Shell/METC High-Temperature, High- Pressure Filtration Program

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DISCLAIMER

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ABSTRACT

The purpose of this paper is to present the program objectives and non-proprietary results of the high temperature, high pressure filtration work done under the Shell/METC Cooperative Research and Development Agreement (CRADA) 93-011. The primary purpose of this CRADA was to collect data relevant to the design and operation of dry particulate solids filters employing rigid ceramic (silicon carbide) filter elements in a gasifying environment at conditions of commercial interest; e.g., temperatures up to 1100 °F and system pressures between 300 and 350 psia. Shell provided the ceramic filter elements and evaluated the exposed filter elements. METC installed the filter elements and operated their 10" Fluid Bed Gasification and Cleanup facility as required for their Hot Gas Clean-up Test Program. Filter elements were removed from service after approximately 254, 525 and 868 hours of on-line operation. The exposed filter elements were analyzed and compared to an unexposed element with respect to changes in physical property.

INTRODUCTION

Coal is an abundant fuel which has been used for the generation of power. Coal combustion or gasification converts the chemical energy of this fuel into power via the Rankine cycle or the combination of the Brayton and the Rankine cycle. The reality of coal combustion or coal gasification is that its intermediate products are dirty and pollute the air, water and the solids by-products. Cleaning up these intermediate products is necessary, complex and costly.

Coal combustion as practiced always involves reducing particulate emissions and sulfur oxide emissions. Improved emissions to the atmosphere means removing "all" of the particulates and/or removing "most" (greater than 95%) of the sulfur oxides. Added to this cleanup is removal or avoidance of nitrogen oxide formation, halide removal, and mercury removal. In coal gasification, sulfur is easily converted to elemental sulfur; particulates are removed to less than .01% wt.; and nitrogen compounds are converted to basic nitrogen or must be reduced by selective catalytic reduction. Halides, alkali, trace elements and mercury are removed by solution or absorption to extremely low levels.

Integrated coal gasification (IGCC) is being demonstrated in various forms at locations around the world. Removal of contaminants to very low levels has been practiced in "cold gas cleanup" unit operations (usually at ambient to moderate process temperatures). Cold gas cleanup has been practiced in such gasification technologies developed by Destec, Prenflo, Texaco and Shell. Cold gas cleanup equipment and operations are not very costly compared to other process steps such as high temperature heat transfer equipment. There remains the desirability of dry gas cleanup technology development at high to moderate temperatures to improve thermal efficiency and, hopefully, reduce capital and operating costs.

The objective of dry gas cleanup is to keep the syngas dry, the solids dry, and reduce solids/water contact and thus avoid potential leaching or hazardous waste generation. It is always desirable to reduce water effluent generation and contamination and reduce water cleanup costs. (It must be noted that coal gasification is at least one to two orders of magnitude cleaner than coal combustion.)

Shell Oil and Shell Internationale (SIPM) demonstrated and reported on the success of clay bonded silicon carbide porous ceramic candles in dry particulate service in 1989 to 1991. The 4175-hour demonstration of these porous ceramic filter elements in the reducing atmosphere of the Shell entrained bed gasifier showed that ceramic candle filters could be used to effectively remove particulate solids at 400 to 500°F and 350 to 450 psia. At these conditions, particulate removal exceeded 99.5 -99.95% weight on a particulate solids basis or 99.99% on a gas mass flow rate basis. The average inlet particulate loading, depending upon the process configuration, was in the range of 2-20 g/Nm^3 or 150-1500 lb/hr in a 60,000-65,000 lb/hr gas stream.

Shell Oil contracted with Westinghouse Science and Technology Center to evaluate the physical structure and chemical composition of the new and used filter elements. Results from this evaluation showed after 4175 hours of operation that the clay bonded silicon carbide filter elements maintained their physical integrity in low temperature (< 500 °F) gasification conditions [1]. There were, however, some microstructural changes that might affect the ultimate service life of the material. Although there were no signs of pore plugging, there was evidence that submicron particles have an affinity for adhering along the pore cavity binder surface.

Filter system design variations were studied and resulted in the construction of a single, large vessel capable of processing the equivalent of 1400 MMSCFD of syngas at the SEP Buggenum Plant in Holland,

The Department of Energy has developed a mechanism in which an industrial partner can cooperate with the Morgantown Energy Technical Center, and similar centers, in research and development of materials, catalysts, technology, and demonstration for use in a commercial venture. These CRADAs (Cooperative Research and Development Agreements) are designed to effectively transfer technology developed through government funding to industry, and to encourage industrial participation in federal programs.

