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APPLICATION OF CERAMIC MEMBRANES IN ADVANCED COAL-BASED POWER GENERATION SYSTEMS

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ABSTRACT

The U.S. Department of Energy is researching high-temperature ceramic gas separation membranes. DOE will demonstrate the feasibility of using these membranes to remove the sulfur and nitrogen contaminants found in gas streams of advanced coal-based power generation systems. These contaminants must be removed to protect not only the turbine system components but also the environment. This paper discusses the integration of passive, facilitated, and catalytic membranes, and the expected benefits of applying this membrane technology.

INTRODUCTION

The Morgantown Energy Technology Center (METC) of the U.S. Department of Energy (DOE) is sponsoring research to develop advanced coal-based power generation technologies that use coal more efficiently, more economically, and with lower environmental emissions than conventional, pulverized-coal power plants. Two emerging coal-based power generation systems under development are the integrated, coal-gasification combined cycle (IGCC) and direct coal-fueled turbine (DCFT) systems. In support of this effort, METC is sponsoring the development of high-temperature, high-pressure ceramic membranes that can function as a means to clean the hot contaminant gases produced in these coal conversion systems. By operating at high temperatures and pressures, these membranes could improve the economics of advanced power generation systems by significantly reducing gas cleanup and separation costs.

METC initiated the high-temperature ceramic membrane development program in 1988. The program logic, provided in Figure 1, follows a step-by-step scaling-up approach with the most near-term membranes undergoing investigation and development first. Work is currently being performed to evaluate passive and electrochemical membranes in IGCC and DCFT environments. If these membranes can successfully operate under simulated environments at lab-scale, membrane modules will be fabricated and tested under actual coal gasification and combustion conditions at larger scale. Development of the more advanced catalytic and facilitated transport membranes is just now beginning, but will also be brought along in the systematic logic of the membrane development program.

As shown in Figure 2, two types of gas separations are being investigated: bulk separation of valuable products such as hydrogen (H_2) (a minor emphasis for power generation systems), and the selective removal of gaseous contaminants such as ammonia (NH_3), hydrogen sulfide (H_2S), and oxides of nitrogen (NO_x) and sulfur (SO_x), which are found in coal-derived gas in low concentrations. The membrane operating conditions of interest are temperatures between 540 and 1,230 °C, and pressures between 1 and 7 MPa (150 and 1,000 psia).

SYSTEM DESCRIPTIONS

A central mission of DOE/METC is the development of advanced coal conversion systems for the production of power. Contaminants produced during the conversion of coal to gaseous and particulate forms are related to deposition, component erosion, and corrosion problems in DCFT and IGCC systems. Figure 3 shows a schematic of both systems.

Direct Coal-Fueled Turbine Systems

The DCFT system uses dry pulverized coal or a coal-water slurry (CWS) as the fuel. The coal is burned directly in the combustor, and the gas is expanded in the turbine. In this system, the combustor is generally external to the turbine and particles with mean diameters greater than 10 μm must be removed from the exhaust gases between the combustor and the turbine inlet. Depending on the specific system, contaminants need to be removed at temperatures between 980 and 1,230 °C and at pressures of 0.8 to 3.5 MPa (120 to 500 psig) (1). It is believed that particles and alkali and sulfur compounds represent the most significant control problems (2). Protection of the turbine components and pollution control are of primary importance.

DCFTs are in their initial stages of development, and contaminant control requirements and operating regimes have not firmly been established (Table 1). Recent developments in the METC Heat Engines Program have shown effective operation in component testing at bench-scale facilities using highly beneficiated CWS with low sulfur and ash contents. The METC Gas Stream Cleanup Program is

