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**Thermal/Chemical Degradation of Ceramic
Cross-Flow Filter Materials, Phase I
September 1988 - November 1989**

Topical Report

**M.A. Alvin
J.E. Lane
T.E. Lippert**

November 1989

Work Performed Under Contract No.: DE-AC21-88MC25034

**For
U.S. Department of Energy
Office of Fossil Energy
Morgantown Energy Technology Center
Morgantown, West Virginia**

**By
Westinghouse Electric Corporation
Westinghouse Science and Technology Center
Pittsburgh, Pennsylvania**

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Pittsburgh, Pennsylvania 15235**

November 1989

CONTENTS

Abstract	xx
Executive Summary.....	S-1
1. Introduction.....	1-1
2. Project Summary.....	2-1
3. Technical Discussion.....	3-1
3.1 Task 1: Identification of Long-Term High Temperature	
Degradation Mechanisms.....	3-3
3.1.1 Technology Review.....	3-3
3.1.1.1 Coal Process Systems.....	3-3
3.1.1.2 Ceramic Materials.....	3-40
3.1.2 Materials Characterization.....	3-83
3.1.2.1 Cross-Flow Filter Materials.....	3-85
3.1.2.2 Process Char and Ash.....	3-144
3.1.3 Phase Stability Assessment.....	3-174
3.1.3.1 Projected Char or Ash Phase	
Compositions and Reaction with	
Volatile Alkali.....	3-174
3.1.3.2 Projected Thermal Stability of	
Ceramic Cross-Flow Material Phases	
and Potential Reaction with	
Process Gases.....	3-201
3.1.3.3 Projected Char and Ash Fines Reactions	
with Ceramic Cross-Flow Filter	
Material Phases.....	3-222
3.1.4 Cross-Flow Filter Test Experience.....	3-242
3.1.4.1 Chemical Affinity of Alumina/Mullite	
for Sodium.....	3-242

3.1.4.2	Alumina/Mullite Filter Tests in a Bench-Scale Fluid-Bed Gasifier.....	3-252
3.1.4.3	Alumina/Mullite Cross-Flow Filter Materials Fabricated for Use at the Subpilot-Scale Pressurized Fluidized-Bed Combustor at New York University..	3-291
3.1.4.4	Alumina/Mullite Cross-Flow Filter Materials Fabricated For Use at the Texaco Entrained-Bed Gasifier.....	3-312
3.1.4.5	Variation in the Physical Properties and Principal Chemical Phases in the Alumina/Mullite Filter Material.....	3-315
3.1.4.6	Conclusions.....	3-326
3.2	Task 2: Evaluation of Potential Long-Term High Temperature Degradation Mechanisms.....	3-328
3.2.1	Thermodynamic Assessment.....	3-328
3.2.2	Chemical/Mechanical Assessment.....	3-355
3.2.3	Summary.....	3-362
4.	Conclusions	4-1
5.	Recommendations.....	5-1
6.	Acknowledgment.....	6-1
7.	References	7-1
	Appendix A - Thermodynamic Equilibrium Process Calculations.....	A-1
1.0	Fixed-Bed Gasification.....	A-2
2.0	Fluid-Bed Gasification.....	A-5
3.0	Entrained-Bed Gasification.....	A-24
4.0	Direct Coal Fired Turbines.....	A-27
5.0	Pressurized Fluidized-Bed Combustion.....	A-30

LIST OF FIGURES

S.1	Ceramic Cross-Flow Filter Element.....	S-2
3.1	Fixed-Bed Gasification System.....	3-6
3.2	Fluid-Bed Gasification System.....	3-7
3.3	Entrained-Bed Gasification System.....	3-8
3.4a	Direct Coal Fired Turbine, Slurry-Fired System.....	3-9
3.4b	Direct Coal Fired Turbine, Gas-Fired System.....	3-10
3.5a	Pressurized Fluidized-Bed Combustion System.....	3-11
3.5b	Adiabatic Fluidized-Bed Combustion System.....	3-12
3.6	Chemical Pathways in Coal Combustion Systems.....	3-18
3.7	Deposition Pathways in Coal Combustion Processes.....	3-20
3.8a	Phase Stability Diagrams for Si-O, Al-O, and Fe-O.....	3-35
3.8b	Phase Stability Diagrams for Al_2O_3 - SiO_2 , CaO - SiO_2 , and CaO - Al_2O_3	3-36
3.8c	Phase Stability Diagrams for Fe-Si-O, FeO- Al_2O_3 , Ca-Fe-O, and Fe-Mg-O.....	3-37
3.8d	Phase Stability Diagrams for Na_2O - SiO_2 , $NaAlO_2$ - Al_2O_3 , and SiO_2 - K_2O - SiO_2	3-38
3.8e	Phase Stability Diagrams for $CaCO_3$, $MgCO_3$, and $CaCO_3$ - $MgCO_3$	3-39
3.9	RBSN Oxidation Model for Materials with Small and Large Pores.....	3-49
3.10	Percent Weight Gain and Percent Conversion of RBSN to SiO_2 as a Function of Time and Temperature for Materials with Densities of 2.10, 2.31, and 2.39 g/cm ³	3-51

3.11	Sections Removed from a Mid-Ribbed Alumina/Mullite Cross-Flow Filter.....	3-91
3.12a	Scanning Electron Micrographs Showing Fractured Surface of an Alumina/Mullite Cross-Flow Filter Mid-Ribbed Area...	3-92
3.12b	Higher Magnification Scanning Electron Micrographs Showing the Fractures Surface of the Alumina/Mullite Mid-Ribbed Area.....	3-93
3.12c	Scanning Electron Micrograph Showing Internal Surface of a Pore in the Alumina/Mullite Mid-Ribbed Area.....	3-94
3.12d	SEM/EDAX Analysis Characterizing the Various Phases in the Alumina/Mullite Mid-Ribbed Area.....	3-95
3.12e	SEM/EDAX Analysis Characterizing the Fractured Mid-Ribbed Surface of the Alumina/Mullite Filter.....	3-96
3.13a	Scanning Electron Micrographs Showing the Gas Flow Channel Surface of an Alumina/Mullite Mid-Ribbed Filter.....	3-97
3.13b	SEM/EDAX Analysis Characterizing the Gas Flow Channel Surface of an Alumina/Mullite Mid-Ribbed Filter.....	3-98
3.14a	Scanning Electron Micrographs Showing the Fractured Surface Beneath the Mid-Rib Area in an Alumina/Mullite Filter.....	3-99
3.14b	SEM/EDAX Analysis Characterizing the Fractured Surface Beneath the Mid-Rib Area in an Alumina/Mullite Filter.....	3-101
3.15a	Scanning Electron Micrographs of the Cordierite Plate Surface.....	3-104
3.15b	High Magnification Scanning Electron Micrographs of the Cordierite Plate Surface.....	3-105
3.15c	Higher Magnification Scanning Electron Micrographs of the Cordierite Plate Surface.....	3-106
3.15d	Area Scan of the Cordierite Plate Surface Using Energy Dispersive X-Ray Analysis.....	3-107
3.15e	Localized Energy Dispersive X-Ray Analyses Along the Cordierite Plate Surface.....	3-108
3.16a	Scanning Electron Micrographs of the Aluminosilicate Foam Cross-Flow Filter Material.....	3-112

3.16b	High Magnification Scanning Electron Micrographs of the Aluminosilicate Foam Cross-Flow Filter Material.....	3-113
3.16c	Higher Magnification Scanning Electron Micrographs of the Aluminosilicate Foam Cross-Flow Filter Material.....	3-114
3.16d	Energy Dispersive X-Ray Analyses of Various Phases Present in the Aluminosilicate Foam.....	3-115
3.17a	Scanning Electron Micrographs of the Cordierite-Silicon Nitride Plate Surface.....	3-117
3.17b	Scanning Electron and Back-Scattering Electron Micrographs of the Cordierite-Silicon Nitride Plate Surface.....	3-118
3.17c	High Magnification Scanning Electron and Back-Scattering Electron Micrographs of the Cordierite-Silicon Nitride Plate Surface.....	3-119
3.17d	Higher Magnification Scanning Electron and Back-Scattering Electron Micrographs of the Cordierite-Silicon Nitride Plate Surface.....	3-120
3.17e	Energy Dispersive X-Ray Analysis of the Cordierite-Silicon Nitride Surface.....	3-121
3.18a	Scanning Electron Micrographs of the Reaction Bonded Silicon Nitride Plate (RBSN) Surface.....	3-125
3.18b	Scanning Electron Micrographs of the Dense Particle Formations along the RBSN Surface.....	3-126
3.18c	Scanning Electron Micrographs of the Whisker Formations in Both the Dense Particle and Cracked Regions Along the RBSN Surface.....	3-127
3.18d	Higher Magnification Scanning Electron Micrographs of the Whisker Formations in the Cracked Areas of the RBSN Surface.....	3-128
3.18e	Higher Magnification Scanning Electron Micrographs of the Whisker Formations in Both the Dense Particle and Cracked Regions Along the RBSN Surface.....	3-129
3.18f	Energy Dispersive X-Ray Analysis of RBSN Particles and Whiskers.....	3-130
3.18g	Scanning Electron Micrograph and Energy Dispersive X-Ray Analysis of the RBSN Whiskers.....	3-131

3.19a	Scanning Electron Micrograph and Major Ash Composition of the NYU Pittsburgh Combustor Ash Fines.....	3-149
3.19b	Scanning Electron Micrographs of the NYU Pittsburgh Combustor Ash Fines.....	3-150
3.19c	High Magnification Scanning Electron Micrographs of the NYU Pittsburgh Combustor Ash Fines.....	3-151
3.19d	Higher Magnification Scanning Electron Micrographs of the NYU Pittsburgh Combustor Ash Fines.....	3-152
3.20a	Scanning Electron Micrograph and Major Ash Composition of the KRW Gasifier West Virginia Char Fines.....	3-153
3.20b	Scanning Electron Micrographs of the KRW Gasifier West Virginia Char Fines.....	3-154
3.20c	High Magnification Scanning Electron Micrograph of the KRW Gasifier West Virginia Char Fines.....	3-155
3.21a	Scanning Electron Micrograph and Major Ash Composition of the KRW Gasifier Pittsburgh, Ireland Seam Char Fines.....	3-156
3.21b	Scanning Electron Micrographs of the KRW Gasifier Pittsburgh, Ireland Seam Char Fines.....	3-157
3.21c	High Magnification Scanning Electron Micrographs of the KRW Gasifier Pittsburgh, Ireland Seam Char Fines.....	3-158
3.22a	Scanning Electron Micrograph and Major Ash Composition of the KRW Gasifier, Pittsburgh Aloe Seam Char Fines.....	3-159
3.22b	Scanning Electron Micrographs of the KRW Gasifier, Pittsburgh Aloe Seam Char Fines.....	3-160
3.22c	Scanning Electron Micrographs of the KRW Gasifier, Pittsburgh Aloe Seam Char Fines.....	3-161
3.23a	Scanning Electron Micrograph and Major Ash Composition of the KRW Gasifier Wyoming Char Fines.....	3-162
3.23b	Scanning Electron Micrographs of the KRW Gasifier Wyoming Char Fines.....	3-163
3.24a	Scanning Electron Micrograph and Major Ash Composition of the Texaco Gasifier Pittsburgh No. 8 Char Fines.....	3-164
3.24b	Scanning Electron Micrographs of the Texaco Gasifier Pittsburgh No. 8 Char Fines.....	3-165