In 1993, Shell Oil joined with the Department of Energy Morgantown Energy Technical Center (METC) in a cooperative research and development agreement (CRADA) to test ceramic candles at high temperature (1000 °F) in a reducing atmosphere, high pressure, fluidized bed gasifier. The purpose of these tests was to identify the feasibility of ceramic candle filtration in syngas service and add to the overall knowledge of high temperature solids filtration.

HIGH TEMPERATURE HIGH PRESSURE FILTRATION

Objectives

The purpose of this effort is to collect process data relevant to the design and operation of dry particulate solids filters employing rigid ceramic filter elements in a gasifying (reducing) environment at temperatures between 1,000 and l,l00 °F, system pressures between 300 and 350 psia, filter pressure differentials between 1 and 10 psig, filter superficial face velocities between 5 and 10 fpm, and solids loadings in the range of 2-30 g/Nm^3 (1.25 x 10^{-4} - 18.75 x 10^{-4} lbs/ft^3).

Experimental

In conjunction with shakedown, operation, and desulfurization testing at the Morgantown Energy Technology Center (METC) 10" Fluid Bed Gasification and Cleanup facility, a series of tests was completed in cooperation with Shell Synthetic Fuels Incorporated to obtain data relevant to the design and operation of dry particulate solids filters.

Shell Synthetic Fuels Incorporated provided 60 mm O.D. x 40 mm I.D. x 0.5 m long silicon carbide Industrial Filter and Pump (IFP) LayCer® 70/3 candles for use in filtering coal gas from the METC gasifier. METC installed the filters in a vessel existing in the DOE/METC cleanup facility and provided process data in exchange for ceramic filter characterization. Details of the cooperative research and development agreement (CRADA) are found in CRADA #93-011.

Seven gasifier runs were conducted over an 18 month period using five different feed stocks, as shown in Table 1, to accumulate 868 hours of operation. During this time, 3 filters were used two at a time (see Table 2) to give individual candle usage of 254, 525, and 868, respectively. During one 89-hour test, one LayCer 70/3 candle was in-line with a 3M ceramic composite filter. The face velocity through the candles was maintained nominally at 2.5 ft/min throughout the testing. This velocity is lower than the 5-10 fpm stated in the objective because going to 5 fpm would mean that only one filter element could be tested at a time.

Limiting testing to one element at a time would have limited the amount of information that could be obtained over a given run length and increased the risk of gaining no information if something should happen to the one element before the test could be completed and the material analyzed. Thus, two filter elements were always in service at any given time. Average operating conditions are given in Table 3. The blowback cycle for the filters was approximately once per hour for 100-200 msec duration. A typical analysis of the gas to the filter is given in Table 4.

Results

Proximate, Ultimate, Ash Mineral and Trace Metals for typical fly ash samples are given in Table 5, and Coulter Counter particle size analyses are given in Table 6.

Shell Oil again contracted with Westinghouse Science and Technology Center to evaluate the physical structure and chemical composition of the new and used filter elements. Figure 1 shows a scanning electron microscope photograph of a cross-section of an "as-manufactured" IFP LayCer 70/3 clay bonded silicon carbide filter element. The fine outer membrane can be seen on the far left side of the photograph. Dirty gas would flow from the left or membrane side to the right or coarse substrate side. Figures 2, 3 and 4 show photographs taken at similar (NOT identical magnifications) after 254, 525 and 868 hours of filtration service in synthesis gas from the METC MCGR 10" gasifier.

A thin layer of char remains on the outer surface (left side of the photo). Although there is some penetration of fine particles through the barrier membrane, there is no sign of filling or blocking of the coarser silicon carbide substrate. Higher magnification photographs indicate that some phase changes (i.e., crystallization) occurred along the surface of the residual binder phase that coats the silicon carbide grains in the membrane of the filter element. Scanning electron microscopy/energy dispersive x-ray analysis (SEM/EDAX) indicates that the crystal formation may have resulted from oxidation of the surface of the silicon carbide grain. This crystallization is thought to be the cause of the tensile strength loss as indicated by the room temperature and high temperature C-ring tension and compression tests shown in Figure 6 From these figures it appears that the residual strength of the matrix may have plateaued. Thus, the LayCer 70/3 filter elements appear to be approaching their "conditioned" strength.

