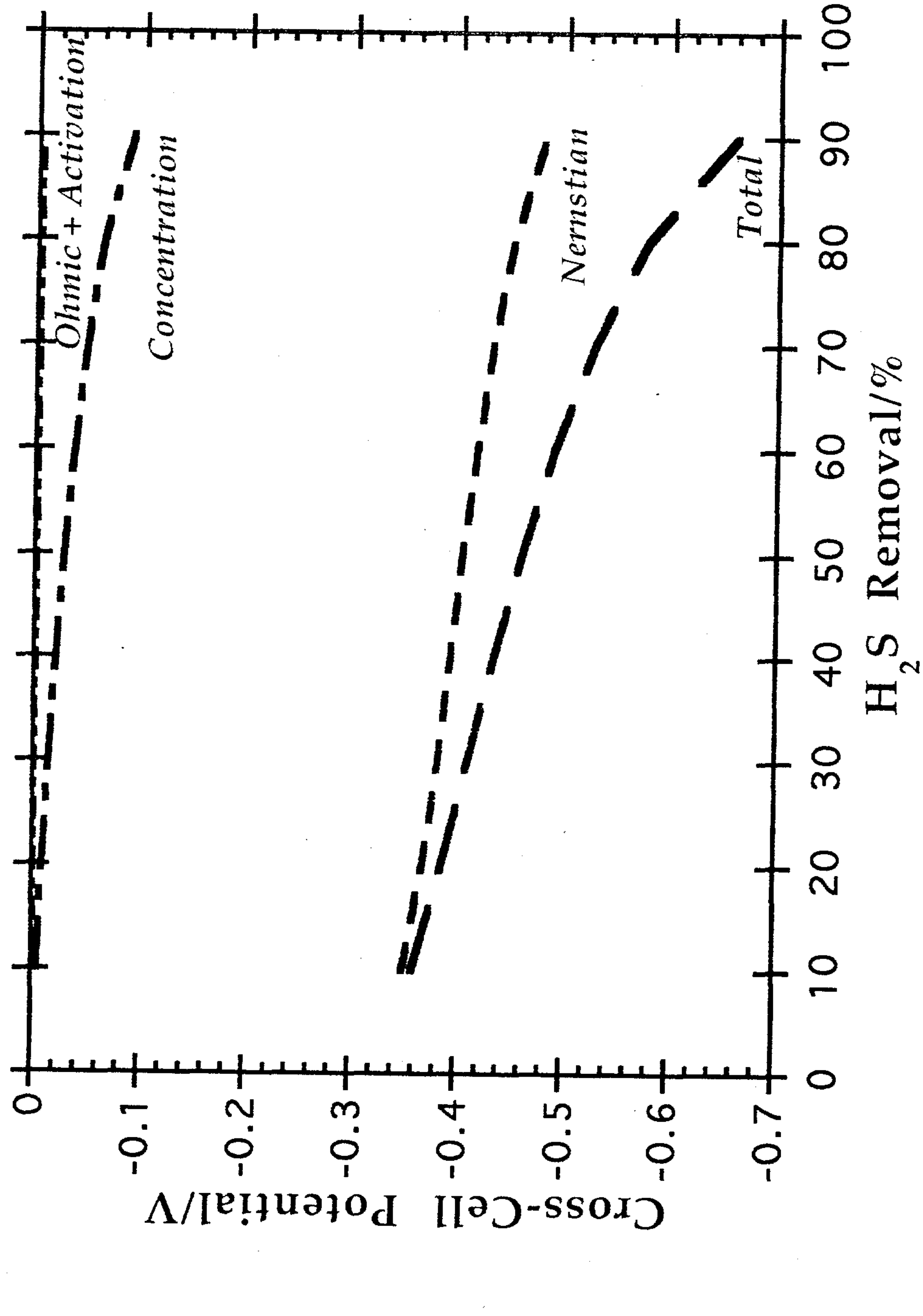

Figure 3. Theoretical Cross Cell Potential vs % H_2S Removal

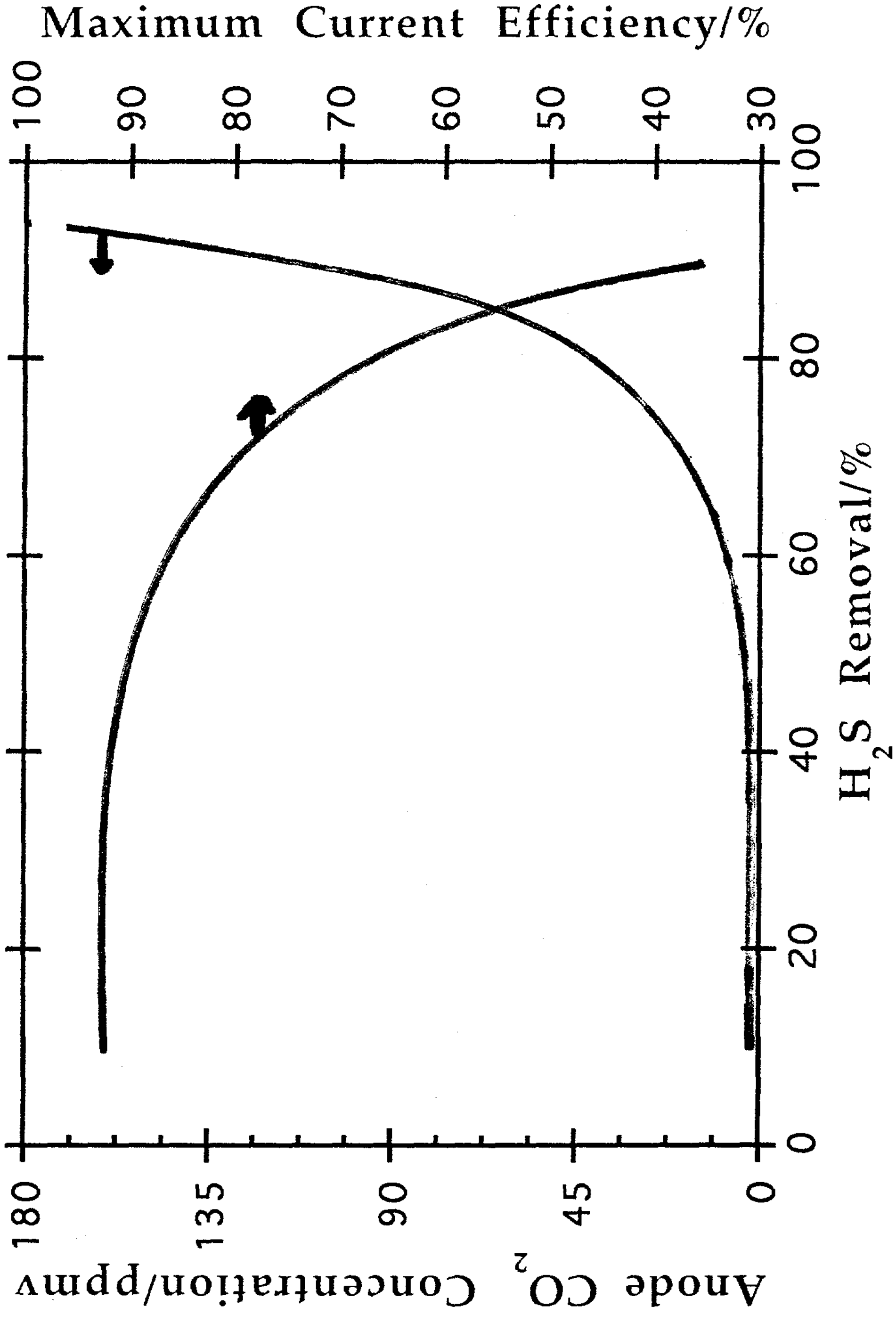

Figure 4. Predicted Anodic CO_2 Production and Maximum Current Efficiency vs H_2S Removal