3.24c	Scanning Electron Micrographs of the Texaco Gasifier Pittsburgh No. 8 Char Fines.....	3-166
3.25	Char and Ash Particle Size Distribution.....	3-170
3.26	Condensed Alkali Phases Projected in Fixed-Bed Gasification Systems.....	3-178
3.27	Condensed Alkali Phases Projected in Fluid-Bed Gasification Systems.....	3-179
3.28	Condensed Alkali Phases Projected in Entrained-Bed Gasification Systems.....	3-180
3.29	Condensed Alkali Phases Projected in Direct Coal Fired Turbine Systems.....	3-181
3.30	Condensed Alkali Phases Projected in Pressurized Fluidized-Bed Combustion Systems.....	3-182
3.31	Scanning Electron Micrographs and Energy Dispersive X-Ray Analysis of Alumina/Mullite Filter No. 427 Surface.....	3-244
3.32	Scanning Electron Micrographs and Energy Dispersive X-Ray Analysis of Alumina/Mullite Filter No. 485 Surface.....	3-245
3.33	Section Removed from the WCXF2 Alumina/Mullite Filter after Exposure to the METC Fluid-Bed Gasifier Process Gas (8/16/85).....	3-253
3.34	Section Removed from the WCXF4 Alumina/Mullite Filter After Exposure to the METC Fluid-Bed Gasifier Process Gas (11/5/85).....	3-256
3.35	Cross-Section of the Ribbed Surface of the WCXF2 Alumina/Mullite Filter Exposed in the METC Gasifier (8/16/85).....	3-258
3.36	Scanning Electron Micrographs and Energy Dispersive X-Ray Analysis of a Clean Gas Channel Surface in the WCXF2 Alumina/Mullite Filter Exposed at METC.....	3-259
3.37	Scanning Electron Micrographs and Energy Dispersive X-Ray Analysis of a Dirty Gas Channel Surface in the WCXF2 Alumina/Mullite Filter Exposed at METC.....	3-263
3.38	Scanning Electron Micrographs and Energy Dispersive X-Ray Analysis of a Cross-Sectioned Rib Surface in the WCXF2 Alumina/Mullite Filter Exposed at METC.....	3-265

3.39	Cross-Section of the Ribbed Surface of the WCXF4 Alumina/Mullite Filter Exposed in the METC Gasifier (11/5/85).....	3-267
3.40	Scanning Electron Micrographs and Energy Dispersive X-Ray Analysis of a Clean Gas Channel Surface in the WCXF4 Alumina/Mullite Filter Exposed at METC.....	3-269
3.41	Scanning Electron Micrographs and Energy Dispersive X-Ray Analysis of a Dirty Gas Channel Surface in the WCXF4 Alumina/Mullite Filter Exposed at METC.....	3-271
3.42	Scanning Electron Micrographs and Energy Dispersive X-Ray Analysis of a Cross-Sectioned Rib Surface in the WCXF4 Alumina/Mullite Filter Exposed at METC.....	3-273
3.43	Microprobe Analysis of the Cross-Sectioned Rib Surface in the WCXF4 Alumina/Mullite Filter Exposed at METC.....	3-275
3.44	WCXF2 Four-Point Bend Fracture Surface.....	3-278
3.45	WCXF4 Four-Point Bend Fracture Surface.....	3-279
3.46a	Scanning and Back Scattering Electron Micrographs of the WCXF2 Four-Point Bend Fracture Surface.....	3-281
3.46b	Higher Magnification Scanning and Back Scattering Electron Micrographs of the WCXF2 Four-Point Bend Fracture Surface.....	3-283
3.47a	High Magnification Scanning and Back-Scattering Electron Micrographs of the WCXF2 Four-Point Bend Fracture Surface Showing the Synergism Between Phases.....	3-284
3.47b	Energy Dispersive X-Ray Analysis of the Light Phase(s) Along the WCXF2 Four-Point Bend Fractured Surface.....	3-285
3.48	Microprobe Analysis of the WCXF2 Four-Point Bend Fractured Surface.....	3-287
3.49	X-Ray Diffraction Analysis of the WCXF2 Alumina/Mullite Filter Material After Exposure at METC.....	3-292
3.50	X-Ray Diffraction Analysis of the Alumina/Mullite Material in Filters Fabricated for Use at the New York Combustor...	3-293
3.51a	Scanning Electron Micrographs of a Cross-Sectioned Area from a Rib in an Alumina/Mullite Filter Fabricated for Use at the New York Combustor.....	3-295

3.51b	Higher Magnification Scanning Electron Micrographs of a Cross-Sectioned Area from a Rib in an Alumina/Mullite Filter Fabricated for Use at the New York Combustor.....	3-296
3.52a	Scanning Electron Micrographs of a Fracture Surface in an Alumina/Mullite Filter Exposed in the New York University Combustor.....	3-297
3.52b	Higher Magnification Scanning Electron Micrographs of a Fracture Surface in an Alumina/Mullite Filter Exposed in the New York University Combustor.....	3-298
3.52c	Scanning Electron Micrographs Showing the Crystal Formations and Ash Deposits along the Alumina/Mullite Fracture Surface from a Filter Exposed in the New York University Combustor.....	3-299
3.52d	Scanning Electron Micrographs Showing the Crystal Formations and Ash Deposits along the Alumina/Mullite Fracture Surface and Within Pores of a Filter That Was Exposed to the New York University Combustor Process Gases.....	3-300
3.52e	Energy Dispersive X-Ray Analysis Area Scan of the Alumina/Mullite Fracture Surface.....	3-301
3.53a	Scanning Electron Micrographs of the Crystal Formations Along the Alumina/Mullite Fracture Surface.....	3-303
3.53b	Energy Dispersive X-Ray Analysis of the Various Phases Along the Alumina/Mullite Fracture Surface.....	3-304
3.54a	High Magnification Scanning Electron Micrographs Illustrating the Ash Deposit-Ceramic Matrix Interface	3-308
3.54b	Energy Dispersive X-Ray Analysis of the Ash Deposit and Alumina/Mullite Matrix.....	3-307
3.55	Scanning Electron Micrograph and Energy Dispersive X-ray Analysis of an Ash Deposit Extending into the Pore Cavity in the Alumina/Mullite Filter That Had Been Exposed to the New York University Combustor Process Gases.....	3-308
3.56	Scanning Electron Micrographs Illustrating Dense Ash Deposit Areas Along the Alumina/Mullite Matrix after Exposure in the NYU Combustor.....	3-309
3.57	X-Ray Diffraction Analysis of the Alumina/Mullite Filter Material after Exposure in the New York University Combustor.....	3-310

3.58	X-Ray Diffraction Analysis of the Alumina/Mullite Filter Material Before and After Exposure to the New York University Combustor Process Gases.....	3-311
3.59	Scanning Electron Micrographs and Energy Dispersive X-ray Analysis of a Cross-Section From a Rib in an Alumina/Mullite Filter Fabricated for Use at Texaco.....	3-318
3.60	X-Ray Diffraction Analysis of Alumina/Mullite Filter Material Fabricated for Use at Texaco.....	3-316
3.61	Ceramic Material Porosity-Strength Relationship.....	3-325
3.62	Phase Stability Diagram for $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$ Composite System.....	3-356
3.63	Phase Stability Diagram for $\text{Na}_2\text{O}\cdot\text{Al}_2\text{O}_3\cdot 2\text{SiO}_2\text{-CaO}\cdot\text{Al}_2\text{O}_3\cdot 2\text{SiO}_2\text{-SiO}_2$ Composite System.....	3-358
3.64	Phase Stability Diagram for $\text{MgO-Al}_2\text{O}_3\text{-SiO}_2$ Composite System.....	3-359
3.65	Phase Stability Diagram for $\text{Na}_2\text{O}\cdot\text{Al}_2\text{O}_3\cdot 2\text{SiO}_2\text{-MgO}\cdot\text{Al}_2\text{O}_3\text{-SiO}_2$	3-360
3.66	Long-Term Ceramic Material Assessment - Thermal Degradation.....	3-363
3.67	Long-Term Ceramic Material Assessment - Chemical Degradation (Alkali).....	3-364
3.68	Long-Term Ceramic Material Assessment - Char/Ash Fines Degradation.....	3-365
3.69	Long-Term Ceramic Material Assessment - Phase Change/Crystallization.....	3-366
3.70	Long-Term Ceramic Material Assessment - Mechanical Properties (Material Strength).....	3-367
3.71	Long-Term Ceramic Material Assessment - Thermal Shock Resistance (Thermal Cycling).....	3-368

Appendix

A.1	Fixed-Bed Gasification.....	A-4
A.2	Thermodynamic Equilibrium Projections Illustrating the Composition of Gas/Solid Phases Released during Fluid-Bed Gasification of Upper Freeport Coal.....	A-7
A.3	Thermodynamic Equilibrium Projections Illustrating the Composition of Gas/Solid Phases Released during Fluid-Bed Gasification of Western Kentucky Coal.....	A-11
A.4	Thermodynamic Equilibrium Projections Illustrating the Composition of Gas/Solid Phases Released during Fluid-Bed Gasification of Brookville Coal.....	A-15
A.5	Thermodynamic Equilibrium Projections Illustrating the Composition of Gas/Solid Phases Released during Fluid-Bed Gasification of North Dakota Lignite.....	A-19
A.6	Entrained-Bed Gasification.....	A-26
A.7	Schematic of the Coal Gasification System That Supplies Hot Coal Gas to the Gas Turbine.....	A-28
A.8	Pressurized Fluidized-Bed Combustion.....	A-32
A.9	Release of Sodium from Sulfur Sorbent Materials as a Function of Temperature.....	A-36
A.10	Release of Potassium from Sulfur Sorbent Materials as a Function of Temperature.....	A-37
A.11	Partial Pressure of Volatile Equilibrium Phases Formed in Pressurized Fluidized-Bed Combustion Systems.....	A-46
A.12	Principal Reaction Pathways of Trace and Minor Elements During Combustion.....	A-47

LIST OF TABLES

S.1	Coal Process/Filter Parameters.....	S-4
S.2	Cross-Flow Filter Material Characterization.....	S-5
S.3	Process Char and Ash Characterization.....	S-7
3.1	Process System Characterization.....	3-5
3.2	Thermodynamic Equilibrium Projections of the Kellogg Rust-Westinghouse Gasifier Effluent Gas Composition.....	3-14
3.3	Sulfur Release from Coal as a Function of Process Temperature.....	3-16
3.4	Concentration of Alkali and Chlorides in Pittsburgh No. 8 Coal	3-17
3.5	Thermodynamically Projected Effluent Gas Compositions Formed During Combustion of Pittsburgh No. 8 Coal.....	3-23
3.6	Process System Data Illustrating Alkali Release.....	3-28
3.7	Coal Ash Compositions.....	3-32
3.8a	Elemental Reaction in Pittsburgh Seam Coal Ash During Processing.....	3-33
3.8b	Elemental Reaction in Texaco Coal Ash During Processing...	3-34
3.9	Properties of Dense and Reaction Bonded Silicon Nitride Ceramics.....	3-44
3.10a	Cross-Flow Filter Material Characterization.....	3-86
3.10b	Cross-Flow Filter Material Characterization.....	3-88
3.11	Four-Point Bend Strength Test Data for the Alumina/ Mullite Cross-Flow Filter Material.....	3-102
3.12	Four-Point Bend Strength Test Data for the Cordierite Cross-Flow Filter Material.....	3-110