Figure 5 shows the inside diameter of the filter element exposed for 868 hours. There is negligible penetration of fine particles. Although observed, changes in the morphology, however, were limited to the binder ligaments that bind two grains together.

SUMMARY/CONCLUSIONS

The results of 868 hours of testing at 1000 °F can be summarized as follows: 1) there were no broken clay bonded silicon carbide filter elements, 2) some fine particles penetrated the outer porous membrane, 3) there were no signs of blinding of pores, 4) C-ring tensile and compression strength tests run at room temperature and 1000 °F indicate that the clay bonded silicon carbide matrix lost some strength but appears to be approaching its "conditioned" strength.

These results were expected and are consistent with similar observations made after 4175 hours of exposure with Schumacher candle filters and 821 hours exposure with Industrial Pump and Filter (IFP) candle filters at 500 °F at the Shell Deer Park Demonstration Plant (SCGP-1) between November of 1989 and April 1991. Specifically, there was no strength loss of C-ring sections from the conditioned candle filters when they were tested at room temperature and 500 °F, but C-ring sections of the same conditioned elements did show some strength loss when tested at 1000 ° F.

TABLES

TABLE 1a
FILTER TEST FEED COAL CHARACTERIZATION

COAL TYPE	MONT. #5	MONT. #6	MONT. #7	ILL. #6	COKE BREEZE
PROXIMATE ANALYSIS (% wt. ON AS RECEIVED COAL)					
HMO	4.19	7.12	3.46	3.38	0.46
ASH	8.94	10.24	12.79	8.26	9.72
VOLATILES	38.32	36.85	36.18	26.34	3.28
FIXED CARBON (BY DIFFERENCE)	48.55	45.79	47.57	62.02	86.54
HEATING VALUE (BTU/lb)	10992	10901	11126	12294	12316
SULFUR (%)	0.56	1.24	2.19	1.98	0.78
ALKALI AS SODIUM OXIDE	0.07	0.1	0.11	N/A	N/A
ULTIMATE ANALYSIS (% wt. ON AS RECEIVED ASH)					
HMO	4.19	7.12	3.46	3.38	0.46
CARBON	65.85	62.43	63.83	73.39	85.84
HYDROGEN	4.55	4.36	4.22	3.6	1.22
NITROGEN	0.99	1.01	1.01	1.26	1.01
SULFUR	0.56	1.24	2.19	1.98	0.78
CHLORINE	0.0	N/A	N/A	N/A	N/A
ASH	8.94	10.24	12.79	8.26	9.72
OXYGEN (BY DIFFERENCE)	14.92	13.6	12.5	8.13	0.97
ASH MINERAL ANALYSIS (% wt. ON IGNITED ASH BASIS ASH)					
SiO_2	39.14	35.16	23.54	39.1	N/A
Al_2O_3	19.24	12.85	14.49	779	N/A
Fe_2O_3	3.77	12.88	23.02	1.74	N/A
CaO	15.79	13.72	14.92	3.14	N/A
MgO	4.21	3.96	3.71	0.92	N/A
TiO_2	0.89	1.03	0.54	0.24	N/A
K_2O	0.42	0.3	0.09	1.5	N/A
Na_2O	0.52	0.74	0.8	N/A	N/A
P_2O_5	0.43	0.16	0.29	0.41	N/A
SO_3	14.85	18.27	16.47	N/A	N/A
SrO	0.40	0.5	0.28	N/A	N/A
BaO	0.13	0.14	1.01	N/A	N/A
MnO	0.21	0.06	0.13	N/A	N/A
undetermined	0	0	0	NA	N/A
TYPE (lignitic, etc.)	LIGNITIC	N/A	N/A	N/A	N/A
SILICA VALUE	62.22	N/A	N/A	N/A	N/A
BASE:ACID RATIO	0.42	N/A	N/A	N/A	N/A
FOULING INDEX	0.52	N/A	N/A	N/A	N/A
T_{250} TEMPERATURE (°F)	2391	N/A	N/A	N/A	N/A