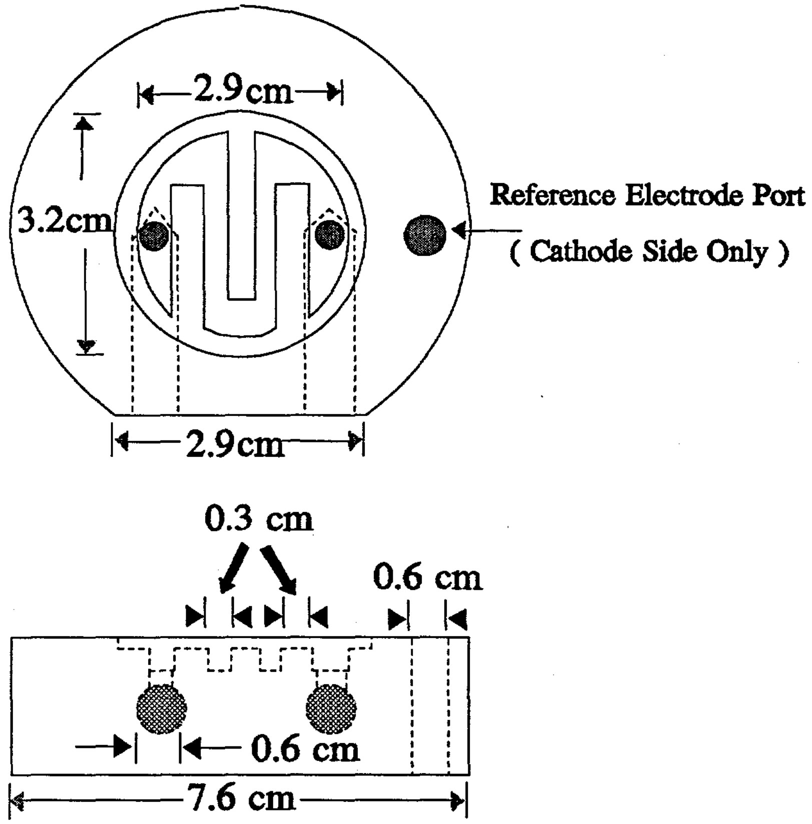

Figure 5. Cell Housing Configuration

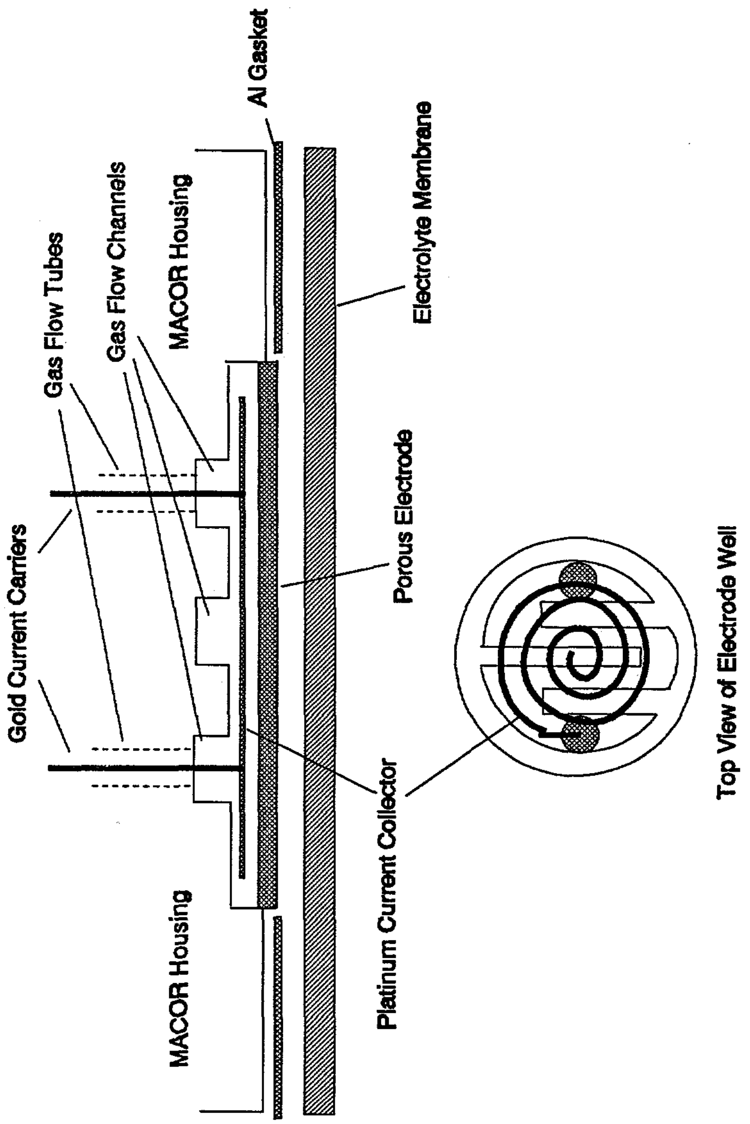

Figure 6. Housing/Current Collector / Electrode / Gasket / Membrane Configuration