3.13	Four-Point Bend Strength Test Data for the Cordierite-Silicon Nitride Cross-Flow Filter Material.....	3-123
3.14	Chemical Resistivity of Alumina, Silica, Mullite, Silicon Nitride, and Silicon Carbide.....	3-134
3.15	Characterization of Process Char and Ash Fines.....	3-146
3.16	Ultimate Analysis and Melt Fusion Temperatures of Combustor and Gasifier Fines.....	3-172
3.17	Projected Mole Fractions of Alkali Species Formed in Fixed-Bed Gasification Systems.....	3-183
3.18	Projected Mole Fractions of Alkali Species Formed in Fluid-Bed Gasification Systems.....	3-186
3.19	Projected Mole Fractions of Alkali Species Formed in Entrained-Bed Gasification Systems.....	3-189
3.20	Projected Mole Fractions of Alkali Species Formed in Direct Coal Fired Turbine Systems.....	3-192
3.21	Projected Mole Fractions of Alkali Species Formed in Pressurized Fluidized-Bed Combustion Systems.....	3-195
3.22	Thermodynamically Projected NYU Ash Composition.....	3-202
3.23	Projected Alkali Equilibrium Concentrations Released at the KRW Gasifier.....	3-204
3.24	Thermal Stability of Ceramic Cross-Flow Materials in Nitrogen at Filter Operating Conditions.....	3-208
3.25	Stability of Ceramic Cross-Flow Filter Materials in Process Gases at Operating Conditions.....	3-209
3.26	Projected Condensed Phases Resulting from the Reaction of Alumina with Sodium and Sulfur at Filter Process Conditions.....	3-210
3.27	Projected Condensed Phases Resulting from the Reaction of Mullite with Sodium and Sulfur at Filter Process Conditions.....	3-211
3.28	Projected Condensed Phases Resulting from the Reaction of Cordierite with Sodium and Sulfur at Filter Process Conditions.....	3-212

3.29	Projected Condensed Phases Resulting from the Reaction of Silicon Nitride with Sodium and Sulfur at Filter Process Conditions.....	3-213
3.30	Thermodynamically Projected Stable Solid Phases Resulting from the Reaction of Ash Fines with Ceramic Cross-Flow Filter Material Phases.....	3-223
3.31	Thermodynamically Projected Stable Solid Phases Resulting from the Reaction of Char Fines with Ceramic Cross-Flow Filter Material Phases in Fixed-Bed Gasification Systems.....	3-226
3.32	Thermodynamically Projected Stable Solid Phases Resulting from the Reaction of Char Fines with Ceramic Cross-Flow Filter Material Phases in Fluid-Bed Gasification Systems.....	3-227
3.33	Thermodynamically Projected Stable Solid Phases Resulting from the Reaction of Char Fines with Ceramic Cross-Flow Filter Material Phases in Entrained-Bed Gasification Systems.....	3-228
3.34	Thermodynamically Projected Stable Solid Phases Resulting from the Reaction of Char Fines with Ceramic Cross-Flow Filter Material Phases in Direct Coal Fired Turbine Systems	3-229
3.35	Thermodynamically Projected Stable Solid Phases Resulting from the Reaction of Char Fines with Ceramic Cross-Flow Filter Material Phases in Pressurized Fluidized-Bed Combustion Systems.....	3-230
3.36	Thermodynamically Projected Stable Solid Phases Resulting from the Reaction of Ash Fines with Ceramic Cross-Flow Filter Material Phases in Fixed-Bed Gasification Systems.....	3-231
3.37	Thermodynamically Projected Stable Solid Phases Resulting from the Reaction of Ash Fines with Ceramic Cross-Flow Filter Material Phases in Fluid-Bed Gasification Systems.....	3-232
3.38	Thermodynamically Projected Stable Solid Phases Resulting from the Reaction of Ash Fines with Ceramic Cross-Flow Filter Material Phases in Entrained-Bed Gasification Systems.....	3-233
3.39	Thermodynamically Projected Stable Solid Phases Resulting from the Reaction of Ash Fines with Ceramic Cross-Flow Filter Material Phases in Direct Coal Fired Turbine Systems.....	3-234

3.40	Thermodynamically Projected Stable Solid Phases Resulting from the Reaction of Ash Fines with Ceramic Cross-Flow Filter Material Phases in Pressurized Fluidized-Bed Combustion Systems.....	3-235
3.41	Summary of the Thermodynamic Projections Illustrating Ceramic Cross-Flow Filter Material Stability with Acidic Char/Ash.....	3-240
3.42	Summary of the Thermodynamic Projections Illustrating Ceramic Cross-Flow Filter Material Stability with Basic Char/Ash.....	3-241
3.43	Emission Spectroscopy Analysis of Alumina/Mullite Filter Materials.....	3-246
3.44	Atomic Absorption Analysis of Alumina/Mullite Filter Materials.....	3-247
3.45	Atomic Absorption Analysis of Exxon 3 rd Stage Cyclone Catch PFBC Ash.....	3-249
3.46	Atomic Absorption Analysis of the Alumina/Mullite Filter Materials after Exposure to Alkali and PFBC Ash.....	3-250
3.47	Cross-Flow Filter Test Conditions at the METC Fluid-Bed Gasifier.....	3-254
3.48	Principal Phase Characterization of the Alumina/Mullite Filters Exposed to the METC Fluid-Bed Gasifier Process Gases.....	3-289
3.49	Emission Spectroscopy Characterization of the Alumina/Mullite Filters Exposed to the METC Fluid-Bed Gasifier Process Gases.....	3-290
3.50	Four-Point Bend Strength Test Data for an Alumina/Mullite Filter Element after Exposure in the New York University Combustor.....	3-318
3.51	Porosity and Density Data for an Alumina/Mullite Filter Element after Exposure in the New York University Combustor.....	3-320
3.52	Chemical and Physical Properties Characterization of Various Alumina/Mullite Filter Materials.....	3-322
3.53	Four-Point Bend Strength Test Data for the Texaco Alumina/Mullite Filters.....	3-323

3.54	Long-Term Ceramic Cross-Flow Filter Degradation Mechanisms - Fixed-Bed Gasification.....	3-330
3.55	Long-Term Ceramic Cross-Flow Filter Degradation Mechanisms - Fluid-Bed Gasification.....	3-334
3.56	Long-Term Ceramic Cross-Flow Filter Degradation Mechanisms - Entrained-Bed Gasification.....	3-338
3.57	Long-Term Ceramic Cross-Flow Filter Degradation Mechanisms - Direct Coal Fired Turbine Systems.....	3-342
3.58	Long-Term Ceramic Cross-Flow Filter Degradation Mechanisms - Pressurized Fluidized-Bed Combustion.....	3-347

Appendix

A.1	Thermodynamic Equilibrium Product Distribution Formed During Fixed-Bed Gasification of a Pittsburgh Seam Coal...	A-3
A.2	Thermodynamic Estimates of Alkali and Chloride Release Concentrations at the Fluid-Bed Gasifier Outlet.....	A-23
A.3	Thermodynamic Equilibrium Product Distribution Formed During Entrained-Bed Gasification of a Pittsburgh Seam Coal.....	A-25
A.4	Gas Composition at Various Locations in the Direct Coal Fired Turbine System.....	A-29
A.5	Thermodynamic Equilibrium Product Distribution Formed During Pressurized Fluidized-Bed Combustion of a Kittanning Coal.....	A-31
A.6	Concentration of Ca, Mg, Na, K, and Cl in Sulfur Sorbent Materials.....	A-35
A.7	Summary of Trace and Minor Element Reactions in Fluidized-Bed Combustion Systems.....	A-39
A.8	Percent Distribution of Trace and Minor Elements in 10% Excess Air, 0% Sulfur Removal, Fluidized-Bed Combustion Systems.....	A-41
A.9	Percent Distribution of Trace and Minor Elements in 300% Excess Air, 99% Sulfur Removal, Fluidized-Bed Combustion Systems.....	A-43

A.10	PFBC Projections for Eastern Coals Containing Low Trace and Minor Element Concentrations.....	A-48
A.11	PFBC Projections for Eastern Coals Containing High Trace and Minor Element Concentrations.....	A-49
A.12	PFBC Projections for Western Coals Containing Low Trace and Minor Element Concentrations.....	A-50
A.13	PFBC Projections for Western Coals Containing High Trace and Minor Element Concentrations.....	A-51

ABSTRACT

This report summarizes the 14-month, Phase I effort conducted by Westinghouse on the Thermal/Chemical Degradation of Ceramic Cross-Flow Filter Materials program under DOE Contract DE-AC21-88MC25034. In Phase I expected filter process conditions were identified for a fixed-bed, fluid-bed, and entrained-bed gasification, direct coal fired turbine, and pressurized fluidized-bed combustion system. Ceramic cross-flow filter materials were also selected, procured, and subjected to chemical and physical characterization. The stability of each of the ceramic cross-flow materials was assessed in terms of potential reactions or phase change as a result of process temperature, and effluent gas compositions containing alkali and fines. In addition chemical and physical characterization was conducted on cross-flow filters that were exposed to the METC fluid-bed gasifier and the New York University pressurized fluidized-bed combustor. Long-term high temperature degradation mechanisms were proposed for each ceramic cross-flow material at process operating conditions. An experimental bench-scale test program is recommended to be conducted in Phase II, generating data that support the proposed cross-flow filter material thermal/chemical degradation mechanisms.

EXECUTIVE SUMMARY

Westinghouse is currently developing ceramic cross-flow filters for application in advanced fossil energy power generation systems (Figure S.1). As part of this effort, a two phase program is being conducted to identify potential long-term, high temperature degradation mechanisms in the various ceramic materials during cross-flow filter operation. Should material's degradation occur during the expected operating life of the cross-flow filter to the extent which limits both filter performance and use, an attempt will be made to identify alternate materials that will provide long-term durability.

As part of the two phase program which identifies potential long-term, high temperature degradation characteristics of ceramic cross-flow filter materials, this report documents the efforts conducted during Phase I of this contract. This includes (1) a review of the process literature identifying filter operating parameters (i.e., temperature, pressure, gas and particulate chemistry, etc.) in the various coal process systems, as well as a review of the advancements made in the ceramics technology; (2) selection, procurement, and chemical and physical characterization of current state-of-the art ceramic cross-flow filter materials; (3) a thermodynamic equilibrium phase stability assessment of the ceramic cross-flow filter materials at process operating conditions; and (4) a preliminary chemical and physical characterization of several cross-flow filter elements which had operated under sub-pilot scale conditions. An experimental bench-scale test program will be conducted in Phase II of this contract. The experimental bench-scale tests are intended to generate data which will support the proposed potential ceramic material degradation mechanisms. Kinetic data will be generated which reflect the rate of the various potential degradation mechanisms. These data will be used in development of models that ultimately project cross-flow filter operating life and performance. A summary of the Phase I effort follows.

Figure S.1 - Ceramic Cross-Flow Filter Element

Identification of the filter operating process parameters is essential in the selection and assessment of filter element material stability. Table S.1 presents a generic overview of the various process parameters which the cross-flow filter is expected to experience during operation in fixed-bed, fluid-bed, and entrained-bed gasification systems, and in direct coal fired turbine and pressurized fluidized-bed combustion systems.