TABLE 1b
FILTER TEST FEED COAL CHARACTERIZATION

TRACE ELEMENT (ppm):	MONT. #5	MONT. #6	MONT. #7	ILL. #6	COKE BREEZE
ANTIMONY, (Sb)	<4			N/A	N/A
ARSENIC, (As)	<1			N/A	N/A
BERYLLIUM, (Be)	0.2	0.6	<0.3	N/A	N/A
BORON, (B)	180			N/A	N/A
CADMIUN, (Cd)	<0.2	<0.3	<0.3	N/A	N/A
CHROMIUM, (Cr)	2	6	1	N/A	N/A
COBALT, (Co)	<1			N/A	N/A
COPPER, (Cu)	7	10	8	N/A	N/A
FLUORIDE, (F)	30			N/A	N/A
LEAD, (Pb)	6	12		N/A	N/A
MANGANESE, (Mn)		36	120	N/A	N/A
MERCURY, (Hg)	0.08			N/A	N/A
MOLYBDENUM, (Mo)	<3			N/A	N/A
NICKEL, (Ni)	<1	4	<1	N/A	N/A
SELENIUM, (Se)	<1			N/A	N/A
SILVER, (Ag)	<0.2			N/A	N/A
THALIUM, (Tl)	<1			N/A	N/A
TIN, (Sn)	<4			N/A	N/A
URANIUM, (U)	1.2			N/A	N/A
VANADIUM, (V)	8	12	7	N/A	N/A
ZINC, (Zn)	<1	20	3	N/A	N/A
ZIRCONIUM, (Zr)	17			N/A	N/A

TABLE 2
FILTER TEST OVERVIEW

CAMPAIGN NUMBER	OPERATING HOURS	FILTER ELEMENTS	FEED COAL	ASH SAMPLE
1	108	C34 C35	MONTANA #5	93MGC04
2	145	C34, C35	MONTANA #6	93MGC05
3	130	C34, C36	MONTANA #6	93MGC06
4	119	C34, C36	MONTANA #6	94MGC07
5	191	C34, C36	MONTANA #6	94MGC08
6	85	C34, C36	MONTANA #6, MONTANA #7, COKE BREEZE, ILLINOIS #6	94MGC09
7	89	C34, C36	MONTANA #6, MONTANA #7	94MGC10

TABLE 3
AVERAGE PROCESS CONDITIONS DURING FILTER TESTS

	CAMP. 1 93MGC 04	CAMP. 2 93MGC 05	CAMP. 3 94MGC 06	CAMP. 4 94MGC O7	CAMP. 5 94MGC 08	CAMP. 6 94MGC 09	CAMP. 7 94MGC 10
PRESSURE IN (psia)	308.4	308.5	313.2	305.2	304.7	306.7	304.7
BLOWBACK PRESSURE (psia)	429.3	432.7	502.0	480.2	467.7	471.7	464.7
DIFFERENTIAL PRESSURE (psid)	6.3	5.2	7.5	3.5	3.22	4.1	6.34
TEMPERATURE IN (°F)	1017	1066	1089	1089	926	1128	1053
TEMPERATURE OUT (°F)	1027	1126	1106	1047	1043	1074	1024
GAS MASS FLOW RATE (lb/hr)	121	120	127	118	134	138	131
GAS VOL. FLOW RATE (scfm/acfm)	28.8/4.4	28.5/4.5	30.3/4.8	28.1/4.5	32.0/4.6	33.0/5.5	31.2/4.95
AVE. SOLIDS FLOW RATE IN (LB/HR)	0.0 35	0.033	0.018	0.03	0.04	0.03	0.03