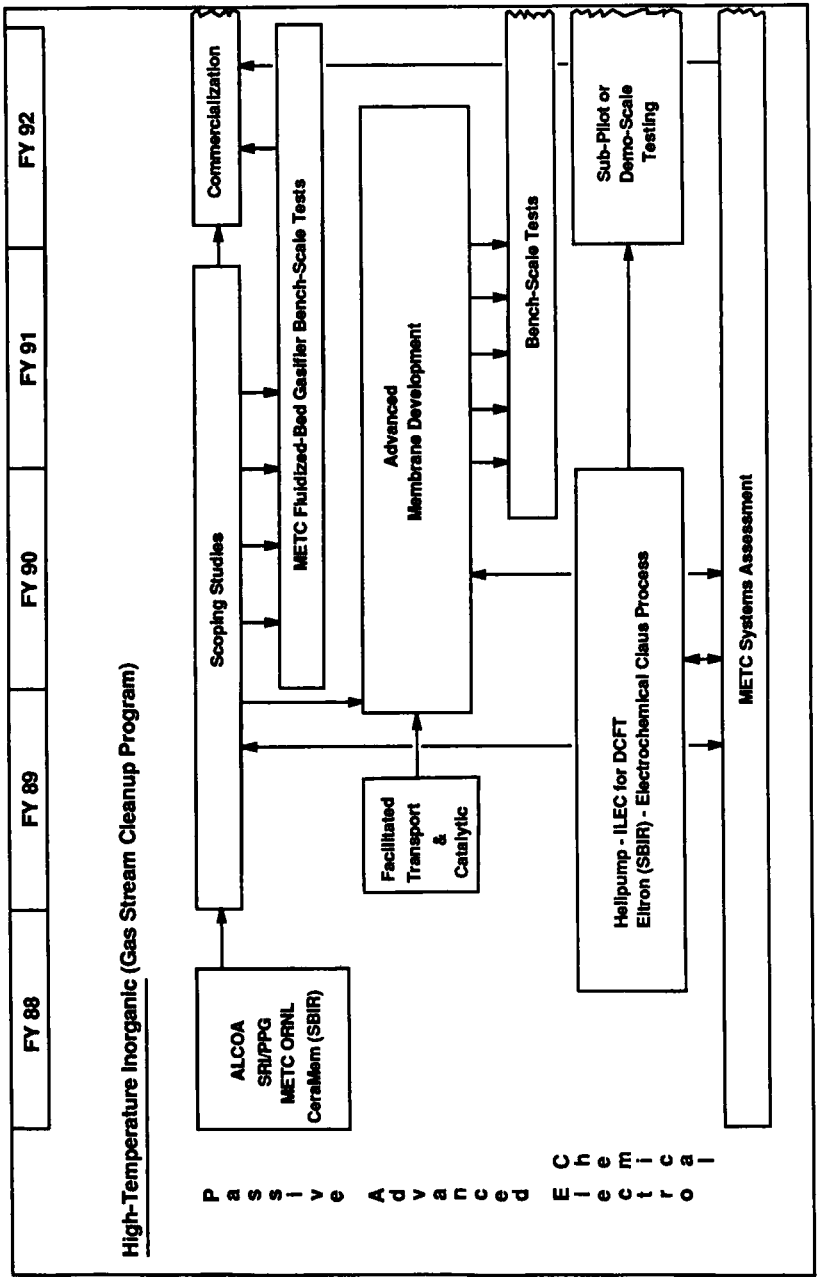


Figure 1. Membrane Development Program

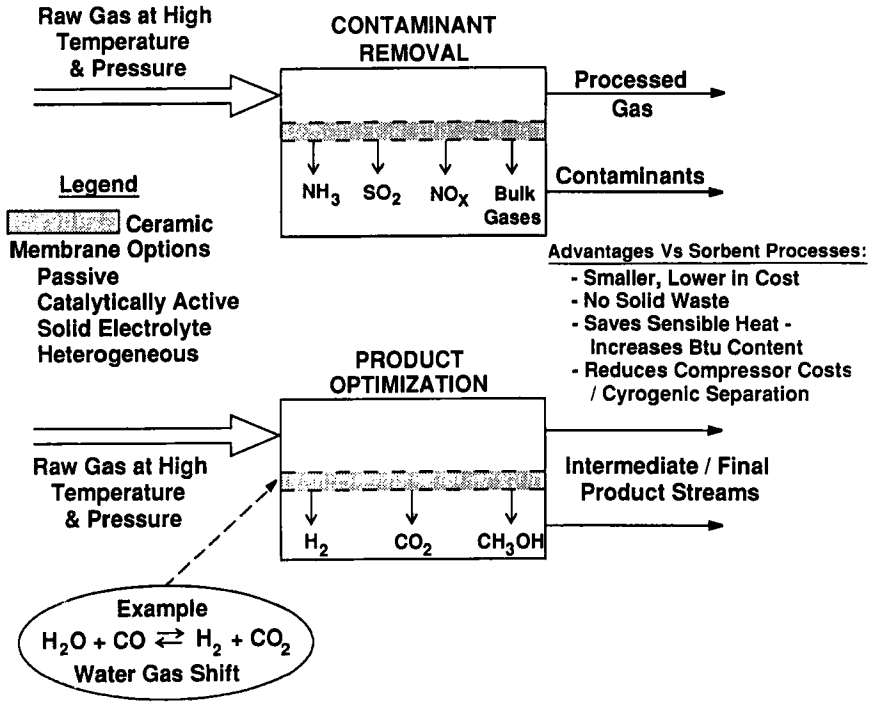
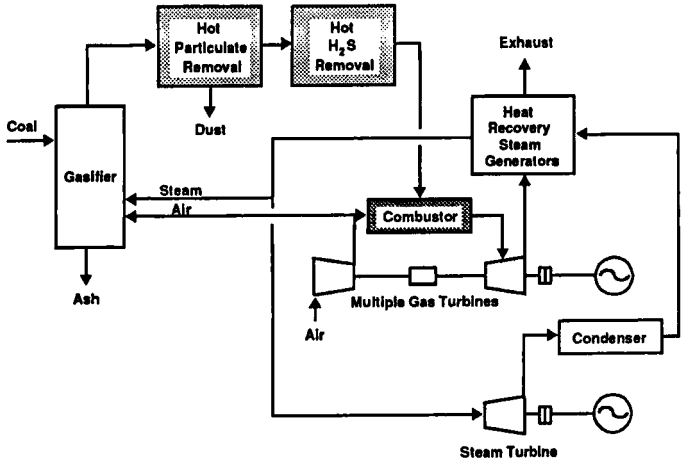


Figure 2. Membrane Separation of Gases

Table 1. Preliminary Conditions/Goals of the Direct Coal-Fired Turbine System

Temperature:	980-1,230 °C
Pressure:	0.8-3.5 MPa (120-500 psig)
Uncontrolled Particulate Loading:	
	Undefined g/scf[a]
Outlet Particulate Loading:	
	1 > 5μm ppmw[b]
Sulfur:	≤ NSPS[c] Limits
Alkali:	TBD[d]
Ammonia (Nitrogen):	*[e]
Halogen Compounds (HCl, etc):	*

a These are nominal loadings after one stage of cyclones; b At the outlet of the particulate control device; c New Source Performance Standards for electric utility solid fuels; d To be determined; e Controlled without hot gas cleanup.