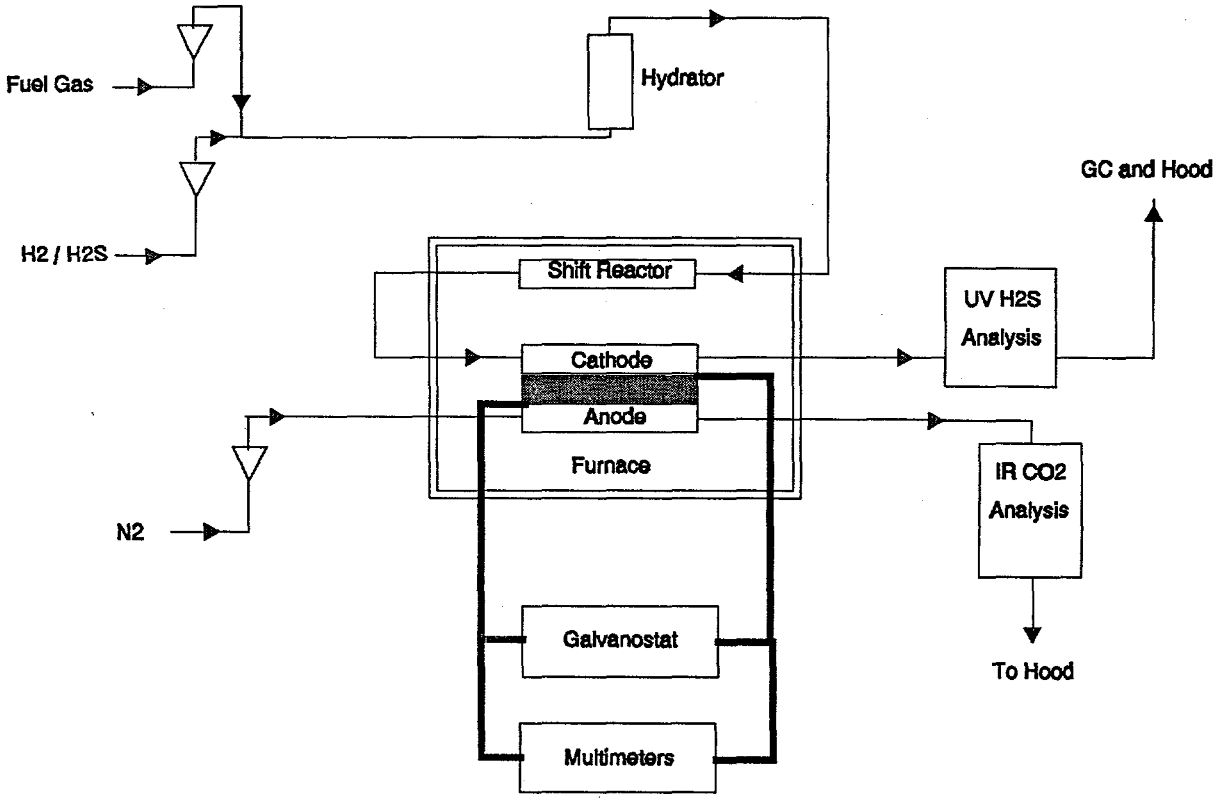

Figure 7. Experimental Apparatus Configuration for Coal Gas Polishing

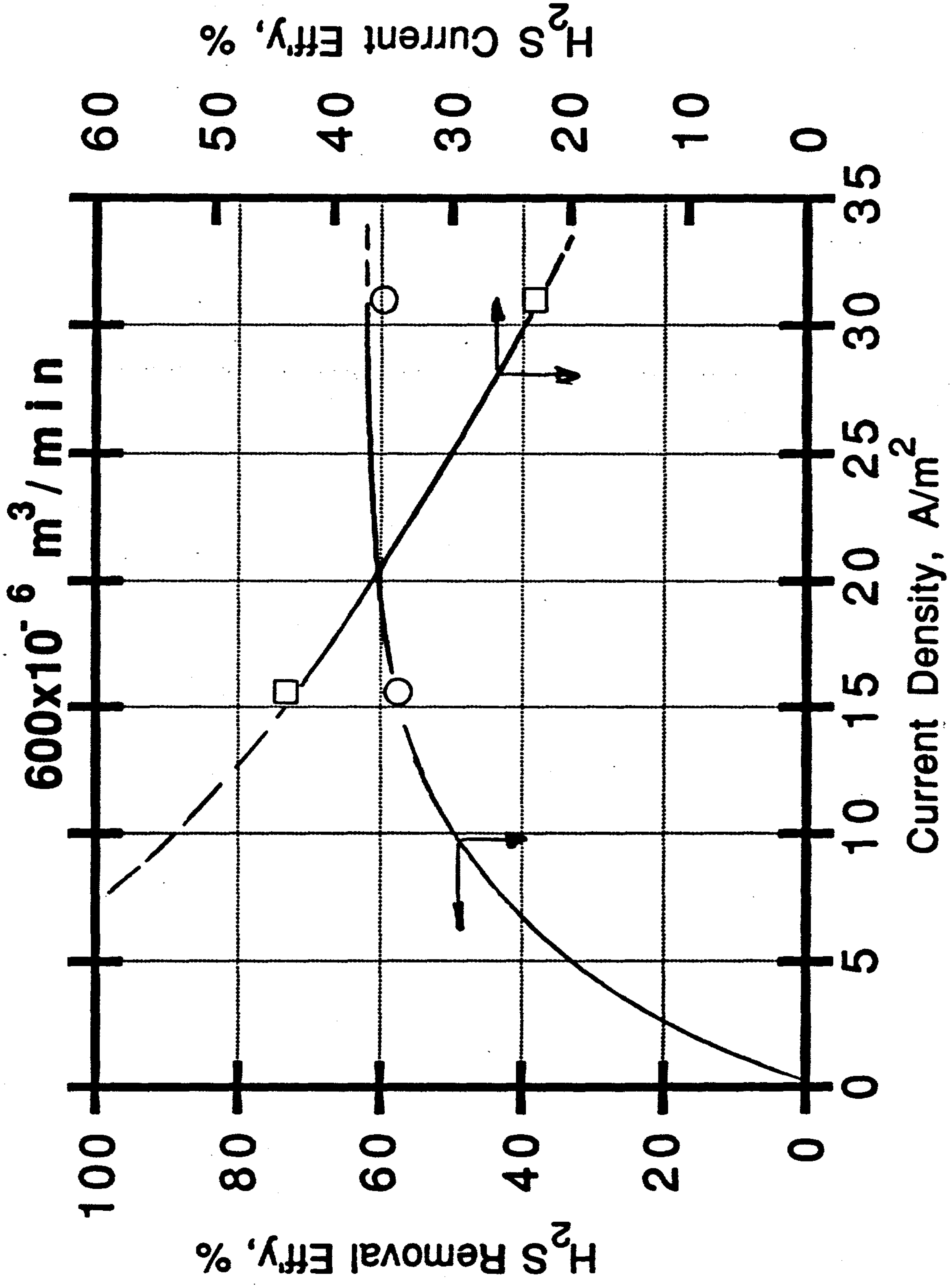

Figure 8. H_2S Removal and Efficiency vs Applied Current Density, 100 ppm H_2S, 600 x 10^{-6} m^3-min^{-1}