Ceramic materials which possess excellent mechanical properties, as well as good thermal shock and corrosion resistance have been considered for use in fabricating cross-flow filter elements. In Phase I, five ceramic materials were selected for chemical and physical characterization, and evaluated based on their potential long-term high temperature stability. These materials include both oxides and non-oxide ceramics which are either currently being developed for or have been used in the fabrication of cross-flow filter elements.

Compositions range from a relatively high alumina-containing silica material, to an oxide-nonoxide composite, to a silicon nitride material. These materials include alumina/mullite, cordierite, aluminosilicate foam, cordierite-silicon nitride, and reaction bonded silicon nitride. Table S.2 summarizes the chemical and physical properties of the current state-of-the-art cross-flow filter materials.

Desirable physical properties [i.e., MOR: 2000-9000 psi; pressure drop of 10 in. water at gas flow rates of 10 ft/min at 815°C (1500°F)] are demonstrated for the alumina/mullite and cordierite materials. Further development is, however, needed to increase porosity within the cordierite-silicon nitride and reaction bonded silicon nitride materials. Because of the low strength of the aluminosilicate foam, its durability in cross-flow filter applications needs to be demonstrated.

TABLE S.1
COAL PROCESS/FILTER PARAMETERS

System	Fixed-Bed Gasification	Fluid-Bed Gasification	Entrained- Bed Gasification	Direct Coal Fired Turbines	Pressurized Fluidized Bed Combustion
Gasifier / Combustor Temperature, °C	400-600	700-800	1,300	1,000-1,350	800-1,000
Filter Temperature, °C	590	700	870	980	870
Filter Pressure, psig	300	300	450	180	150
Gas Composition					
Oxidizing	-	-	-	X	X
Reducing	X	X	X	-	-
Particulate Load, ppm	1,000-2,000	1,000-10,000	4,000	1,000	1,000-10,000

TABLE S.2

CROSS-FLOW FILTER MATERIAL CHARACTERIZATION

	Alumina/ Mullite ^(a)	Cordierite	Cordierite/ Si ₃ N ₄	Alumino- Silicate Foam	Reaction Bonded Si ₃ N ₄
<hr/>					
X-Ray Diffraction					
Analysis,					
Major Phases:	Mullite ^(b)	Cordierite	β -Si ₃ N ₄	Mullite	β -Si ₃ N ₄
Minor Phases:	Corundum	Amorphous	Si ₂ ON ₂	Amorphous	α -Si ₃ N ₄
	Anorthite		α -Cordierite		Amorphous
	Amorphous		Amorphous		
<hr/>					
4-Point Bend					
Strength, psi	2,162+234- 8,995+738	1,967+125	48,459+ 15,632	(c)	(d)
<hr/>					
Density, g/cm ³					
True	3.087	2.678	(d)	2.928	(d)
Bulk	2.26+0.02	1.42+0.01		0.447	
Percent	73.1+0.5	53.1+0.5		15.3	
<hr/>					
Porosity, %					
Open	18.8+1.7	43.2	(d)	83.1	(d)
Closed	8.1+1.3	3.8+0.6		1.6	

(a) Phase composition and MOR, density, and porosity values varied with filter material production lots.

(b) Materials range from 95% mullite/5% corundum, to 70% mullite/17% anorthite/12% corundum/amorphous.

(c) Inherently low strength material. Demonstration of adequate material strength at filter operating conditions is required.

(d) Not analysed since materials are undergoing further development.

Char or ash fines that were generated at the Kellogg Rust-Westinghouse fluid-bed gasifier and at the pressurized fluidized-bed New York University combustor, and which were collected along ceramic filters were also subjected to chemical and physical characterization. Details of these analyses are provided in Table S.3.

In order to assess the stability of each of the ceramic cross-flow materials during filter operation, the public domain thermodynamic equilibrium NASA CET86 computer code was used to project process gas phase composition, including alkali, chloride, and sulfur levels, as well as the composition of char or ash fines that could potentially result in each of the gasification and combustion systems. A parametric series of calculations was also performed for each process system, identifying the fate of alkali carryover from the gasifier or combustor outlet to the filter element surface.

Thermodynamic equilibrium calculations, as well as bench-scale testing conducted at Westinghouse have demonstrated the affinity for reaction of the alumina/mullite cross-flow filter material with gas phase alkali. Similarly equilibrium calculations have identified the possible chemical interaction of char or ash fines with the various ceramic material phases.

In order to assess the potential chemical degradation mechanisms for each cross-flow filter material, consideration is given to not only composition, but also to the nature of the grain boundary phase in each material. The alumina/mullite, cordierite, and cordierite-silicon nitride materials are considered to have an amorphous or "glassy" grain boundary phase, which is compositionally different from the ceramic matrix. It is at this site where reaction with volatile alkali species is expected to occur, and where capture and adherence of fines, phase crystallization, and increased residual stress could result. In both the alumina/mullite and cordierite materials, alkali is expected to

TABLE S.3
PROCESS CHAR AND ASH CHARACTERIZATION

Process	Fluid-Bed Gasification	Fluid-Bed Gasification	Pressurized Fluidized-Bed Combustion
Coal	Pittsburgh Ireland	West Virginia	Kittanning
Atomic Absorption Analysis, wt% Ash			
Al ₂ O ₃	15.93	18.76	19.09
SiO ₂	23.05	34.03	35.54
Fe ₂ O ₃	21.50	9.18	5.05
CaO	15.89	24.45	18.98
MgO	4.28	4.88	7.43
Na ₂ O	0.28	0.68	1.45
K ₂ O	1.88	1.04	0.88
Ash, wt%	17.64	16.33	99.67
Moisture, wt%	0.33	0.19	0.05
50% Mass Point, μ	3.4	5.2	4
Ash Transformation Temp., °C:			
Softening	1160	1177	1154
Fluid	1254	1254	1243
XRD Phase Analysis:			
Major	Amorphous	Amorphous	CaSO ₄ , SiO ₂
Minor	CaSO ₄	CaSO ₄ FeS, Fe ₂ O ₃	Fe ₂ O ₃

dissolve within the amorphous grain boundary phase, forming low melting temperature eutectic compositions which enhance dissolution of adjacent grains, and which subsequently may lead to loss of material strength. Although the "glassy" grain boundary phase is expected to be present in the cordierite-silicon nitride material, the presence of a Mg-SiAlON structure at the grain boundary interface is expected to prevent dissolution of adjacent grains during alkali absorption. Loss of material strength which may result in cordierite, is not expected to occur as dramatically after long-term high temperature exposure of the cordierite-silicon nitride material to volatile alkali.

Uncoated glass fibers in the aluminosilicate foam are considered as potential sites for reaction with volatile alkali, leading to devitrification of the fibers through the formation of soda-aluminosilicate complexes. If this sequence of reaction occurs, shrinkage and cracking of the fibers, and ultimately structural failure may result.

Reaction bonded silicon nitride presents a unique material which is not expected to have a separate grain boundary phase, provided that during fabrication, nitridation of fine grained silicon has resulted successfully. The inherent oxide layer present along the external surface of the filter element, as well as in the reaction bonded silicon nitride pores is the potential site for reaction with volatile alkali species. The oxidation kinetics of the reaction bonded silicon nitride material has been shown to be very slow at temperatures below 900-1000°C (1650-1830°F) which implies material's stability in the fixed-, fluid-, and entrained-bed gasification, and pressurized fluidized-bed combustion systems.

Potential phase transitions within the principal phases (i.e., alumina, mullite, cordierite, and silicon nitride) of the ceramic materials are not expected to occur during filter operation since each

material initially experienced a firing temperature that is higher than the expected filter process temperature. The presence of the glass phase, however, which has been shown to be the site for phase crystallization in the alumina/mullite material, may serve as the site for residual stress within the porous ceramic structure after long-term exposure to process conditions. During thermal cycling of the filter element which is either induced by process perturbations or pulse jet cleaning, cooling and crystallization of the "glassy" phases could introduce stress corrosion cracks, and subsequently flaws within the filter element structure.

Limited chemical and physical characterization data of in-field tested alumina/mullite filters suggest a potential loss in material strength. Further characterization of strength variation not only in a given filter element, but between filter elements within a given fabrication lot, and for filters from various fabrication lots are needed to confirm the strength reduction data. Similarly, the influence of steam, and possibly the reaction of volatile sulfur and chloride species, particularly with the non-oxide ceramics, as well as the reaction kinetics of alkali and associated change in material's strength all require further investigation.

Based on the information and data generated during Phase I of this contract, the following mechanisms are considered to represent the principal, potential, synergistic, long-term, high temperature degradation modes that could occur in the current state-of-the-art ceramic cross-flow filter materials:

- Reaction of volatile alkali species with grain boundary phases
- Oxidation of non-oxide ceramic phases at elevated temperatures
- Phase crystallization.

Each of these mechanisms could potentially introduce residual stresses within the porous ceramic matrix, particularly within the "glassy" grain boundary phases, which could lead to subsequent stress corrosion crack formation and flaw propagation. Ceramic cross-flow filter material degradation may also be influenced by:

- The interaction of the ceramic matrix with steam
- Possibly thermal cycling
- Possibly the interaction of fines which adhere to the "glassy" or amorphous phase present in each ceramic cross-flow filter material.

In developing the long-term, high temperature cross-flow filter element life performance models, the following critical issues have been identified:

- Definition of the alkali reaction(s) and kinetics for the various ceramic cross-flow filter material glass phases.
- Definition of the relationship between the alkali reaction and subsequent change in the ceramic material properties.
- Definition of an acceptable change or loss in the critical physical and mechanical properties that govern long-term cross-flow filter element integrity.

1. INTRODUCTION

To meet environmental regulations and equipment specifications in advanced power generating systems, studies are underway for developing and optimizing the use of advanced high temperature, high pressure particle control devices. The Federal New Source Performance Standards (NSPS) govern the concentration of utility or industrial emissions released. For turbines, a major operating requirement is minimal concentration of particles carried over into the expander. Excess particles are likely to cause erosion of the blade and vane metal surface. Therefore, consideration has been given to various configurations of particulate removal systems. For example:

- Cyclones (i.e., conventional and advanced concepts as electrified and rotating cyclones)
- Barrier filters (i.e., metal and ceramic)
- Granular filters (i.e., fixed shallow bed concepts, recirculating solid concepts)
- Ceramic bag filters (i.e., woven or felted concepts)
- Electrostatic precipitators.

Direct application of the high performance, high temperature particulate control devices will be of benefit to the advanced fossil fuel processes, selected high temperature industrial processes, and waste incineration processes.

Commercially available metal filters that are generally constructed of high temperature alloys undergo sulfidation of the metal surfaces when exposed to sulfur-laden combustion or gasification environments. Previous efforts at Westinghouse have demonstrated that, for sintered metal Inconel 671 filter tubes that were exposed to

gasification conditions at the Kellogg Rust-Westinghouse gasifier, excessive subsurface sulfidation resulted from the formation of an impervious metal sulfide eutectic layer which ultimately restricted gas passage. In order to prevent sulfidation of conventional filter metals, several ceramic filter concepts have been identified. These include woven fabric, felted, or batted bag filters, ceramic candle filters, and ceramic cross-flow filters.