TABLE 4
TYPICAL ANALYSIS OF GAS TO FILTER

COMPONENT	MOL %
CO	10
CO_2	11
H_2	15
H_2O	12
N_2	49
CH_4	2.4
H_2S	0.3
Ar	0.3

TABLE 5a
FILTER ASH CHARACTERIZATION

SAMPLE NUMBER	93MGC05A	93MGC05B	93MGC06	94MGC07	94MGC08	94MGC09	94MGC10
PROXIMATE ANALYSIS (% wt. ON AS RECEIVED COAL)							
HMO	1.54	1.42	1.31	1.57	0.89	1.04	1.05
ASH	61.96	62.8	64.09	62.53	62.89	60.73	62.09
VOLATILES	4.8	2.91	3.77	4.35	3.4	3.69	2.36
FIXED CARBON (BY DIFFERENCE)	31.7	32.87	30.83	31.55	32.82	3.54	34.5
HEATING VALUE (BTU/lb)	4968	4899	4976	4843	5081	5310	5308
SULFUR (%)	0.6	0.6	1.05	0.77	0.41	0.28	0.3
ALKALI AS SODIUM OXIDE	1.21	1.22	1.84	1.32	1.15	0.31	0.31
ULTIMATE ANALYSIS (% wt. ON AS RECEIVED ASH)							
HMO	1.54	1.42	1.31	1.57	0.89	1.04	1.05
CARBON	34.42	33.86	32.86	34.18	35.02	37.13	35.75
HYDROGEN	0.36	0.39	0.31	0.37	0.25	0.2	0.31
NITROGEN	0.39	0.33	0.33	0.3	0.25	0.28	0.27
SULFUR	0.6	0.6	1.04	0.77	0.41	0.28	0.3
CHLORINE	N/A	N/A	N/A	N/A	N/A	N/A	N/A
ASH	61.96	62.8	64.94	62.53	62.89	60.73	62.09
OXYGEN (BY DIFFERENCE)	0.73	0.6	0.06	0.28	0.29	0.34	0.23
ASH MINERAL ANALYSIS (% wt. ON IGNITED ASH BASIS ASH)							
SiO_2	41.19	40.65	39.85	42.26	41.1	33.39	35.8
Al_2O_3	17.74	17.71	21.99	18.12	18.73	17.04	16.68
Fe_2O_3	4.93	4.84	4.44	5.49	4.32	3.59	3.35
CaO	22.17	22.44	17.41	20.04	22.11	29.03	28.48
MgO	7.14	7.25	5.67	6.53	7.11	9.93	9.89
TiO_2	1.71	1.73	1.89	1.75	1.7	1.79	1.74
K_2O	0.38	0.36	0.61	0.44	0.38	0.07	0.11
Na_2O	1.7	1.7	2.47	1.82	1.56	0.47	0.42
P_2O_5	0.13	0.13	0.07	0.1	0.14	0.58	0.5
SO_3	0.13	2.19	2.72	2.5	1.88	1.57	1.37
SrO	0.78	0.82	0.66	0.72	0.78	1.21	0.18
BaO	0.08	0.09	0	0	0.11	0.27	0.26
MnO	0.1	0.09	0.07	0.1	0.09	0.22	0.22
undetermined	0	0	0	0	0	0	0
TYPE (lignitic, etc.)	LIGNITIC	N/A	N/A	N/A	N/A	N/A	N/A
SILICA VALUE	54.61	N/A	N/A	N/A	N/A	N/A	N/A
BASE:ACID RATIO	0.6	N/A	N/A	N/A	N/A	N/A	N/A
FOULING INDEX	1.7	N/A	N/A	N/A	N/A	N/A	N/A
T_{250} TEMPERATURE (°F)	2247	N/A	N/A	N/A	N/A	N/A	N/A

TABLE 5b FILTER ASH CHARACTERIZATION							
TRACE ELEMENT (ppm):	93MGC 04	93MGC 05	93MGC 06	94MGC 07	94MGC 08	94MGC 09	94MGC 10
BERYLLIUM, (Be)	8.2	19	11	14	17	7.9	6.6
CADMIUN, (Cd)	<2	<2	<2	<2	<2	<2	<2
CHROMIUM, (Cr)	84	100	230	120	87	82	84
COPPER, (Cu)	48	67	81	79	29	21	380
LEAD, (Pb)	39	31	53	81	32	14	77
MANGANESE, (Mn)	420	460	360	430	410	1100	1000
NICKEL, (Ni)	130	310	760	330	120	80	180
VANADIUM, (V)	130	140	110	140	140	160	130
ZINC, (Zn)	130	350	5800	1500	90	1800	2700

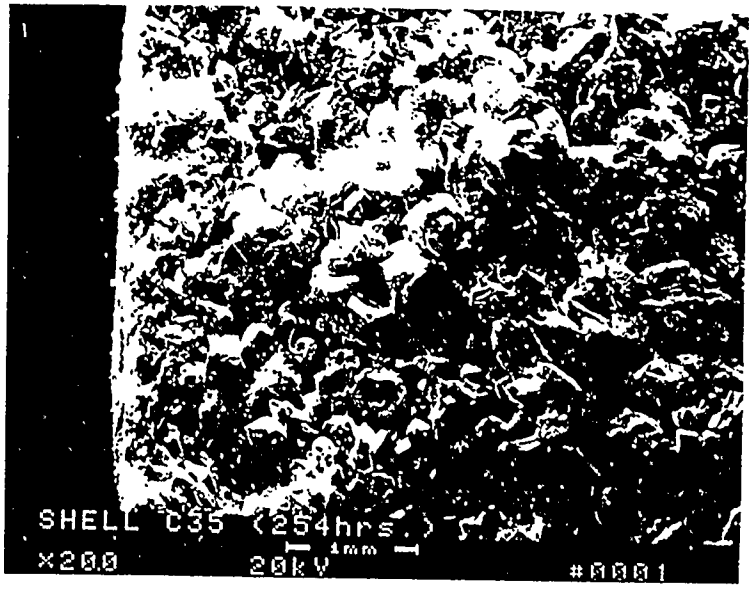
TABLE 6 PARTICLE SIZE DISTRIBUTION ANALYSIS OF ASHES (MICRONS)							
PERCENT LESS THAN	93MGC 05	93MGC 05	94MGC 06	94MGC O7	94MGC 08	94MGC 09	94MGC 10
90	3.089	2.848	3.768	3.696	3.714	3.184	3.133
75	2.655	2.458	3.207	3.157	3.193	2.787	2.737
50	2.167	2.013	2.625	2.525	2.661	2.317	2.308
25	1.689	1.570	2.035	1.894	2.074	1.836	1.852
10	1.282	1.207	1.536	1.404	1.534	1.423	1.443