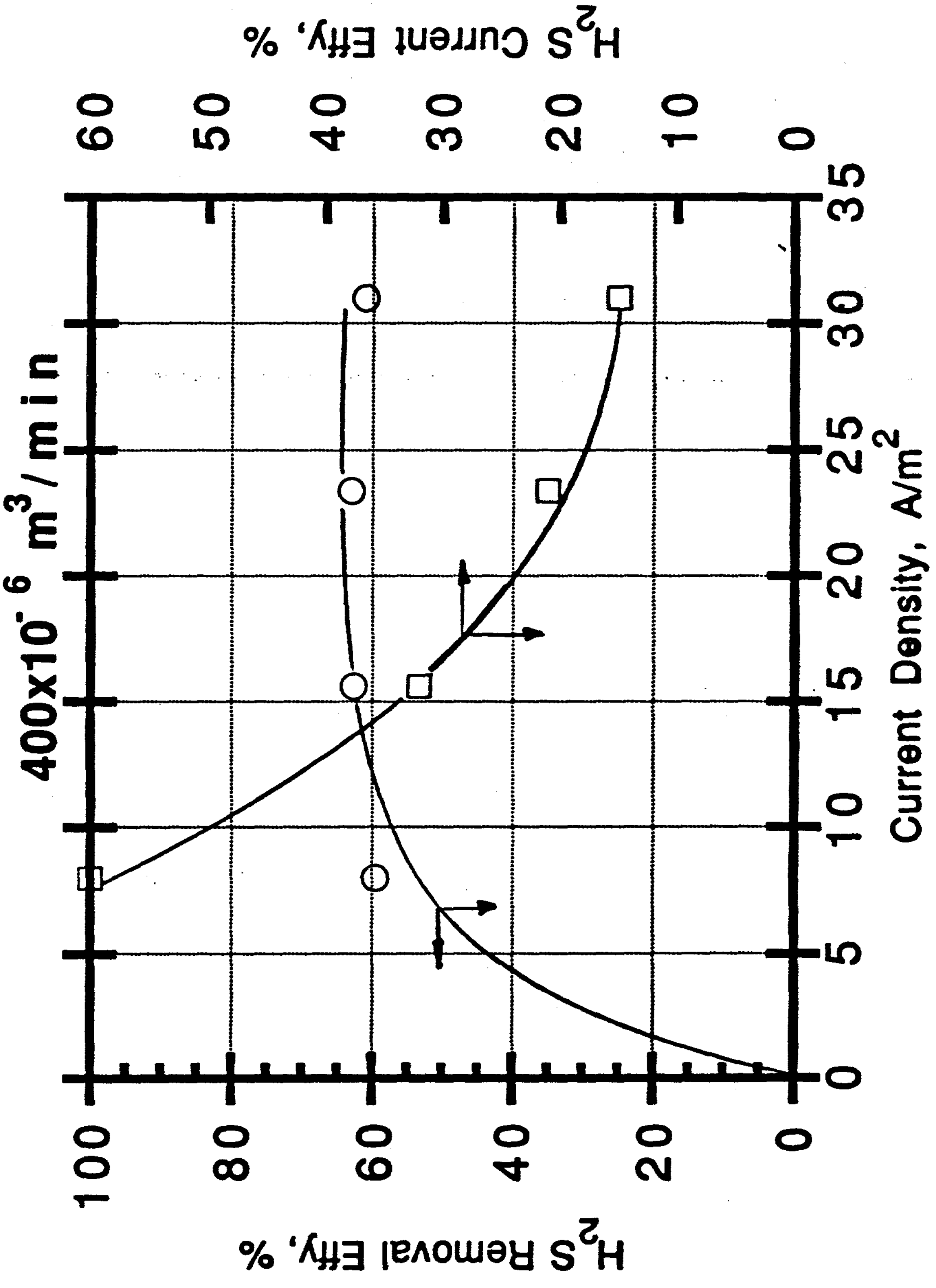

Figure 9. H$_2$S Removal and Efficiency vs Applied Current Density, 100 ppm H$_2$S,400 x 10^{-6} m^3-min^{-1}