Fabric bag filters which are made of ceramic fibers are an apparent analogue to conventional bag filters. Fabric filters are fabricated from:

- Silica fibers
- Alumina fibers
- Aluminosilicate fibers.

The basic types of fabrics used in the construction of the ceramic bag filters include felted or matted bag materials and woven cloths. Filter collection efficiency, cleanability, and durability are primary characteristics associated with the evaluation of these materials during operational filter life. In addition to these characteristics, the chemical and thermal integrity of the filter materials when exposed to high temperature coal gasification or combustion environments is also a critical issue. Factors that affect fabric durability can be divided into chemical aspects as temperature stability, oxidation resistance, corrosion resistance, interaction with fines, and embrittlement, as well as to physical aspects as breaking strength, impact resistance, pin holing, crush strength, flexural rigidity, abrasion, impingement, and burst strength.

Ceramic fibers are inherently brittle, making their mechanical processing into conventional fabric forms difficult. During testing, the felted fabric bag filter design demonstrated high particle collection efficiency, but are difficult to clean by reverse pulse-jet methods. During repeated cleaning cycles, large tufts of felt material

can be dislodged, causing thinning or tearing. The woven ceramic bag filters not only have high particle collection efficiencies, but can also be cleaned effectively by simple pulse-jet methods. Failure of the woven ceramic bags, however, results due to particle impingement and abrasion.

The dual requirement of mechanical durability and chemical resistance to the gasification or combustion environments can conceivably be satisfied through the use of rigid barrier filters as the ceramic candle or cross-flow filter. Generally the candle filters are manufactured as closed-base, open flanged tubes, and are considered to be much stronger than woven ceramic fibers. Currently candle filters are fabricated from:

- Alumina fibers bound by a fused clay binder
- Silicon carbide grains encapsulated with clay binder and aluminosilicate fiber tufts
- Aluminosilicate grains embedded in a clay binder.

Silicon carbide candle filters are available from Schumacher'sche Fabrik of Bietigheim, Didier in the Federal Republic of Germany, and Industrial Filter and Pump (Refractron). Test programs previously conducted at Westinghouse demonstrated near absolute particulate removal capability (>99.9+%) for these filters. Failures, however, were experienced with the candles and were predominantly with fracture of the candle at the tubesheet array mounting flange. Possible failure mechanisms which were considered included:

- Flow induced vibration
- Thermal shock
- Flow-thermal distributions
- Slug momentum impact
- Chemical interactions
- Thermo-mechanical impact
- Material degradation.

After performing detailed analysis of failed candles, failure was attributed to thermal shock caused by thermal stress induced by rapid heating and cooling, and by the generation of solid slugs which were formed during pulse purging which ultimately impacted the candle with sufficient momentum to produce high stress regions near the tube sheet. Additional post exposure analysis of failed candles indicated high and low density bands of the silicon carbide material along the tube length. No significant voids or inclusions were apparent. The flange section appeared to consist of a higher density, more uniform material. Analysis of the candle fracture surface indicated that the silicon carbide filter material was bonded together with a clay binder that could react with volatile alkali or other process gas phase constituents.

The ceramic cross-flow filter also represents an attractive technology for high temperature particulate removal. This is primarily due to the excellent high temperature material's properties (i.e., strength, thermal shock resistance, and relative chemical inertness), compact filter element geometry, and >99.9% particulate removal efficiencies. The cross-flow filter consists of multiple layers of thin, flat, porous ceramic sheets that have parallel channels formed on one side, and which are stacked with adjacent layers oriented perpendicularly to each other. When in use, the particle-laden gas deposits a layer of fines along the channel surfaces, which can be periodically backpulsed. Cross-flow filters are currently being fabricated from:

- Mixed oxides containing alumina, mullite, and anorthite
- Oxides as cordierite or aluminosilicates.

Advanced concepts include the use of:

- Nonoxides as reaction bonded silicon nitride
- Mixed oxides-nonoxides as cordierite-silicon nitride.

In operation, multiple filter elements are connected to an exhaust manifold with the gas exit end of each filter element attached to the manifold. A major problem which arises during use of the cross-flow filter element is delamination along rib-to-plate seams. If sharp corners exist, stress analyses have shown that the stresses at the gas path channel corners during pulse cleaning can approach the cross-flow material's strength. These stresses are considered to result from thermal shock of the cold cleaning pulse impinging on the hot cross-flow material surface, and from the overpressure caused by the high pressure cleaning pulse. Other failures which have been observed during bench-scale or pilot scale testing of the cross-flow filters include:

- Crack formation at the base of the flange
- Collapse of the rib-to-plate channels.
- Crack formation perpendicular to dirty gas channel caused by thermal shock.

Further efforts are required for development of an effective means for bonding adjoining filter element surfaces (i.e., rib-to-plate), or to development of a manufacturing process which forms a monolithic structure. Success in either of these areas would ultimately minimize or alleviate the problem of filter delamination. Failures as delamination and crack formation along the filter flange reflect critical design and fabrication issues encountered in the production of the complex, porous, filter element. Once these issues are resolved, the stability of the filter element will depend on its ability to withstand mechanical stresses induced during process operation, and to changes that would possibly result through either thermal and/or chemical interactions.

2. PROJECT SUMMARY

Westinghouse has undertaken a 14-month Phase I, base program effort under DOE Contract DE-AC21-88MC25034, in order to identify potential long-term, high temperature [538 to 1370°C (1000 to 2500°F)], degradation mechanisms that could occur in ceramic cross-flow filter elements during operation in fixed-bed, fluid-bed, and entrained-bed gasification, direct coal fired turbine, and pressurized fluidized-bed combustion systems. Specific objectives of the Phase I effort include identification of the influence of:

- Ceramic cross-flow filter material composition on the thermal and/or chemical degradation.
- Temperature and exposure duration on possible phase transitions which may occur within the various ceramic cross-flow filter materials.
- Reactant gas chemistry (i.e., volatile alkali and/or sulfur, reducing or oxidizing gas conditions) on ceramic cross-flow filter material stability or degradation.
- Ash chemistry (i.e., pressurized fluidized-bed combustion ash or gasifier coal char) on ceramic cross-flow filter material stability or degradation.
- Reaction kinetics for chemical degradation of the various ceramic filter material.

The Phase I effort which began in October 1988 was structured such that in Task 1 a plan for identification and evaluation of the long-term degradation mechanisms was devised. The plan included:

- Identification of the process operating parameters (i.e., temperature, pressure, bulk gas chemistry, etc.) which the cross-flow filters would likely experience.
- Conduct of a general ceramic, patent, and process literature review, emphasizing ceramic fabrication and processing, and possible thermal and/or chemical interactions.
- Selection, procurement, and characterization of ceramic cross-flow filter materials.
- Thermodynamic phase stability assessment identifying the thermal influence, and possible interaction of bulk gas, volatile trace constituents, and fines with the various ceramic cross-flow filter materials.

This information was assimilated in Task 2, and an evaluation of the potential degradation mechanisms was performed, relating the influence of process temperature, bulk gas, trace constituent, and fines interactions with the various filter material phases. Task 3 documents the Task 1 and 2 efforts in this Topical Report.

Phase II of this contract is intended to experimentally demonstrate the proposed thermal/chemical degradation mechanisms identified in Phase I for the various cross-flow filter materials. The resulting experimental bench-scale data will be correlated with in-field filter exposure test data (Task 4). Predictive models will be developed which project ceramic filter performance and life during long-term operation (Task 5). A Final Report will be issued at the conclusion of Task 5, assimilating the bench-scale and in-field test data, and the predictive modeling effort.

3. TECHNICAL DISCUSSION

The overall objective of Phase I is to identify the potential thermal and/or chemical degradation mechanisms that are likely to occur in ceramic cross-flow filter materials during operation at high temperature [538 to 1370°C (1000 to 2500°F)] in coal gasification and combustion environments. Phase II of this contract will assess the influence of these degradation mechanisms on filter operating performance and life.

To begin identifying the potential thermal and/or chemical degradation mechanisms, an understanding of both process and filter operating conditions is needed. Similarly an understanding of thermal and chemical stability of candidate ceramic materials used in the fabrication of cross-flow filter elements is needed. A review of both of these technology areas is presented in Section 3.1.1.

Chemical and physical characterization of cross-flow materials which are used in filter element fabrication provides fundamental information which can be used to project material stability at process conditions. Similarly, characterization of process chars and ashes also provides fundamental information which can be used to project potential reactions with the various ceramic cross-flow filter materials. Characterization data which have been generated from analysis of the candidate cross-flow materials, and process chars and ashes are detailed in Section 3.1.2.

Thermodynamic equilibrium calculations have traditionally been used to establish a first level approximation of chemical reactions that are likely to occur at process conditions. This approach has been used

in Section 3.1.3 and Appendix A to project the effluent gas and solid phase chemistry emitted from the coal gasification and combustion systems; the effect of process gas chemistry, temperature, and pressure on ceramic cross-flow filter material stability; the effect of trace emissions as alkali and chlorides on ceramic cross-flow filter material stability; and the effect of char and ash chemistry on potential interactions with various phases present in the ceramic cross-flow filter materials. The validity of the equilibrium models is a function of not only the thermodynamic data which is used, but also the manner in which the calculation is designed to simulate process conditions, and the interpretation which follows of the generated phase and concentration projections.

Section 3.1.4 presents a discussion of bench-scale and in-field test experience which supports and extends the information generated in the technology review, materials characterization, and phase stability assessment sections.

Utilizing the information generated in Task 1, potential long-term high temperature degradation mechanisms are identified for each of the candidate cross-flow filter materials during operation in the fixed-bed, fluid-bed, and entrained-bed gasification systems, and in the direct coal fired turbine, and pressurized fluidized-bed combustion systems. A discussion of these mechanisms is presented in Task 2, Section 3.2. This document serves to fulfill the contract requirement in Task 3, for assimilation of all data and information generated during conduct of the Phase I, Task 1 and 2 efforts.

3.1 TASK 1: IDENTIFICATION OF LONG-TERM HIGH TEMPERATURE DEGRADATION MECHANISMS

3.1.1 Technology Review

3.1.1.1 Coal Process Systems

Chemical degradation of the cross-flow materials potentially includes the interaction of the ceramic filter material with the advanced energy conversion plant process gases; with trace and minor species as volatile alkali and sulfur compounds; and with particulates through either gas phase condensation of eutectics or molten salts, or entrained ash fines. A review of the literature is presented in this Section illustrating the variability in process gas chemistry, in the concentration of process trace and minor element emissions, and in the ash or char particulate composition. Appendix A presents thermodynamic models that either were previously generated, or were generated during the course of this contract. The models reflect the projected equilibrium bulk gas and particulate fines chemistry released into the effluent streams of the fixed-bed, fluid-bed, and entrained-bed gasification, direct coal fired turbine, and pressurized fluidized-bed combustion systems.

Process Gas Phase Chemistry

During combustion, volatiles including pyrolyzed organics are released from the coal particle as either attached or detached flames. The chemical transformations which occur within the organic material during rapid heating and combustion are kinetically limited for particles smaller than 100 microns, and diffusion limited for larger particles. Initially, conditions at the particle surface are reducing, with limited diffusion of oxygen through the boundary layer. Nonvolatiles may be trapped within the organic matrix, remain bonded with the organic compounds, or are released directly into the effluent gas stream.