REFERENCE:

1. J. A. Salter and J. L. Monsavoir, "SCGP-1 High Temperature Filtration Experience,"Proceedings: Second EPRI Workshop on Filtration of Dusts from Coal-Derived Reducing and Combustion Gases at High Temperature," San Francisco, California, March 11-13, 1992.

FIGURES

Figure 1 - Cross-section of "as manufactured clay bonded silicon carbide filter matrix. The fine outer surface membrane and the underlying coarse support silicon carbide grains are evident.



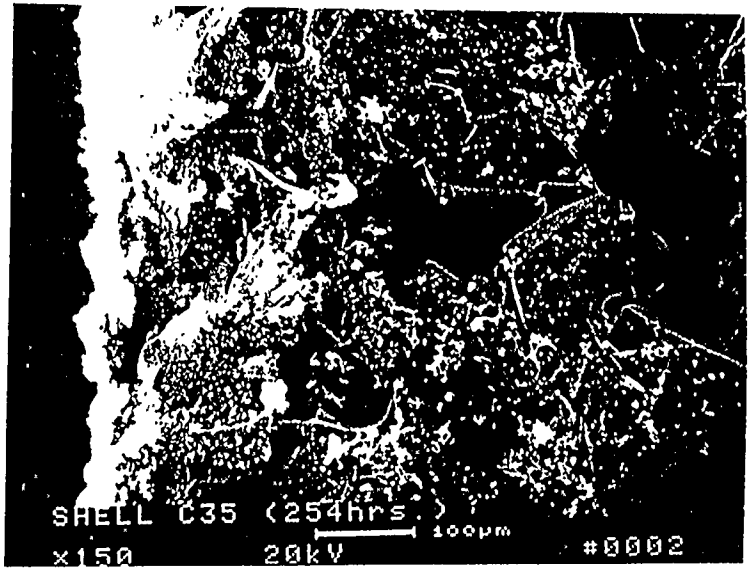
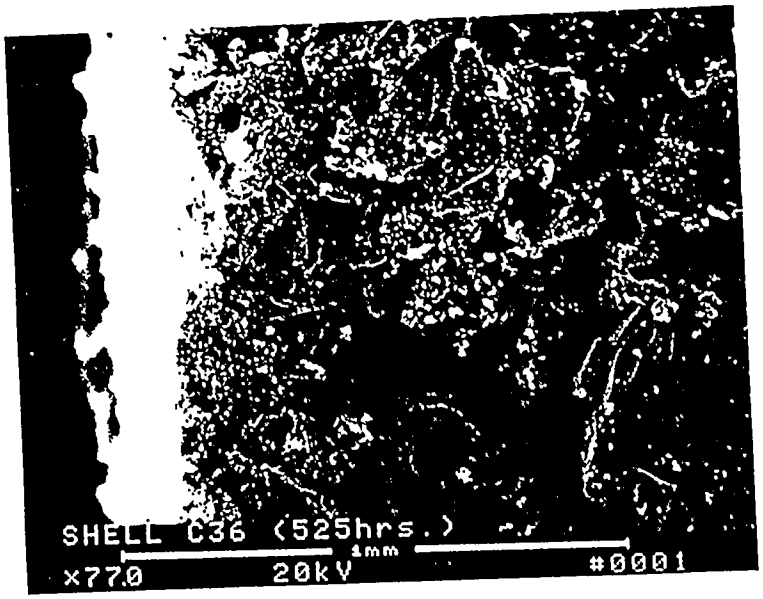


Figure 2 - Morphology of the 254 hour gasifier exposed clay bonded silicon carbide candle filter matrix.



