A multi-sheet module with about 0.5 ft^2 membrane area was prepared and tested continuously with a laboratory-blended FCC H_2/HC mixture (containing 20% H_2, 20% CH_4, 16% C_2's and 44% C_3's) over a six month period. No decrease in membrane performance was observed (1).

Thus, as a part of the proof of concept, it was demonstrated that the SSF membrane can be reproduced on porous graphite sheets and that these membranes are stable with continued use with a clean H_2/HC mixture.

3.0 MEMBRANE FABRICATION SCALE-UP

The objectives of the membrane fabrication scale-up were to develop the following:
(i) A support for coating membranes that is scalable, commercial and cost effective,
(ii) A membrane preparation method that is reproducible, scalable and cost effective,
(iii) A 1 ft^2 area membrane for demonstration of scalability and field testing,
(iv) Membrane performance data for process engineering, design, and first pass economics.
The following sections discuss the results for each of these objectives.

3.1 Substrate for Coating Membrane

The list of requirements for a scalable support for the SSF membrane is shown in **Table 2**. Several different types of porous supports meet the requirements, including tubes, multi-channel structures and hollow fibers. **Table 3** summarizes the supports that were evaluated and also indicates the ones on which the SSF membranes could be coated successfully. In the evaluation of the various porous supports, the pore size, pore size distribution, porosity, coating thickness and multiple coatings were investigated. Some of the criteria listed in **Table 2** were developed based on the results from these screening evaluations. Based on the support cost and membrane performance, it was decided that the focus for detailed studies would be on ceramic tubes and monoliths with homogeneous structures. The concept of tailoring ceramic tubes for coating gas separation membranes is not widely practiced. Most researchers developing ceramic gas separation membranes have focused on coating commercial alumina tubes used in liquid microfiltration and ultrafiltration applications. These tubes are typically asymmetric structures with a large pore (~ 100 micron pore) α-alumina base, coated with multiple layers of γ-alumina coated from γ-alumina sols to prepare tubes with surface pores ranging from 40 A to 2000 A (e.g., Ref 8). Recently there have been some efforts in sol-gel coating of cordeirite monoliths (multi-cell structures) with γ-alumina for use of the structures as particulate and liquid filtration devices (9). The above supports are expensive -- typically \$ 500-2,000/ft^2 of membrane area -- and have not been used in gas separations because of large membrane area requirements and the corresponding large membrane capital costs. Thus, the development of a low cost (< \$50/ft^2) ceramic support for the SSF membrane is a critical factor in successfully scaling up this membrane.

TABLE 2

REQUIREMENTS FOR SSF MEMBRANE SUPPORT

1. Pore size 50 A to 7,000 A
2. Low surface roughness
3. Narrow pore size distribution - max pore size < 1.5 micron
4. Total Porosity > 20%, preferably about 40%
5. Stable in temperature range 500 C - 1000 C
6. Thermal expansion coefficient 5 - 10 x 10^{-6}/°C
7. Tube ends sealed to prevent by-pass flow through cross-section
8. Can tolerate heating and cooling rates of up to 20°C/min
9. Mechanical strength to withstand $\Delta p > 250$ psig
10. Materials can be carbon, alumina, cordeirite (and other ceramics), glass
11. Cost of support is low

TABLE 3

SUPPORTS EVALUATED FOR COATING SSF MEMBRANE

Support Type	Cost	Success
1. Porous carbon tubes with different pore sizes	H-M	P
2. Hollow porous carbon fibers	M	N
3. Asymmetric α-alumina tubes with different pore sizes	H	Y
4. Cordeirite and mullite tubes	L	Y
5. Multi-channel cordeirite structures coated with γ-alumina	M-L	I
6. α-Alumina tubes with homogeneous structures	L	Y
7. Porous glass tubes	H	N
8. Cordeirite and mullite homogeneous monoliths	L	O

H = High, M = Medium, L= low
P = Partial success
N = not successful
Y = successful
I = incomplete/not successful due to methods used
O = not evaluated

SSF membranes were prepared on alumina, mullite, cordeirite and carbon tubes with pore sizes varying from 0.2 to 5 microns. These tubes are homogeneous in structure and have the same pore size across the tube cross-section. It was determined that membranes with the desired separation properties could be prepared with multiple coats on supports with pores < 1.0 micron. It was also determined that a narrow pore size distribution was critical in preparing a membrane with target separation properties, and pores > ~1.5 micron were undesirable. It was very significantly determined that a membrane with target properties could be reproducibly prepared in a single coat on a ceramic support with a pore size of ~0.3 micron and a maximum pore size <1.0 micron. The total porosity in such supports is >20%. Thus, the outcome of the screening work was to focus on the development of the alumina tubes for optimization of the membrane properties.

3.2. Alumina Tubes for SSF Membranes

In the optimization of the alumina tubes, the following tube characteristics were varied : (i) porosity, (ii) strength, (iii) binder type (iv) alumina particle size (v) tube end finish. The concentrations of the alumina/binder/lubricant/water were not varied in these experiments. The variations in the porosity and strength were achieved by firing the green extruded ceramic tube at different temperatures. The alumina tubes were prepared at a variety of conditions by the tube supplier.