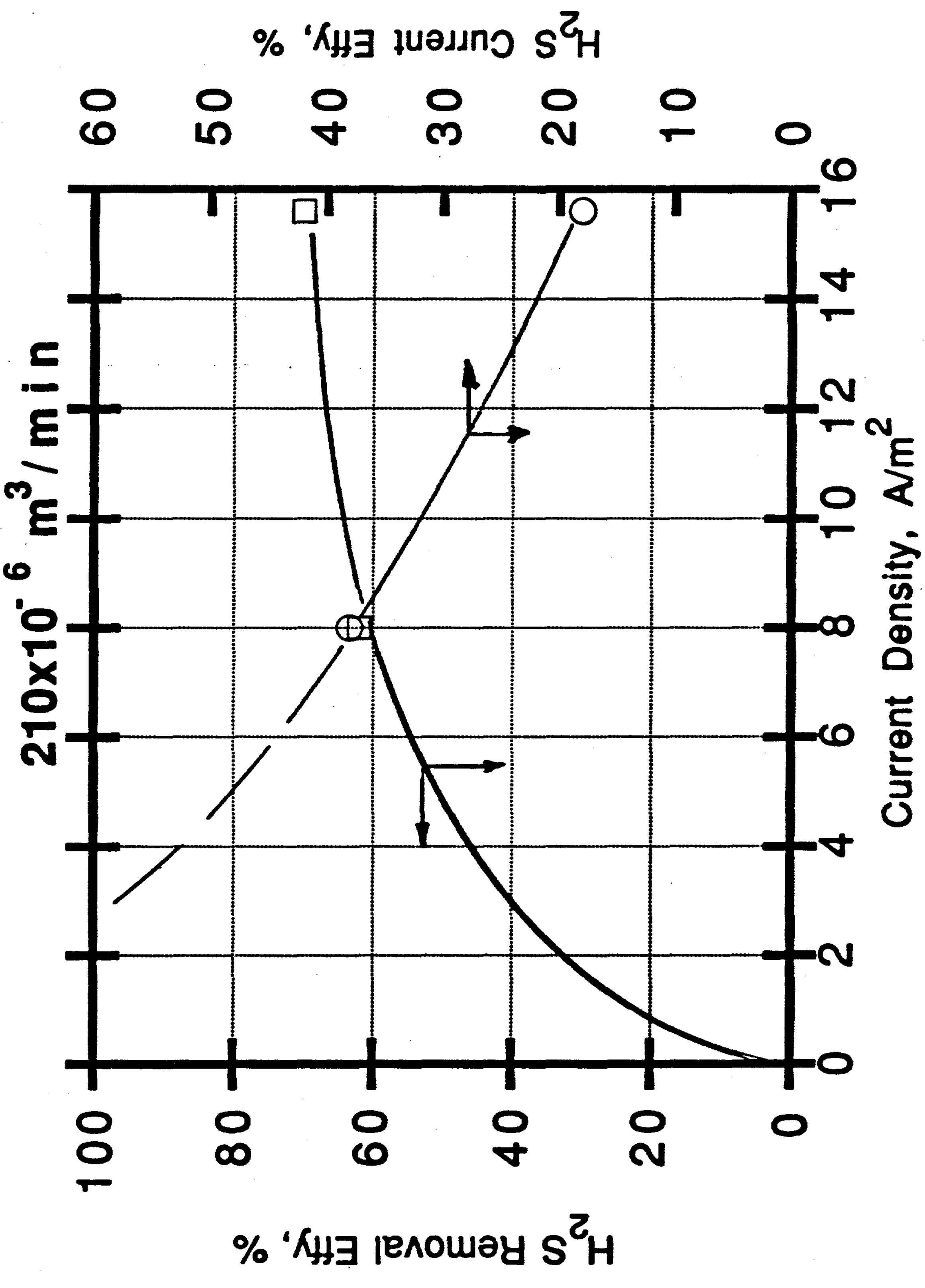

Figure 10. H_2S Removal and Efficiency vs Applied Current Density, 100 ppm H_2S, 210 x 10^{-6} m^3-min^{-1}