The coal particle fractures during combustion as a result of internal burning, forming liquid ash droplet agglomerates. The ash agglomerates may expand through release of internal gases, forming hollow cenospheres, or may burst releasing a shower of submicron particles. Alternately, the cenospheres may coalesce with adjacent particles. Entrapped within the melted matrix of the cenosphere are volatile species, which can undergo a secondary transition, forming an ashed-sphere packed with smaller spheres (plerospheres).

Not all of the trace elements contained in the coal particle may be volatilized during combustion. Under these conditions a sizeable portion becomes entrapped within the liquid matrix, where volatilization is diffusion limited. Similarly, nonvolatiles that are expected to result in the solid ash residues may be transferred into the effluent gas if associated with the organic matrix.

When the last combustible volatile species is consumed, the condition at the particle surface changes from strongly reducing to a mildly oxidizing environment. Because of the high percentage of oxygen required for total combustion, most of the volatiles exist in an oxidized state following combustion.

In order to assess the stability of the ceramic cross-flow materials during operation in the combustion or gasification environment, consideration is given to the process operating temperature, pressure, gas composition, as well as particulate load and composition which the filters may experience. Table 3.1 presents a summary of process parameters identified for fixed-bed, fluid-bed, and entrained-bed gasification, direct coal fired turbine, and pressurized fluidized-bed combustion systems. Process flow diagrams for the specific systems identified in Table 3.1 are provided in Figures 3.1 through 3.5.⁽¹⁻³⁾ Variability is evident in the expected gas compositions which the ceramic cross-flow filter elements may encounter during hot gas cleaning (i.e., gas phase moisture content is shown to

TABLE 3.1
PROCESS SYSTEM CHARACTERIZATION⁽¹⁻³⁾

System	Fixed-Bed Gasification	Fluid-Bed Gasification	Entrained-Bed Gasification	Direct Coal Fired Turbines	Pressurized Fluidized Bed Combustion
Gasifier/Combustor Temperature, °C	400-600	700-800	1300	1000-1350	800-1000
Filter Temp., °C	590	700	870	980	870
Filter Pressure, psig	300	300	450	180	150
Composition					
Oxidizing	-	-	-	X	X
Reducing	X	X	X	-	-
Gas Composition, %					
(Process)	(Lurgi)	(KRW)	(Texaco)	-	-
O ₂	-	-	-	15.16	3.45
N ₂	0.34	0.1	0.81	70.62	75.25
CO ₂	1.48	12.25	7.95	7.57	13.63
SO ₂	-	-	-	54 ppmv	0.34
H ₂ O	22.70	17.47	25.0	6.63	7.33
CO	44.45	37.00	38.84	-	-
H ₂	23.29	27.97	26.38	-	-
CH ₄	5.94	4.31	0.10	-	-
H ₂ S	1.06	0.90	0.92	-	-
Particulate Loading, ppm	1000-2000	1000-10,000	4000	~1,000	1000-10,000

Station	①	②	③	④	⑤
Pressure, psia	475	415	327	320	300
Temperature, °C	327	100	140	870	650
Composition, Mol %					
CH ₄			6.50	5.94	6.05
H ₂			25.48	23.29	23.71
CO			48.64	44.45	45.27
CO ₂			1.62	1.48	1.51
H ₂ S			1.16	1.06	0.5 ppm
COS			0.05	0.04	
NH ₃			0.76	0.70	
N ₂		2	0.38	0.34	0.35
O ₂		98			
H ₂ O (v)	100		15.41	22.70	23.11

Figure 3.1 - Fixed-Bed Gasification⁽¹⁾

Station	①	②	③	④
Pressure, psia	480	480	450	350
Temperature, °C	300	100	1050	650
<u>Composition, Mol %</u>				
CH ₄			4.31	3.92
H ₂			27.97	25.42
CO			37.00	33.63
CO ₂			12.25	11.14
H ₂ S			0.90	0.5 ppm
COS				
N ₂		0.5	0.1	0.09
O ₂		99.5		
H ₂ O(v)	100.		17.47	25.80

Figure 3.2 - Fluid-Bed Gasification⁽¹⁾

Station	①	②	③
Pressure, psia		450	400
Temperature, °C	150	870	650
Composition, Mol %			
CH ₄		0.10	0.08
H ₂		26.38	27.74
CO		38.84	40.83
CO ₂		7.95	8.38
H ₂ S		0.92	0.5 ppm
COS			
N ₂	1.5	0.81	0.64
O ₂	98.5		
H ₂ O(v)		25.0	22.33

Figure 3.3 - Entrained-Bed Gasification⁽¹⁾

Station	①	②	③
Pressure, psia	282	180	15
Temperature, °C	15	1010	378
Composition, Mol %			
CH ₄			
H ₂			
CO			
CO ₂		7.57	
H ₂ S			
COS			
N ₂		70.62	
O ₂		15.16	
H ₂ O (v)		6.63	
SO ₂		54 ppmv	
SO ₃		14 ppmv	
HCl		14 ppmv	
NaCl		0.07 ppmv	
KCl		0.03 ppmv	

Figure 3.4a - Direct Coal Fired Turbine, Slurry-Fired System⁽²⁾

Station	①	②	③	④
Pressure, psia	282	282	193	15
Temperature, °C	649	649	1093	426
Composition, Mol %				
CH ₄	0.94			
H ₂	24.04			
CO	44.69			
CO ₂	17.59		7.57	
H ₂ S	3455 ppmv			
COS	216 ppmv			
N ₂	0.56		70.62	
O ₂			15.16	
H ₂ O (v)	11.80		6.63	
SO ₂			54 ppmv	
SO ₃			14 ppmv	
HCl	137 ppmv		14 ppmv	
NaCl	0.37 ppmv		0.07 ppmv	
KCl	0.40 ppmv		0.03 ppmv	

Figure 3.4b - Direct Coal Fired Turbine, Gas-Fired System⁽²⁾

Station	①	②	③	④	⑤
Pressure, kPa (psia)	101.4(14.7)	1013.6(147)	965.3(140)	930.8(135)	105.5(15.3)
Temperature, °K (°F)	288(59)	597(614)	1255(1800)	1233(1760)	776(937)
Excess Air, %	—	—	21	21	30
Molar Composition, %					
O ₂	21	21	3.45	3.45	4.61
CO ₂	—	—	13.63	13.63	12.72
H ₂ O	—	—	7.33	7.33	6.85
SO ₂	—	—	0.34	0.34	0.32
N ₂	79	79	75.25	75.25	75.50

Figure 3.5a - Pressurized Fluidized-Bed Combustion^(a)

Station	①	②	③	④	⑤	⑥
Pressure, kPa (psia)	101.4(14.7)	1013.6(147)	972.2(141)	951.5(138)	105.5(15.3)	101.4(14.7)
Temperature, °K (°F)	288(59)	597(615)	1283(1850)	1255(1800)	797(975)	408(275)
Excess Air, %	—	—	250	250	275	275
Molar Composition, %						
O ₂	21	21	14.67	14.67	15.07	15.07
CO ₂	—	—	4.88	4.88	4.57	4.57
H ₂ O	—	—	2.62	2.62	2.44	2.44
SO ₂	—	—	0.11	0.11	0.11	0.11
N ₂	79	79	77.71	77.71	77.81	77.81

Figure 3.5b - Adiabatic Fluidized-Bed Combustion^(*)

range from 6.6 to 25 percent). For all process systems the ceramic cross-flow filter element temperature is below the gasifier or combustor outlet temperature. Expected filter operating pressures are 150 to 450 psig. For each of these process systems, various options exist for both the manner of operation (i.e., in-bed, fine particle injection, equipment external to the gasifier or combustor) and the composition of materials used for desulfurization (i.e., dolomite, zinc ferrite, etc.) alkali (i.e., emathlite, bauxite, etc.) and particulate removal (i.e., cross-flow, candle or fiber filter).

Table 3.2 illustrates that for a particular process system (i.e., the Kellogg Rust-Westinghouse gasifier), changes in operating parameters (i.e., gasification under air-blown as opposed to oxygen-blown conditions, feed materials, etc.) can significantly affect the process gas phase composition.⁽⁴⁾ Not only does the bulk gas chemistry change, but also variations are expected in the total sulfur and alkali emission concentrations that are released into the effluent gas stream.

Process Trace and Minor Gas Phase Emissions

The fate of trace and minor species present in coal during gasification or combustion depends on the affinity, concentration, and distribution of the element within the inorganic or organic-associated coal matrix, as well as the process operating conditions as temperature, pressure, residence time and heating rate of the coal particle in either the gasifier or combustor, and the associated gas scrubber (i.e., sulfur and/or alkali) and particulate control systems.

Sulfur is present in coal as either an inorganic or organic constituent. As an inorganic phase, sulfur exists within the coal structure as iron disulfide (FeS_2), in either a cubic crystalline pyritic or rhombic marcasite structure, and as sulfates of iron and calcium. Numerous organic sulfur species as thiophenes, phenyl disulfides and sulfides, mercaptans, and thioethers are known to be included in the coal matrix. During combustion, coal-contained sulfur

TABLE 3.2

**THERMODYNAMIC EQUILIBRIUM PROJECTIONS OF THE
KELLOGG RUST-WESTINGHOUSE GASIFIER
EFFLUENT GAS COMPOSITIONS (4)**

	Oxygen-Blown	Air-Blown	Air-Blown	Oxygen-Blown	Air-Blown
Coal	Illinois No. 6	Illinois No. 6	Pittsburgh	Wyoming	Wyoming
Temperature, °C	1027	1027	1027	1027	1027
Pressure, atm	15	15	15	15	15
Coal Feed Rate, lb/hr	100,000	100,000	100,000	100,000	100,000
Oxidant, lb/hr	58,420	294,650	324,910	55,040	267,960
Steam, lb/hr	50,000	25,000	25,000	50,000	25,000
<u>Gas Composition, %</u>					
CO	48.86	29.49	29.63	27.9	19.2
H ₂	40.25	20.05	19.19	31.4	17.2
H ₂ O	4.98	0.80	0.77	26.4	10.5
CO ₂	3.49	0.68	0.69	13.5	6.8
CH ₄	0.95	0.44	0.41	0.05	0.01
N ₂	0.72	48.06	48.99	0.56	46.2
H ₂ S	0.68	0.42	0.28	0.15	0.09
HCl	0.03	0.02	0.02	0.001	
COS	0.03	0.02	0.02	0.005	
Na, ppm*	19.4	23.3	10.6	51	34.0
K, ppm*	4.3	12.1	5.5	32	20.1

* As Chloride ; Based on Total (Soluble and Insoluble) Alkali Released from the Feed Material

is released as volatile SO_2 and SO_3 , while during gasification, the principal volatile phase released is H_2S . Chemical species which release sulfur into the effluent gases are dependent on the process temperature. Table 3.3 illustrates several of the sulfur release reactions which are expected to occur at temperatures ranging between 300 and 600°C (572 and 1112°F) for both inorganically and organically bound sulfur.⁽⁵⁾

Efforts have demonstrated that near complete release of sulfur bound within the pyritic structure can be achieved during coal processing.⁽⁵⁾ Release of organically bound sulfur is, however, limited. Organic sulfur appears to be repartitioned within the iron and calcium constituents of the ash matrix, or to be retained within the collapsed carbon structure.