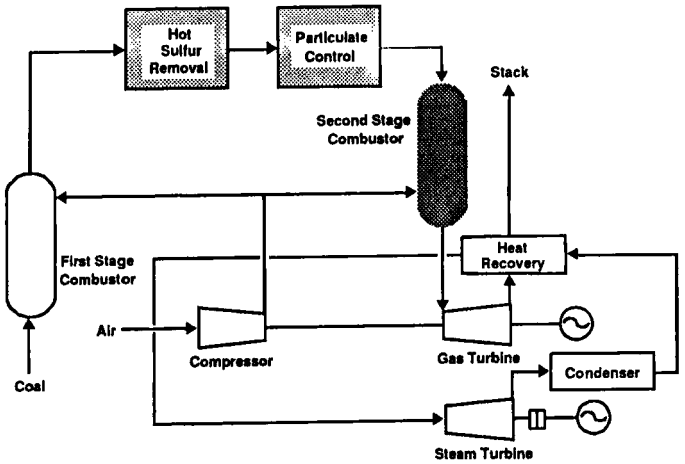


Figure 3. Coal-Fueled Power Generation Systems

closely following the development of the new DCFT systems in order to assist in and identify cleanup requirements. Material of construction problems, and cost effective sulfur and gaseous alkali capture and removal at the high temperatures (more than 1,100 °C) appear to be the primary technical limitations to contaminant control. This is particularly true in the use of minimally-cleaned coal feeds where sulfur, alkali, and particulate loadings are several magnitudes higher.

Integrated Gasification Combined-Cycle System

For power generation from coal, IGCC systems promise to be an efficient and economical route for modular power plants. In IGCC systems, the gasifier converts coal into a gaseous fuel by reaction with an oxidant and steam at a high temperature. To fully integrate the IGCC system, it is necessary to closely couple the temperature and pressure of the gasifier and turbine. Various contaminant control subsystems must be integrated into the IGCC system in order to produce a fuel that contains tolerable levels of contaminants. To preserve system efficiency and reduce capital costs, particles and gaseous contaminants are removed from the fuel gas before the gas is combusted and expanded through the gas turbine.

There are many configurations of IGCC systems. Each type of gasifier requires a different type and level of cleanup. Fixed-bed gasifiers deliver fuel gas at temperatures up to 540 °C, fluidized-bed gasifiers in the 650 to 900 °C range, and entrained-flow gasifiers at temperatures up to 1,540 °C. While some gas cooling may be required, removing sulfur, nitrogen, and gaseous alkali metals at these high temperatures is an area of significant challenge (Table 2). The combination of high fuel feed temperatures and

Table 2. Conditions and Goals for Integrated Gasification Combined Cycle Systems

Temperature:	540-980 °C
Pressure:	0.8-7 MPa 120-1,000 psig)
Uncontrolled Particulate Loading:	200-3,000 ppmw[a]
Outlet Particulate Loading:	1 > 5μm ppmw[b]
Sulfur:	≤ NSPS Limits for SO_2
Alkali:	< 0.02 ppmw
Ammonia (Nitrogen):	≤ NSPS Limits for NOx Following Combustion
Halogen Compounds (HCl, etc.):	*[c]

a These are nominal loadings after one stage of cyclones; b At the outlet of the particulate control device; c Controlled without hot gas cleanup.

NOTE: There are two specifications, i.e., for GT operation and for NSPS.

contaminant control requirements makes it necessary for additional engineering development before IGCC systems incorporating hot gas cleanup can be commercialized.

CERAMIC MEMBRANE APPLICATIONS

In advanced coal-based IGCC and DCFT systems, ceramic membranes act as the primary gaseous contaminant control following particulate removal. Figures 4 and 5 are conceptual IGCC and DCFT system diagrams with ceramic membranes placed in the flowsheets. Integrating these membranes into advanced coal-based systems is expected to allow gas separation without paying the penalties of higher capital costs, energy losses, and wastewater treatment costs associated with the cooling steps required in conventional gas separation operations, particularly using polymeric membranes (3). Coal-based systems require a number of separation steps to remove contaminants such as particulates, SO_x, NO_x, NH_3 or H_2S. H_2 might also be removed for use in liquid product upgrading or the removal of CO_2 might be useful for improved fuel cell operation. In these cases, membranes can be compared with other gas separation methods to determine which most effectively meet system requirements for gas purity, temperature, and pressure and which have the lowest costs. This comparison should be made in terms of capital cost and, as the bottom line, the cost of electricity (COE).

In terms of a typical 250 MWe IGCC system, H_2S removal involves a combination of limestone sorbent in the gasifier bed and external desulfurization with a zinc ferrite sorbent. In this case, H_2S separation units are estimated to cost approximately $93/kW as installed cost or 10% of the total capital cost. The cost in terms of COE (capital and O&M cost components included) would be about 6 mills/kWh in constant 1987 dollars. In DCFT systems, SO_2 would typically be removed with limestone or dolomite in the combustor or in a separate desulfurizer. For such a system, the capital cost in terms of the installed cost is estimated to be about $27/kWe with a COE of about 4 to 5 mills/kWh. These DCFT costs are for a plant of 4 to 5 MWe size and are expected to be somewhat lower for commercial-size DCFT systems. These cost figures provide a target cost that all new sulfur removal methods for IGCC and DCFT systems -- including those with membranes -- must beat.