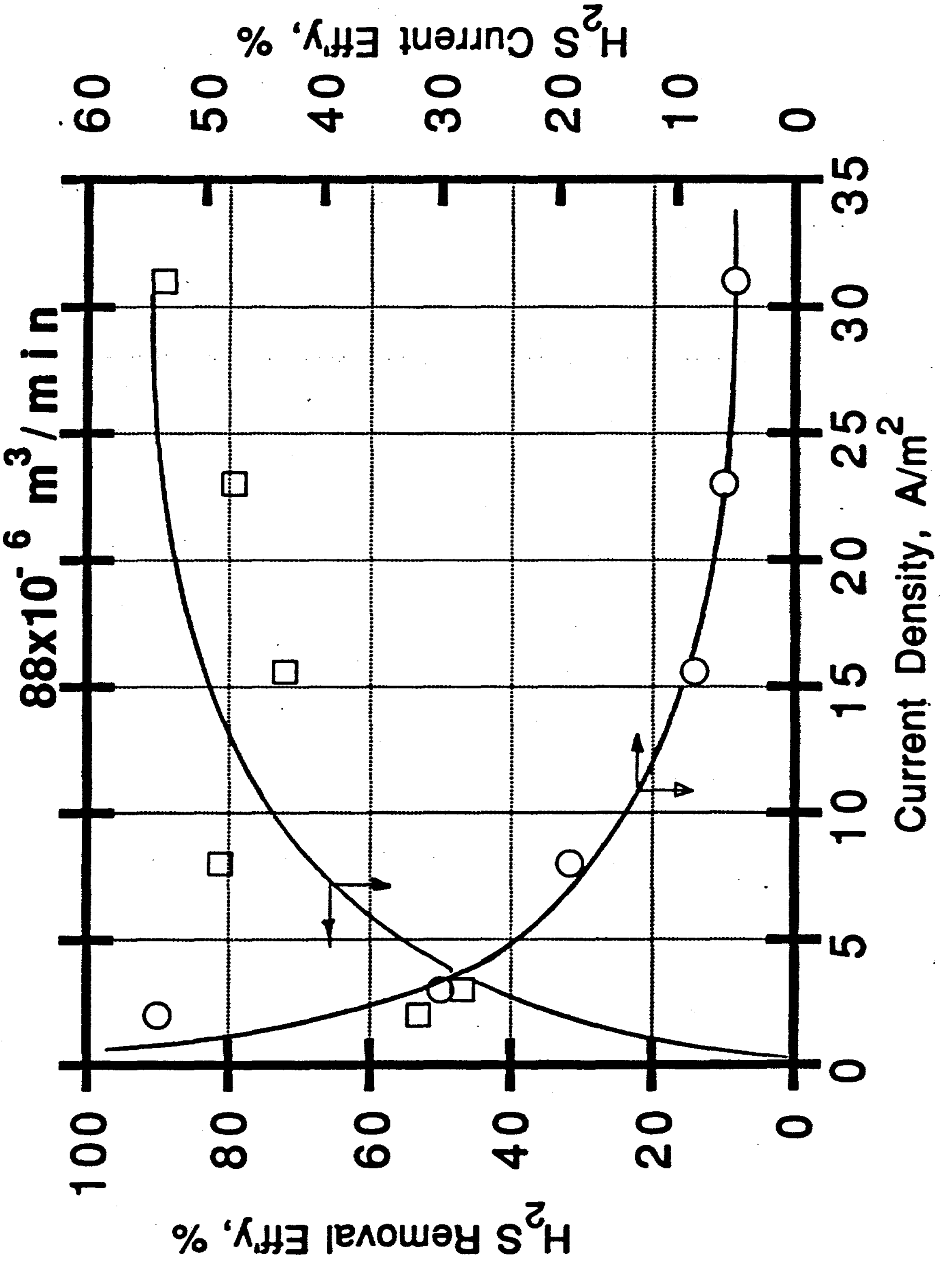

Figure 11. H_2S Removal and Efficiency vs Applied Current Density, 100 ppm H_2S, 88 x 10^{-6} m^3-min^{-1}