Chemical analyses have been performed to demonstrate the concentration and distribution of alkali in the coal structure. Data indicate that alkali is present in two principal phases -- a water soluble phase which includes alkali chlorides, sulfates, carbonates, and hydroxides, and an insoluble aluminosilicate phase which includes the water glasses and feldspars.⁽⁶⁾ The insoluble alkali concentration has demonstrated limited solubility in water, and to a somewhat greater extent is acid leachable. Table 3.4 illustrates an example of this partitioning. Notably, a greater proportion of alkali present in coal is contained within the insoluble structure.

The release of alkali from the coal particle during gasification and combustion has previously been projected by Westinghouse.⁽⁷⁻¹³⁾ In general, the water soluble alkali complexes are expected to be completely released during gasification and combustion, with partial alkali release occurring from the insoluble aluminosilicate lattice. Figure 3.6 illustrates the complex chemistry associated with alkali release during combustion, and subsequent reactions which have been proposed based on thermodynamic equilibrium models.⁽¹⁴⁾ The kinetics for these reactions, however, remains to be determined.

TABLE 3.3

SULFUR RELEASE FROM COAL AS A FUNCTION OF PROCESS TEMPERATURE⁽⁵⁾

<u>Temperature</u>	<u>Reactions</u>
	H_2/N_2
300°C	$FeS_2 \xrightarrow{\hspace{1.5cm}} FeS + H_2S$ $FeSO_4 \xrightarrow{\hspace{1.5cm}} FeO + (SO_2 + H_2SO_4)$ <u>Decomposition:</u> Aliphatic Thiols R-C-S-H 160°-180°C Disulfides R-S-S-R 200°-220°C Aromatic Thiols ϕ -S-H 220°-250°C Aliphatic Sulfides R-S-R 240°-280°C
300°-550°C	Continued Inorganic Sulfur Release <u>Decomposition:</u> Alicyclic Sulfides 290°-330°C Aryl Sulfides 450°-470°C Thiophenic Sulfur 500°-550°C
	$H_2/H_2O/N_2$
550°C	$FeS \xrightarrow{\hspace{1.5cm}} FeO + H_2S$ $FeS \xrightarrow{\hspace{1.5cm}} FeSO_4 + H_2$ $FeSO_4 \xrightarrow{\hspace{1.5cm}} FeO + SO_2$ Continued Organic Sulfur Release
600°C	H_2O/N_2 Continued Organic Sulfur Release

TABLE 3.4

CONCENTRATION OF ALKALI AND CHLORIDES IN PITTSBURGH NO. 8 COAL, Wt%

<u>Coal, Wt. %</u>		<u>Coal, Wt. % (Estimated Wt. % Oxide in Ash)</u>	
C	74.45	Si 1.65	(SiO ₂ 51.17)
H	4.97	Al 1.06	(Al ₂ O ₃ 29.03)
N	1.51	Fe 0.72	(Fe ₂ O ₃ 14.92)
O	6.17	Ca 0.16	(CaO 3.23)
S	3.00	Mg 0.012	(MgO 0.29)
H ₂ O	2.51	Ti 0.056	(TiO ₂ 1.35)
Ash	<u>7.39</u>		
	100.00		

ALKALI AND CHLORIDE DISTRIBUTION, WT. %

	<u>Na</u>	<u>K</u>	<u>Cl</u>
Soluble	0.006	0.006	
Insoluble	0.100	0.270	
Total	0.106	0.276	0.009

Condensation Reactions:

Nucleation Reactions:

* CaO · MgO = Representative of either half- or fully calcined, or sulfated sorbent material
 ** (c) = condensed = solid + liquid

Figure 3.6 - Chemical Pathways in Coal Combustion Systems⁽¹⁴⁾

The thermodynamic equilibrium models project a partitioning of the coal-contained alkali between the flue gas (i.e., principally as volatile chlorides with secondary alkali sulfate and hydroxide formations) and the resulting ash particulates (i.e., alkali aluminosilicates, water glass phases, and feldspar complexes). Bench-scale studies in combustor burner rigs have demonstrated conversion of sodium chloride in the presence of gaseous sulfur dioxide to sodium sulfate within 2.2 milliseconds.⁽¹⁵⁾ The volatile alkali which is released can then either be adsorbed onto the surface of entrained ash fines; nucleate to form aerosol droplets; or condense as either corrosive solid or liquid sulfate or mixed eutectic formations. Any of these alkali formations may result in deposition along process components (i.e., ceramic cross-flow filters) which subsequently has the potential to lead to surface material corrosion (Figure 3.7).

Similar to combustion, alkali which is released from coal during gasification is also considered to be in the form of the volatile chloride phase. Conversion, however, to the sulfate phase is expected to result in the presence of oxygen in the turbine expansion gases. A detailed discussion of the fate of gasifier or combustor alkali emissions is presented in Section 3.1.3.

Based on the literature, alkali volatilizes from the coal structure during processing, probably as a chloride, oxide, or hydroxide. Thermodynamic estimates and/or analytical determinations of the alkali content in the process streams, however, tend to vary. Five major factors have been identified to influence the extent at which alkali is released into the effluent gas streams. These include:

- Process temperature
- The initial quantity and form of alkali present in the coal structure
- The influence of chlorine
- Possible synergistic interactions between the alkali phases
- The influence of alumina, silica, or aluminosilicates present in the ash on alkali capture and retention.

Figure 3.7 - Deposition Pathways in Coal Combustion Processes

Thermodynamic equilibrium calculations have demonstrated that as process operating temperature increases, volatilization of alkali from the water soluble phase increases. Similarly, the potential for conversion and release from the insoluble alkali matrix to the soluble matrix is increased. The higher the concentration of alkali present in the feed material, the greater the potential concentration of alkali released into the effluent gas stream. High chlorine coals have generally been considered to enhance alkali emissions. This is perhaps partly because the chloride content is an indicator of the soluble, releasable alkali content, and partly because excess chloride enhances the release of the non-chloride alkali as shown in the following reactions: (16)

where M is either sodium or potassium.

Reaction of sodium and potassium sulfate has the potential to lead to the formation of low melting temperature, mixed sulfate eutectic complexes within the effluent gas stream passage. Melting temperatures for sodium and potassium sulfate are reported at 884 and 1061°C (1623 and 1942°F), respectively. The formation of a mixed eutectic complex lowers the sulfate melting temperature to approximately 837°C (1539°F).

The presence of alumina, silica, or aluminosilicates in coal ash has the potential to react and retain volatile alkali species. In the presence of water vapor, relatively high alkali capture results through the formation of molten glass phases. (18) The potential stickiness of

these phases can obviously lead to agglomeration of particles upon contact, as well as the formation of tenaciously adherent deposits on process component surfaces. (17)

The following section presents a brief discussion of results that were generated from thermodynamic models previously developed at Westinghouse. These projections illustrate that the concentration of alkali released into the effluent gas stream is dependent on the feed material, feed rate, and the manner in which the process is operated (i.e., oxygen versus air blown). A detailed review of both previously generated Westinghouse thermodynamic projections, and those generated during the course of this contract for each of the five coal process systems is presented in Appendix A.

Alkali Release Thermodynamic Calculations

Several studies have been conducted investigating the thermodynamics of alkali release at various process conditions, with the objectives of obtaining order-of-magnitude projections of alkali release concentrations; predicting the effects of operating conditions on release; and predicting the identities of the released species. The most extensive reported sets of such calculations have been made at Westinghouse and GE.

Calculations performed at Westinghouse (8,7,18,19) have shown that:

- higher temperature increases alkali release
- increased excess chlorine content inhibits liquid sulfate condensation
- the predominant released species are the alkali chlorides.

Table 3.5 illustrates typical projections for a pressurized fluidized-bed combustion system.

TABLE 3.5

THERMODYNAMICALLY PROJECTED EFFLUENT GAS COMPOSITIONS FORMED
DURING COMBUSTION OF PITTSBURGH NO. 8 COAL

Combustor Temp., °C	1010	1370
Pressure, atm	12.4	12.4
Mass Air/Mass Coal	26.32	15.68
CO ₂ (v/o)	6.6593	11.0465
O ₂ (v/o)	10.6623	5.2223
N ₂ (v/o)	79.7572	78.8852
H ₂ O (v/o)	2.8181	4.6747
SO ₂ (v/o)	0.1003	0.1665
HCl (v/o)	0.0025	0.0039
NaCl (g) (ppm)	1.106	4.163
KCl (g) (ppm)	1.519	2.546
Na ₂ SO ₄ (g) (ppm)	0.065	0.001
K ₂ SO ₄ (g) (ppm)	0.080	-----
NaOH (g) (ppm)	0.006	0.448
KOH (g) (ppm)	0.008	0.255
(NaCl) ₂ (g) (ppm)	0.001	-----
(KCl) ₂ (g) (ppm)	0.001	-----
Na (g) (ppm)	-----	0.003
K (g) (ppm)	-----	-----
NaO (g) (ppm)	-----	0.001
KO (g) (ppm)	-----	-----
Na ₂ SO ₄ (c) (ppm)	0.770	-----
K ₂ SO ₄ (c) (ppm)	-----	-----

Westinghouse has also evaluated alkali release under gasification conditions.⁽²⁰⁾ For the Kellogg Rust-Westinghouse gasifier which operated at 1027°C (1880°F) and 15 atm, alkali concentrations of 20 ppm NaCl and 4 ppm KCl were projected. Higher concentrations were projected at higher operating temperatures. For example, a Winkler gasifier operating at 815°C (1500°F) and 2.1 atm is projected to produce a gas containing 15 and 8 ppm NaCl and KCl, respectively, while operating at 1093°C (2000°F), the effluent gas stream is projected to contain 130 and 100 ppm NaCl and KCl, respectively. Calculations⁽⁹⁾ suggest that less than one percent of the coal sodium, and between 3 and 10 percent of the coal potassium will be released during gasification. The Westinghouse thermodynamic model suggests that more alkali will be released from coals which contain low concentrations of alumina in the resulting ash.

Thermodynamic studies at GE also show the importance of coal chlorine concentrations and process operating temperature in determining the magnitude of alkali release, and have mainly focused on the combustion environment. GE used their thermodynamic calculations as the basis for reference design alkali concentrations of 3 ppm volatiles, and 43 ppm water-soluble condensed phase alkali in PFBC off-gases.⁽²¹⁾ Conclusions from the GE studies are as follows:⁽²¹⁻²³⁾

- Alkali present in coal as soluble salts evaporates before equilibrium with the ash aluminosilicate can occur. Comparison of PFBC alkali data with such equilibrium calculations⁽²¹⁾ was used to support this conclusion, and, despite the questionable nature of this PFBC data, this conclusion is believed to be valid. It is also consistent with the lack of effectiveness of in-bed alkali removal or gettering.

- Evaporation results in supersaturation of the gas (once temperature falls below the flame temperature). Condensation occurs via formation of sulfates to restore equilibrium. The alkali volatiles remain primarily as chlorides with less than 20 percent forming gaseous sulfates and hydroxides.
- Just above the bed, there is near-equilibrium with the sulfates.

Gruninger⁽²⁴⁾ at Aerodyne modified the NASA Lewis thermodynamic chemical equilibrium code to consider both ideal solution behavior and pure condensed components. With this modified model, significantly lower alkali volatile emissions were predicted than with the unmodified pure-component model. The authors⁽²⁴⁾ indicated that the predictions may be unrealistic in that they assume complete equilibration with the ash, which is not believed to be true.