To illustrate the comparison of a membrane-based desulfurization system with a conventional calcium-based desulfurization method in a DCFT system, consider a conceptual desulfurization method and its associated costs. Assume a ceramic membrane is used as a separation device in a 207 MWe system to separate 90% of the SO_2 from the main gas stream to meet federal air quality standards. Again, assume the bulk of the SO_2 would go to the permeate, which comprises 10% of the total fuel gas, and the remaining 10% of the SO_2 stays with the retentate, which is then sent to the turbine to produce electricity. The SO_2 in the permeate may be captured by a sorbent or may be converted to sulfur or sulfuric acid. The remaining permeate is either exhausted to the atmosphere or compressed to make it suitable for delivery to the turbine. If the

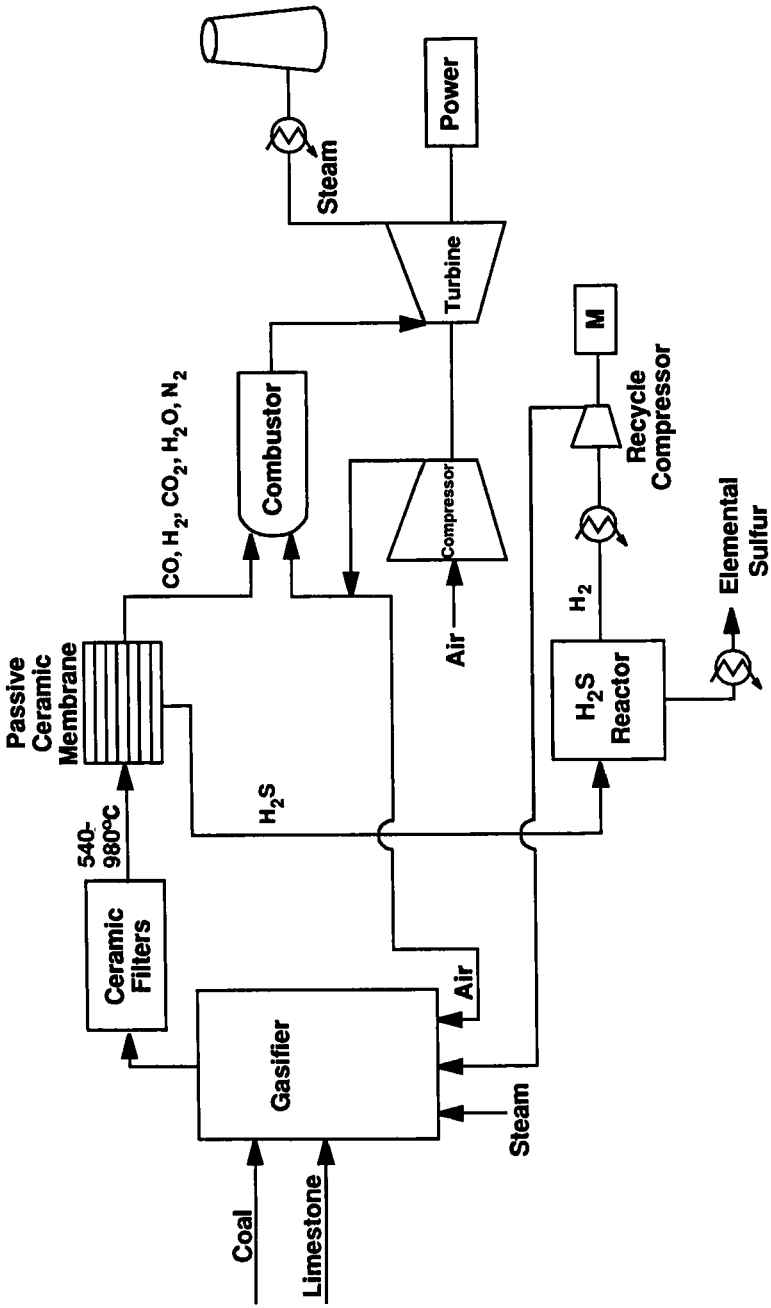


Figure 4. Separation of Acid Gases From IGCC Fuel Gas Streams

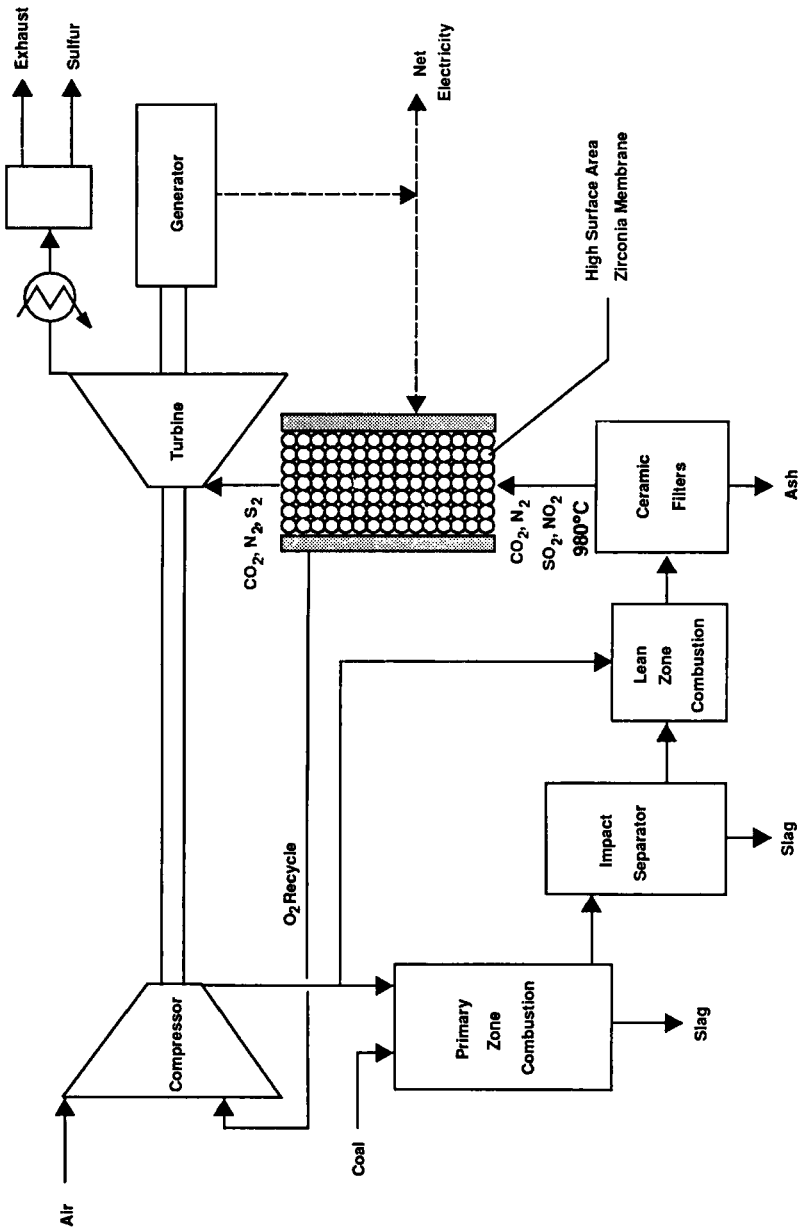


Figure 5. Electrochemical Membrane Removal of SOx/NOx as Applied to Solar Turbines, Inc., Direct Coal-Fueled Turbine

permeate is sent to the atmosphere, mathematical model simulation predicts that the production of electricity is reduced by 10% or 21 MWe. This represents an intolerable loss. If the permeate is recompressed, electricity costs would be about 6 mills/kWh, assuming a conservative 1.4 MPa (200 psi) pressure drop across the membrane. These costs, plus capital costs for the compressor and for a process to remove the SO_2 from the permeate, would yield a desulfurization system cost that is greater than the target calcium sorbent-based process. In this case, the membrane-based system is not the best approach, but a similar procedure could be carried out with other membrane-based systems in a search for economically favorable systems (4).

Many factors must be taken into account to determine the technical and economic feasibility of a membrane-based separation system. This type of assessment is being used to pinpoint the processes worthy of exploration, and to guide experimental work that will determine whether a specific type of membrane has the potential for eventual commercialization.

MEMBRANE DEVELOPMENT PROGRAM