Table 4 shows the tube firing/fusion temperatures of the alumina tubes and the corresponding tube properties. To balance the porosity with the mechanical properties of the tubes, a tube firing temperature of 1430 C was selected with this specific particle size alumina. This alumina allowed one to prepare tubes with the desired pore size and a very narrow pore size distribution. It was noted that the tubes prepared at 1430 C were prone to chipping at tube ends. The problem of tube-end chipping was solved by rounding the tube ends after firing. **Table 4** also compares tubes prepared by using a solid binder vs a gel binder. The use of a solid binder resulted in the formation of pits on the tube surface when the binder volatilized from the surface (**Figure 6**). This resulted in membranes with defects. The problem was solved by replacing a solid binder with a gel binder which coated the surface of the alumina particles and distributed uniformly in the extrusion compound (**Figure 6**).

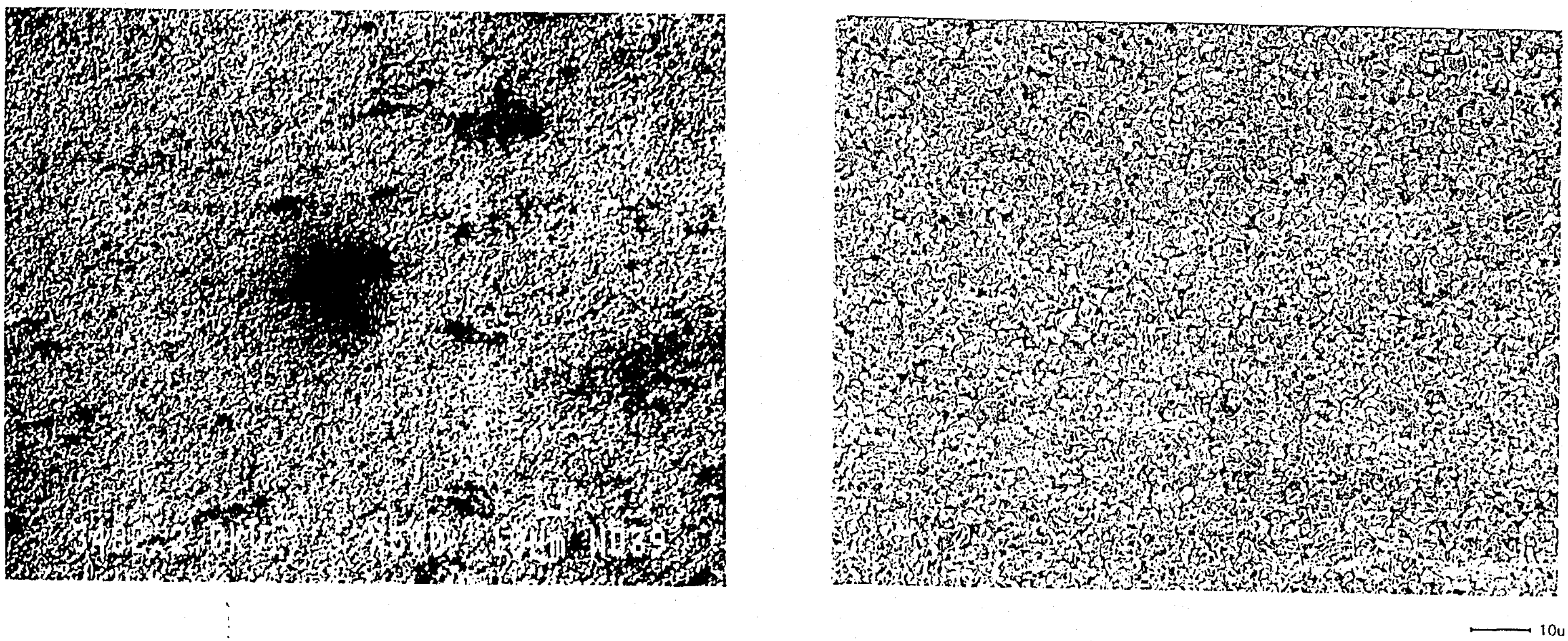
A smaller particle size alumina for preparing the tubes was also evaluated as shown in **Table 4**. Tubes with the smaller particle alumina could be fired at ~ 1200 C while having acceptable mechanical properties. This option was eliminated because of lower gas permeation through these tubes. However, with optimization, these tubes could be possible candidates for separation applications at higher membrane feed pressures.

TABLE 4

OPTIMIZATION OF THE STRUCTURE OF THE ALUMINA TUBES

Firing Temperature, C	Binder	Porosity* %	Pore size* μ	Pore* Volume,cc/g	Mechanical Strength
Tubes with larger particle size alumina :					
975	gel	41.0	0.369	0.192	weak/brittle
1200	gel	37.6	0.276	0.159	weak/brittle
1430	gel	27.5	0.274	0.093	strong/ends chip
1450	gel	26.4	0.290	0.090	strong/ends chip
1470	gel	23.3	0.227	0.073	strong
1550	gel	12.4	0.228	0.036	strong
975	solid	39.1	0.281	0.171	weak
1200	solid	37.2	0.306	0.155	weak
1500	solid	9.7	0.181	0.028	strong
Tubes with smaller particle size alumina :					
975	gel	40.8	0.092	0.183	strong/ends chip
1200	gel	33.4	0.092	0.130	strong
1550	gel	0.4	--	0.001	strong/dense

* Measured by mercury porosimetry



(a) (b)

Figure 6. SEM Micrographs Showing Pits in Alumina Tubes due to Solid Binder (a), and the Absence of Pits with a Gel Binder (b)