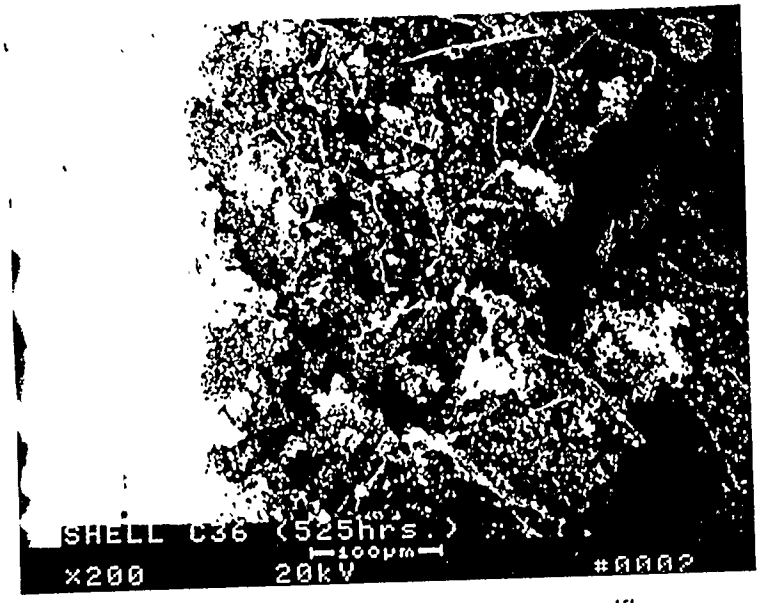


Figure 3 - Morphology of the 525 hour gasifier exposed clay bonded silicon carbide candle matrix. Char particles that were eveident between the first and second grain layer in the support structure may have been a result of sample preparation.

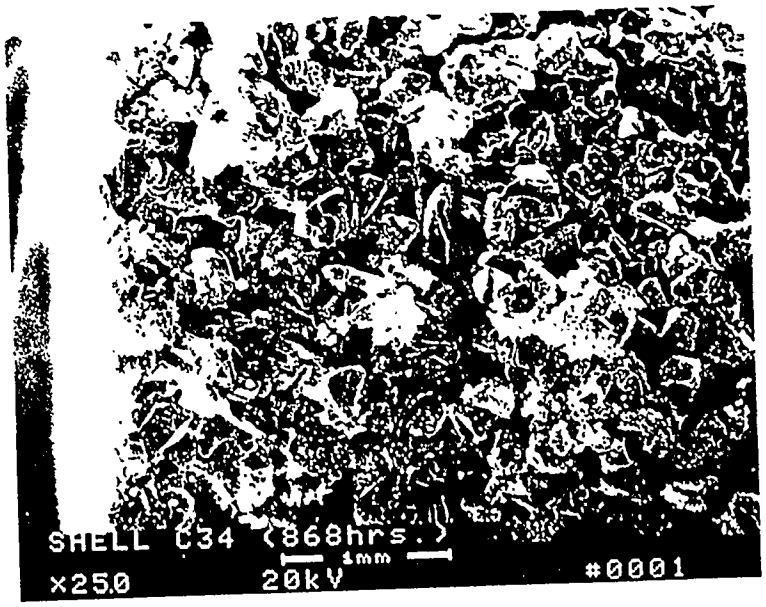


Figure 4 - Morphology of the 868 hour gasifier exposed clay bonded silicon carbide candle filter matrix.

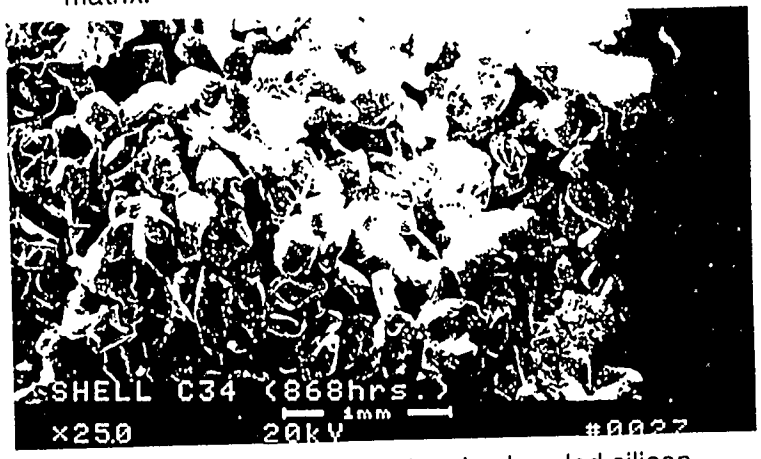


Figure 5 - Morphology of the clay bonded silicon carbide matrix along the ID of the pulse cycled surface of the 868 hour gasifier exposed candle filter.