METC initiated work in ceramic membranes in 1988, with programs to evaluate electrochemical and passive ceramic membranes. The program is now moving into the development of catalytic and facilitated-transport membranes. It is hoped that these membranes will display more effective removal and be more specific for the gases of interest than passive membranes.

Passive Membranes

METC is currently evaluating passive ceramic membranes for their potential to separate gases in the high-temperature process streams of IGCC and DCFT systems. The gas separations of interest in IGCC systems include H_2 separation, CO_2 separation to improving the heating value of the product stream, and the removal of gaseous contaminants such as H_2S and NH_3, which negatively impact the process efficiency, the environment, or the downstream components. The separations of interest in DCFT systems involve the selective removal of SO_x and NO_x.

Two projects are currently underway to evaluate commercially-available passive ceramic membranes for the applications of interest. Alcoa Separations Technology Division is evaluating their 40 Å pore diameter, tubular alumina membranes (Figure 6), and SRI International is evaluating the silica hollow-fiber membranes developed by PPG Industries (Figure 7).

Alcoa has completed a series of thermal stability tests, which demonstrated that the existing membrane is suitable for use in the gas atmospheres expected in IGCC and DCFT systems (5). In addition, current gas separation theory was extrapolated to high temperatures and high pressures to develop a mathematic model, which attributes gas permeation through the membrane to Knudsen dif-

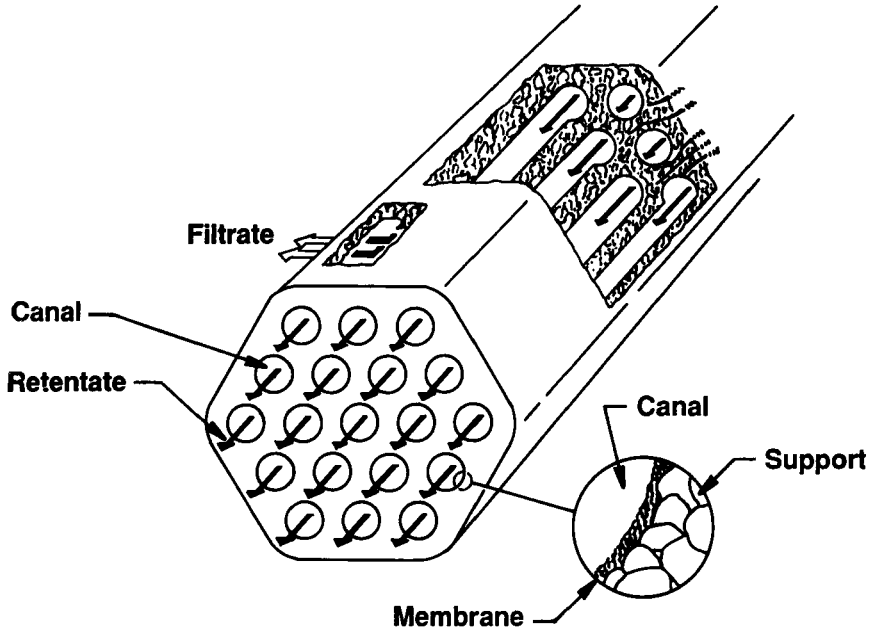


Figure 6. Alcoa Separations Technology Division Membrane Configuration

fusion, Poiseuille flow, and surface diffusion. This model will provide predictive capabilities at the conditions of interest to advanced power generation systems. A high-temperature seal system was developed to connect the ceramic membrane tube to the outer shell assembly in the experimental apparatus. Alcoa is currently conducting screening tests on the membranes to determine the gas permeability at a range of temperatures and pressures, and gas compositions that simulate those found in IGCC and DCFT systems. Based on the results of these tests, the membranes will be modified to enhance gas separation performance, and additional tests will be conducted to determine the performance of the modified membranes.