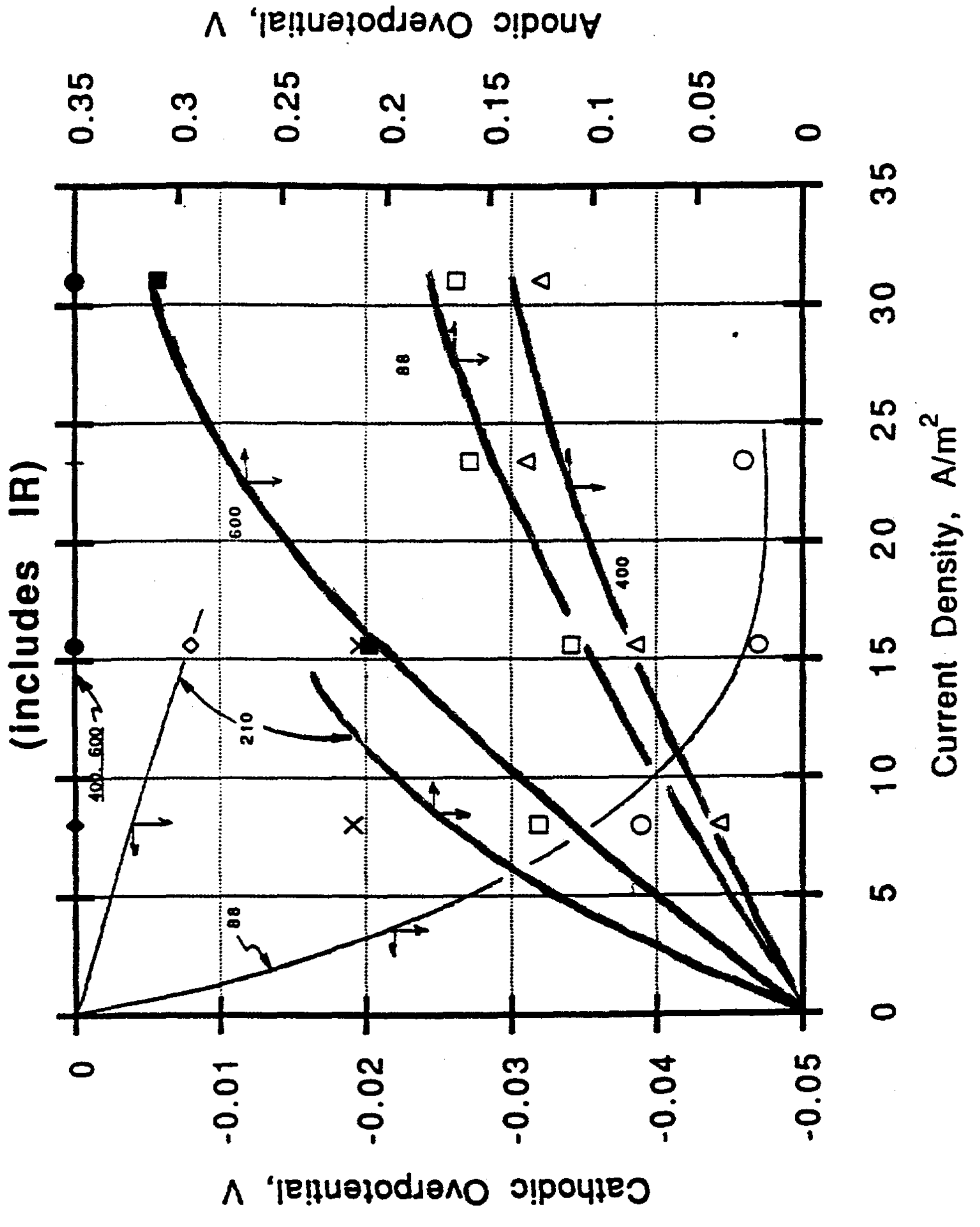

Figure 12. Cell Polarization vs Applied Current, 100 ppm H_2S, Values are Cathodic Flowrate in m^3-min^{-1} x 10^{-6}