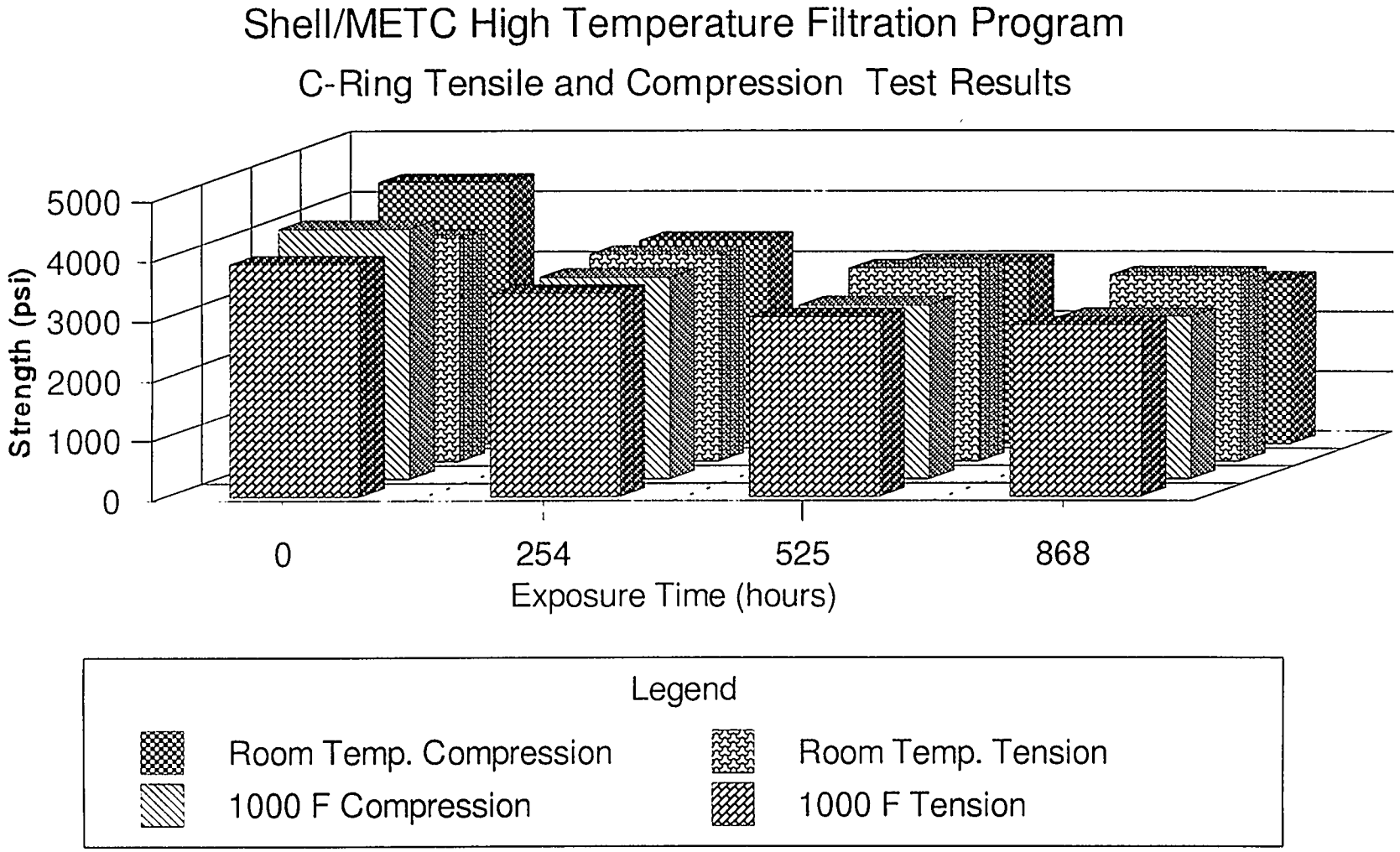


Figure 6 - C-Ring Tension and Compression Tests