At SRI, a mathematical model incorporating ideal adsorbed solution theory to account for multicomponent adsorption and surface diffusion was developed to predict membrane performance. Several high-temperature sealing options have been identified and are being explored. Initial data obtained at room temperature with the silica hollow fiber membrane indicated that the permeability of gas appears to be strongly related to molecular size rather than molecular weight (5). Once the high-temperature seal work is completed, screening tests to determine the gas permeability at feed temperatures up to 870 °C and pressures up to 3.5 MPa (500 psia)

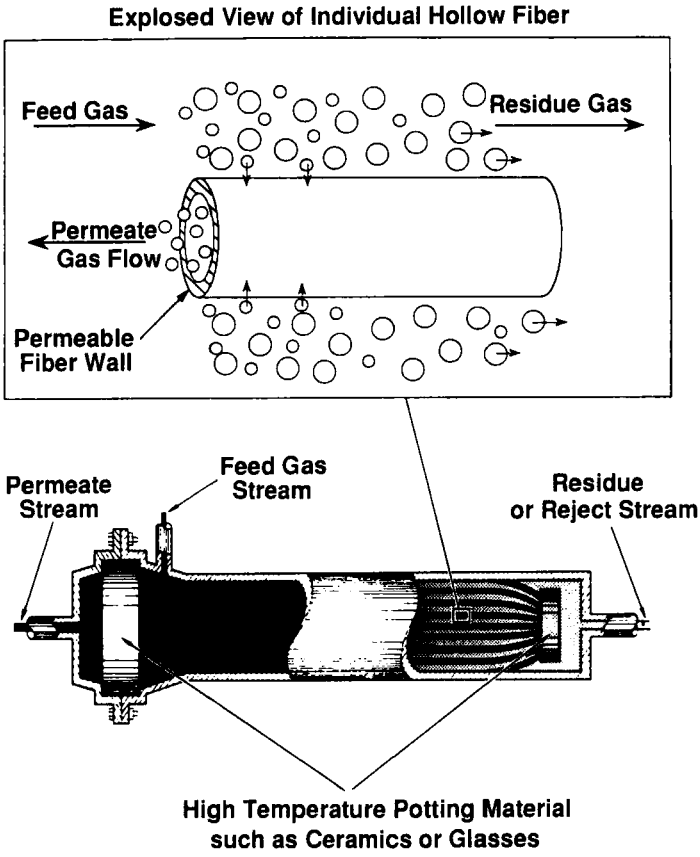


Figure 7. Conceptual Design of High-Temperature Membrane Module Showing Individual Silica Hollow Fiber Membrane

will be initiated. As with the Alcoa project, the results of these tests will lead to membrane modification to enhance performance.

Work is also being performed at Oak Ridge National Laboratory (ORNL) to explore the applicability of ceramic materials technology developed for uranium enrichment to separate gases at high temperatures in IGCC systems. The objective of the program is to develop membrane separation systems to separate H_2 and acid gases such as CO_2 and H_2S from synthesis gas. Tubular alumina membranes are being fabricated at the Oak Ridge Gaseous Diffusion Plant for testing at ORNL. Significant improvements have been made in fabricating these membranes (6). The average pore diameter was successfully reduced

from about 300 Å for the original membranes to 30 to 40 Å for the present membranes. Membrane screening tests at temperatures up to 450 °C and pressures up to 4 MPa (600 psia) are scheduled to begin in October 1989. ORNL is actively pursuing declassification of the uranium enrichment technology and transfer of the membrane technology to industry.

In-house researchers at METC have constructed a lab-scale unit to investigate the separation of H_2 from simulated coal gasification mixtures at temperatures up to 450 °C and pressures up to 1.4 MPa (200 psia). Work to date has been on tubular alumina membranes and tubular Vycor glass membranes. Future plans call for modification (to reduce the pore size) and subsequent testing of the alumina membranes, and the study of catalytic membranes. A pilot plant membrane module (Figure 8) is being planned in 1990 to test membranes under actual fluidized-bed coal gasification conditions. The gasifier has a 152 mm (6 inch) diameter, and operates at temperatures up to 650 °C and pressures up to 3 MPa (440 psia). The membrane module will be placed downstream from a zinc-ferrite sorbent, hot gas desulfurizer unit, and will be capable of processing up to 4 L/s (500 scf/h) of product gas at a temperature of 540 °C. A 25 mm (1 inch) diameter cyclone and two thimble filters will be installed after the desulfurizer and before the membrane to capture particles. The most valuable data to be obtained with this unit will be related to the performance of membrane materials in an actual gasification environment.

Electrochemical Membranes

The Helipump Corporation is developing a NO_x/SO_x removal technology that employs an oxide-ion conductive ceramic to reduce process gas contaminants to their elemental constituents. The Helipump concept is to be used on an integrated basis to clean the combustion product gas contaminants from a DCFT system. As shown in Figure 9, the NO_x/SO_x gases are selectively reacted at the high-surface area cathode in the presence of water, oxygen, and other gases by the application of low voltage. Helipump has fabricated a lab-scale materials test reactor for high temperature, simulated gas evaluation screening.