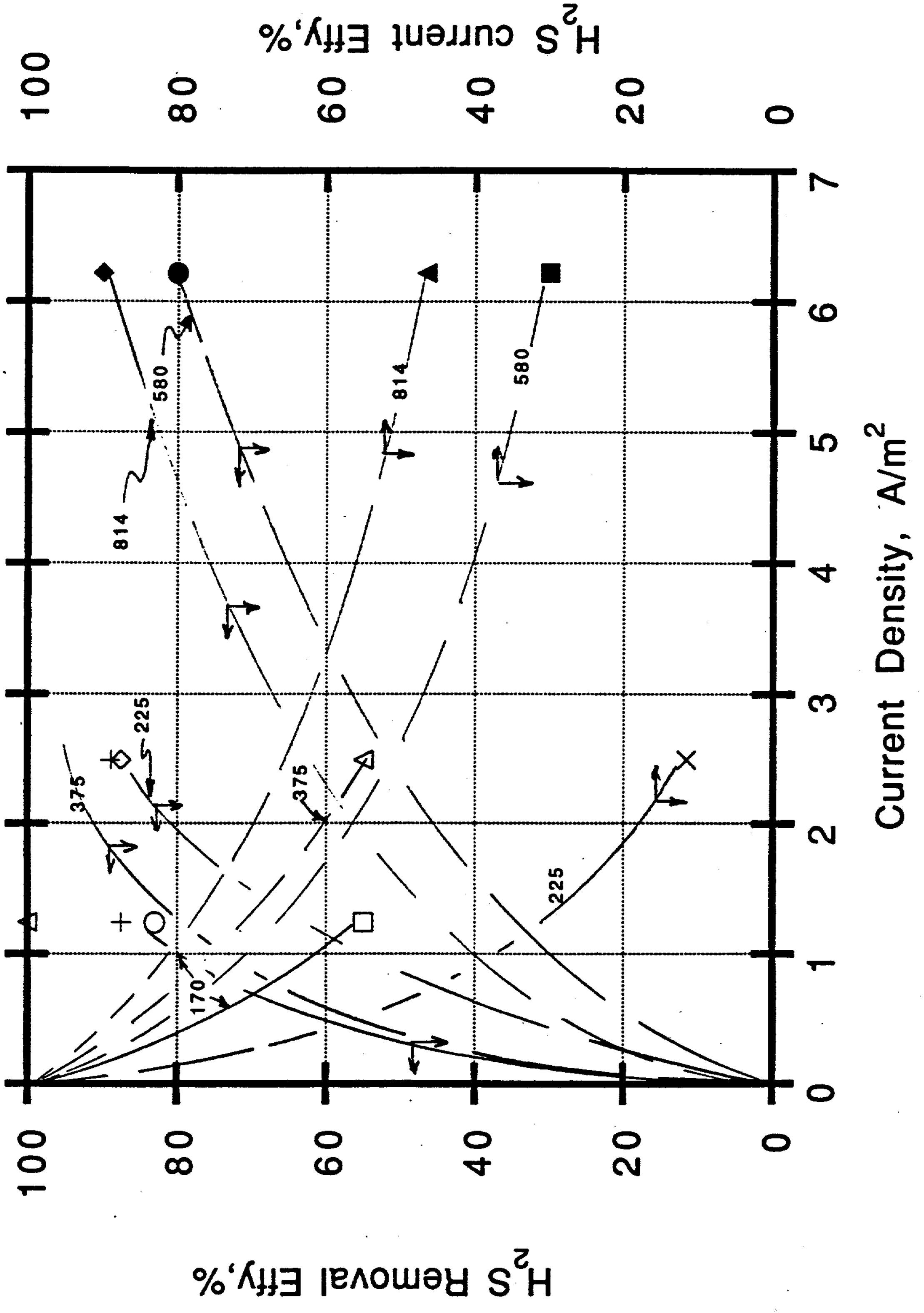

Figure 13. H_2S Removal and Efficiency vs Applied Current Density, 20 ppm H_2S, Parametric Numbers are Cathodic Flowrate in $m^3\text{-}min^{-1} \times 10^{-6}$

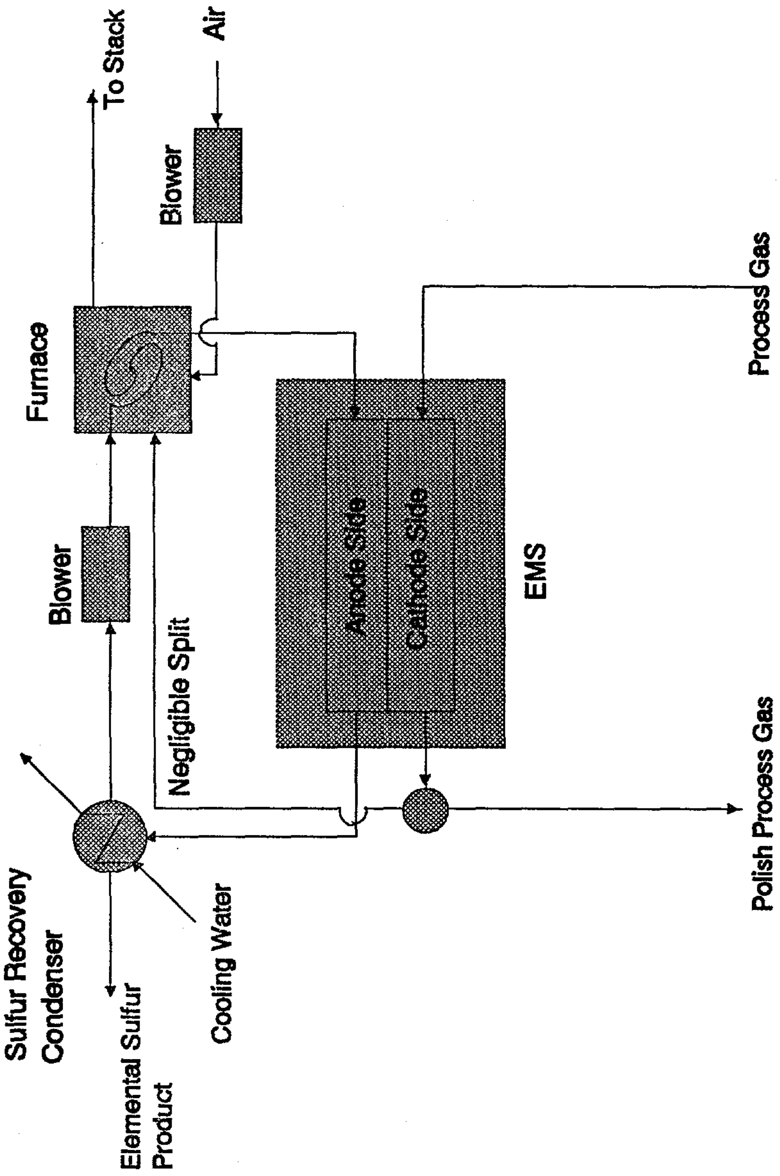

Figure 14. Proposed Coal Gas Sweetening EMS Layout