The experimental efforts to date have centered primarily on the development of electrocatalysts for the selective reduction of NO_x and SO_x. Initial efforts used fully stabilized zirconia discs with transition metal oxide coatings employing applied voltages up to 1.25 V in the presence of various cathodic atmospheres. Subsequent development led to the fabrication and testing of a very high surface-to-volume ratio honeycomb-configured ceramic electrolyte. With the objective to determine the optimum electro-catalyst, Helipump has conducted material screening tests using transition metal electrocatalysts. Tests have been conducted at temperatures of 650 and 1,050 °C and at gas flow rates of 100 and 35 cm^3/min. As the amount of oxygen in the gas stream is increased from 0 to 8%, reduction of NO_x and SO_x is measured. Decreases in

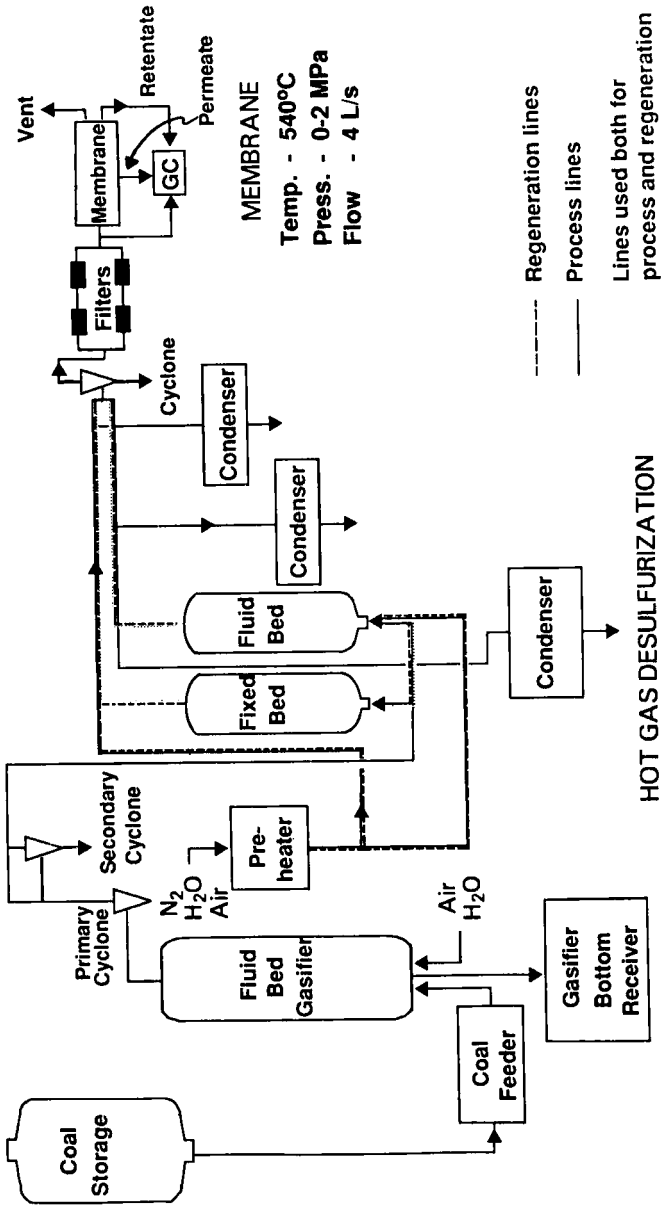
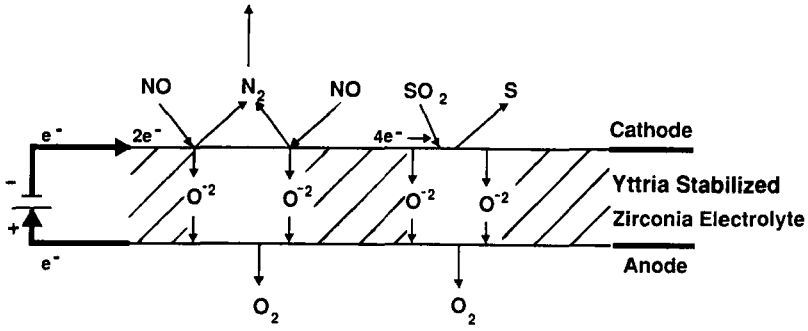


Figure 8. METC Pilot-Plant Membrane Module



$$\text{Cathode} \begin{cases} SO_2 + 4e^- \rightarrow 1/8\ S_8 + 2O^{-2} \\ NO + 2e^- \rightarrow 1/2\ N_2 + O^{-2} \\ NO_2 + 4e^- \rightarrow 1/2\ N_2 + 2O^{-2} \end{cases}$$

$$\text{Anode} \quad \{ 2O^{-2} \rightarrow 4e^- + O_2$$

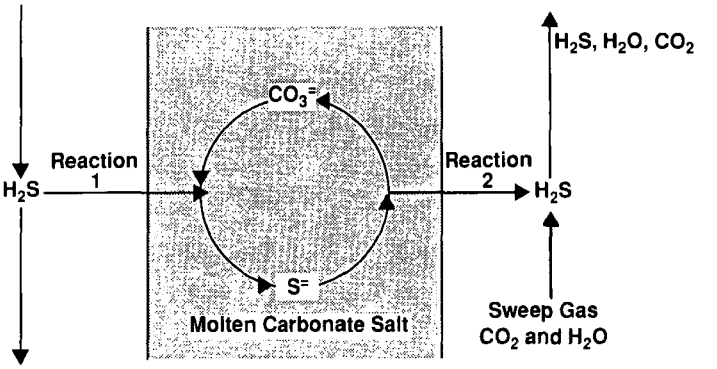
Figure 9. Solid Electrolyte Membrane for SO_2 and NO_x Removal

NO_x ppm concentration as high as 91% and 38% in SO_x have been demonstrated. The screening tests are continuing with other electrocatalysts.

Eltron Research, Inc. recently completed research under the DOE Small Business Innovative Research (SBIR) Program on an electrochemical Claus process for sulfur recovery. The electrochemical oxidation of H_2S to yield sulfur and water was achieved at 900 °C using a fuel-cell-configured reactor. The reactor possessed the general configuration of a yttria-stabilized zirconia electrolyte with a cathode material of perovskite ($LaSrMnO_3$), and a platinum electrode and an anode electrocatalyst. The anode electrocatalysts experimentally investigated for promoting the H_2S oxidation reaction included tungsten disulfide and the thiospinels of $CuNi_2S_4$, $CuCo_2S_4$, $CuFe_2S_4$, $NiCo_2S_4$ and $NiFe_2S_4$. The predominant oxidizable electroactive species present in the cell reactor anode compartment was shown to be H_2, originating from the initial thermal dissociation of H_2S at an operating temperature of 900 °C. Rapid anode kinetics were found. The empirical trend for the anodic reaction, expressed as the exchange currents per geometric area, was observed to be $NiFe_2S_4 > WS_2 > CuCo_2S_4 > CuFe_2S_4 \approx NiCo_2S_4 > CuNi_2S_4$.

Reactive Ceramic Membranes

METC is initiating the development of reactive ceramic membranes for contaminant control at high temperatures and pressures in IGCC systems. Ceramic membranes that employ a facilitated transport or catalytic approach will be developed. Facilitated transport membranes such as that shown in Figure 10 are expected to exhibit increases in selectivity and permeability compared to passive ceramic membranes, using molten alkali carbonate salts as the



Reaction 1

$$H_2S + CO_3^= \leftrightarrow S^= + H_2O + CO_2$$

Reaction 2

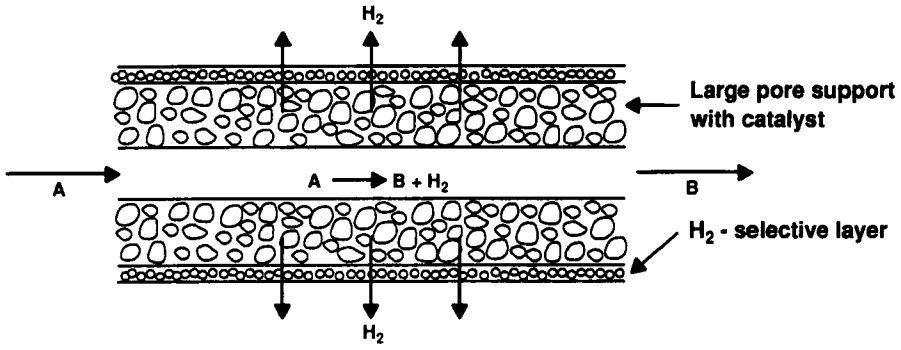
$$S^= + H_2O + CO_2 \leftrightarrow CO_3^= + H_2S$$

Figure 10. Reactive Ceramic Membrane Facilitated-Transport Concept

reactive compound incorporated into ceramic supports (7). Catalytic membranes (Figure 11) are expected to convert gaseous contaminants such as H_2S and NH_3 to products that can then be either used in the process or selectively removed from the system. METC expects that reactive membranes will improve the efficiency of hot gas separation beyond the current state of the art in membrane technology. The initiation of several projects is expected by the end of 1989.

SUMMARY

One can see from the discussions provided here that the METC Membrane Development Program is in its first years of research. In summary, lab-scale facilities have been and are being built to subject individual membranes to the very severe IGCC/DCFT temperatures and pressures. Along with their specific membrane development work, ALCOA and SRI have set out to develop useful tools for the predictive modeling of passive membranes for the IGCC and DCFT applications. ORNL has fabricated a membrane in the 30 to 40 Å pore diameter range and will begin full testing in the near future. METC has likewise completed initial testing of alumina and Vycor



Examples of decomposition reactions

$$H_2 \overset{Cat.}{\leftrightarrow} S + H_2$$

$$2NH_3 \overset{Cat.}{\leftrightarrow} N_2 + 3\,H_2$$

Figure 11. Reactive Ceramic Membrane Catalytic Concepts

glass membranes at lab-scale. METC has planned efforts to test membranes against actual high-temperature/high-pressure coal-gasification gases at pilot-plant scale. This will represent the first bona fide test in the harsh coal-derived gas stream environment. Electrochemical membrane development has shown that NO_x/SO_x in a DCFT environment and H_2S in a fuel cell environment can be selectively reduced to their elemental constituents. Overall system analyses have been initiated. System target costs have been estimated and generalized criteria to determine economic feasibility have been stated.

While there may be potential benefits for inorganic-membrane gas-separation processes, there are obvious data gaps and uncertainties to be addressed; these data gaps and uncertainties point toward research and development opportunities. The hardware development of seals and sealing materials is critical to demonstrating the overall technical feasibility of any membrane component system. Other challenges yet to be faced include the compatibility of high-temperature materials, durability of ceramic membranes above 980 °C, and performance degradation caused by the presence of coal-derived gas contaminants, notably very fine particulate matter and vapor-phase alkali.

Most research efforts to date have yielded only preliminary results. Accordingly, any prediction of the true potential of inorganic-membrane gas separation in DCFT and IGCC systems applications must be considered premature. However, the prospects of

using membrane technology appear quite promising for improving gas separation and contaminant control in advanced coal-conversion processes.

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