Aerodyne^(25,26) performed thermodynamic modeling, including looking at the surface/interior partitioning of the alkali atoms in particles to demonstrate that alkali which was originally part of the aluminosilicate matrix segregates to the outer surface of the particle during combustion. The Aerodyne model was also used to project release rates. Measured alkali levels at CURL were stated to be below equilibrium levels. A kinetic model is claimed⁽²⁶⁾ to have been developed to accurately predict actual measured concentrations.

Thermodynamic calculations at NASA⁽²⁷⁾ resulted in the prediction that gaseous sodium sulfate will exist under fuel-lean conditions. Gaseous alkali chloride (if chlorine is present) and volatile atomic and carbonate alkali species (if no chlorine is present) are also predicted to exist.

Halstead and Raask⁽²⁸⁾ performed simple thermodynamic calculations using published sodium chloride and sodium sulfate vapor pressures and gas phase equilibria involving them, to demonstrate that under combustion conditions with chlorine present, the predominant volatile alkali species is the chloride. At very high temperatures, significant amounts of the alkali hydroxide phase will also be present. Upon cooling, however, the calculations predict that the alkali sulfate phase will predominantly exist.

Many of the thermodynamic studies described above use an ideal solution assumption for the condensed phase. Hastie⁽²⁹⁾ at the National Bureau of Standards performed rigorous thermodynamic studies demonstrating the importance of non-ideal solution behavior on projected alkali release. Using the ideal solution assumption generally resulted in projections of incorrect principal volatile species, and concentrations of alkali vapor that were an order of magnitude too high. Hastie also demonstrated that if chloride were included in the system, alkali release was enhanced by two orders of magnitude relative to the chloride content. This important and real effect is not found with the ideal solution assumption.

Process Alkali Data

Data⁽³⁰⁻⁵⁹⁾ which have been obtained from operational gasification and fluidized-bed combustion process sites are summarized in Table 3.6. Where available a brief description of the unit, feed materials, bed temperature, gas temperature at the sampling site, and the gas phase alkali composition are indicated. Review of this table indicates that alkali concentrations range from several ppb (Curtiss Wright PFBC combined sodium and potassium) to nearly 150 ppm (METC AFBC). Although limited data are presented for gasification systems, alkali concentrations reported to be released are on the order of 25 ppm combined alkali.

Correlation between the various processes, operating parameters, coal feed types, and released alkali concentrations cannot be made using the data shown in Table 3.6. Operation of even the same unit at higher temperatures does not indicate a direct impact on the released alkali concentration as shown for the data generated at the Argonne PFBC (operation at 649-721°C (1200-1330°F) released 5 ppb Na, 30 ppb K; operation at 871-949°C (1600-1740°F) released only 10 ppb Na, 10 ppb K). Similarly at Leatherhead, operation of the PFBC at 888°C (1630°F) released between 2.3-12.2 ppmw Na, and 1.3-5.0 ppmw K, while operations at 952°C (1745°F) released between 1.1-2.7 ppmw Na, and 0.6-2.5 ppmw K.

Similarly, the data presented in Table 3.6 cannot be used to identify the contribution of alkali released from the sulfur sorbent materials. This can be illustrated by comparing the Argonne PFBC data which reported release of 1 ppb Na and 1 ppb K when the unit was operated at 921°C (1690°F) with Sewickley coal and Tymochtee dolomite, and with the Leatherhead PFBC unit data which reported release of 2.3-12.2 ppm Na and 1.3-5.0 ppm K during operation at temperatures of 888°C (1630°F) with Pittsburgh coal and dolomite 1337. Tymochtee dolomite which is known to contain high alkali concentration⁽¹⁴⁾ is expected to release higher concentrations of sodium and potassium in comparison to systems that utilize sulfur sorbents which contain lower alkali concentrations (i.e., Pfizer dolomite or 1337).

Although a direct correlation can not be established for alkali release as a function of process operating parameters, the data reported in Table 3.6 illustrate that alkali release is generally between 0.1 and 10 ppm. These levels are somewhat lower than the thermodynamic equilibrium projected alkali release levels projected in Table 3.2. Consideration is given to the possibility that condensation of volatile alkali has occurred between the gasifier or combustor outlet and the sampling site. Condensation which could have resulted along the entrained ash or char fines, or along the system component surfaces would ultimately lower the concentration of volatile alkali remaining in the effluent gas stream.

TABLE 3.6
PROCESS SYSTEM DATA ILLUSTRATING ALKALI RELEASE

Process System	Description	Feed Materials	Bed Temperature, °F	Off-Gas Temperature, °F	Alkali Analysis	Reference
UK National Coal Board - Cheltenham	12" x 12" "Corrosion" Combustor; AFBC Unit	• Pittsburgh Seam Coal (13.5 wt. % Ash, Containing 0.7 wt. % Na ₂ O, 1.6 wt. % K ₂ O) • Limestone 18	1560	1410-1475	2.7-4.4 ppmw Na 0.7-3 ppmw K	30, 31
		• Illinois No. 6 (11.8 wt. % Ash, 1.7 wt. % Na ₂ O, 1.8 wt. % K ₂ O) • Penrith UK Limestone	1630		0.7-1.2 ppmw Na 0.5-2.0 ppmw K	30
UK National Coal Board - Leatherhead	24" x 48"; 5 atm Unit; PFBC	• Pittsburgh Coal • Dolomite 1337	1470		0.2-1.1 ppmw Na 0.1-0.4 ppmw K	30, 32
		• Pittsburgh Coal • Limestone 18			1.6-2.7 ppmw Na 0.7-0.9 ppmw K	
		• Welbeck Coal (18.2 wt. % Ash Containing 1.8 wt. % Na ₂ O, 3.2 wt. % K ₂ O)			0.4-1.1 ppmw Na 0.2-0.3 ppmw K	33
	36" x 36"; 5 atm Unit; PFBC	• Pittsburgh Coal (13.5 wt. % Ash Containing 0.7 wt. % Na ₂ O, 1.6 wt. % K ₂ O) • Dolomite 1337 (0.4 wt. % Na ₂ O, 0.6 wt. % K ₂ O)	1630 1745		2.3-12.2 ppmw Na 1.3-5.0 ppmw K 1.1-2.7 ppmw Na 0.6-2.5 ppmw K	33 33
		• Illinois Coal (10.9 wt. % Ash Containing 0.56 wt. % Na ₂ O, 1.94 wt. % K ₂ O) • Dolomite 1337	1655-1670		2.1-4.2 ppmw Na 1.2-3.2 ppmw K	33
		• Illinois Coal • UK Limestone (0.18 wt. % Na ₂ O, 0.01 wt. % K ₂ O)	1645-1740		1.3-1.5 ppmw Na 1.1-1.3 ppmw K	33
UK National Coal Board - Leatherhead	12" x 12"; 20 atm Unit; PFBC		1525-1555	1420	0.05-0.2 ppm Na 0.05-0.1 ppm K	34
	12" x 12"; 10-16 atm Unit; PFBC		1385-1720		0.15-0.8 ppmw Na 0.2-1.9 ppmw K	35
Combustion Power Co.	2.2 Sq. Ft., Model AFBC	• Illinois No. 6 Coal • Kaiser Dolomite • Kamlin	1650-1740	1390-1465	3 ppm Na 8 ppm K	16, 36, 37, 38, 39, 40
Essex	PFBC/Miniplant; 9 atm			1540	2.3 ppmw Na 0.3-0.5 ppmw K	41, 42
National Coal Board - IEA Grimsby	PFBC; 6-12 atm	• Pittsburgh No. 8 • Zimex Coal • Plum Run Dolomite	1259-1668		1.9 ppmw Na 20.4-23.4 ppmw K	43, 44
Curtiss-Wright	PFBC		1630		1-10 ppm Total	45, 46, 47
New York University	PFBC				0.2-26 ppm Na 0.03-0.6 ppm K	48, 49

TABLE 3.6
PROCESS SYSTEM DATA ILLUSTRATING ALKALI RELEASE (continued)

Process System	Description	Feed Materials	Bed Temperature, °F	Off-Gas Temperature, °F	Alkali Analysis	Reference
GE	PFBC; 9 atm	<ul style="list-style-type: none"> • Pittsburgh No. 8 Coal (14.4 wt. % Ash Containing 2.02 wt. % K_2O, 0.19 wt. % Na_2O) • Pfizer Dolomite (0.04 wt. % K_2O, 0.07 wt. % Na_2O) 	1650			50
		<p style="text-align: center;">or</p> <ul style="list-style-type: none"> • National Lime and Stone Co. (1 wt. % Na_2O) 			0.09-0.41 ppm Na 0.51-3.21 ppm K	51
MALMO ASEA Stal Laval	15 MW PFBC				No Alkali Reported	52
METC	6" AFBC	<ul style="list-style-type: none"> • Tymochtee Dolomite 	1650		0.2-0.4 ppmw Na 1-2 ppmw K	53, 54
		<ul style="list-style-type: none"> • Tymochtee Dolomite • Pittsburgh No. 8 Coal 			3-30 ppm Na 10-100 ppm K 0.5-2 ppm Na^+ 2-5 ppm K^+ • Continuous Feed	54
APT	AFBC				0.2-1.5 ppmw Total	55
Argonne National Laboratory	PFBC; 9 atm	<ul style="list-style-type: none"> • Sewickley Seam Coal • Tymochtee Dolomite 	1690		1 ppb Na 1 ppb K	56, 57
			1600-1740		10 ppb Na 10 ppb K	57
			1650		20-30 ppb Na 200-500 ppb K	58, 59
			1200-1300		5 ppb Na 30 ppb K	58, 59
W-KRW	Gasifier: 200-300 psig	<ul style="list-style-type: none"> • Upper Freeport Coal • Western Kentucky Coal • Brookville Coal • North Dakota Lignite 	1500-1800		0.18-12.8 ppm Na 0.05-2.4 ppm K	12

Process Fines Chemistry

Table 3.7 illustrates the elemental ash concentration in representative coals.⁽⁶⁶⁾ Although the total ash content for the various feed materials, and the contained elemental concentrations do not dramatically vary, numerous reactions are likely to occur in the char or ash materials during processing under either gasification or combustion conditions. Based on thermodynamic projections, silica which is present in the feed materials may undergo crystalline changes as a function of processing temperature. Similarly, silica has the potential to react with the contained alumina, and form mullite ($3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$) at elevated process temperatures. Alternately, the presence of calcium and/or magnesium in the ash matrix can lead to the formation of localized low melting temperature species which can cause particle agglomeration. The sticky particles can also impact and tenaciously adhere to the surfaces of components. Generally, these low melting temperature species are below the melting temperatures for the respective individual oxide complexes in the ash particle. The eutectic melt temperatures are generally within the process operating temperature range. An example of the potential reactions that are likely to occur within the ash matrix during processing is shown in Table 3.8.⁽⁴⁾ Phase stability diagrams are presented in Figure 3.8 for various aluminum, silicon, iron, calcium, and magnesium systems. The stability diagrams illustrate the transitions which could potentially lead to the formation of low melting temperature complexes within the ash matrix.

The presence of the alkali in the ash matrix similarly has the potential to form low melting temperature glass phases within the ash matrix. Alternately volatile alkali chlorides in the presence of water vapor have been shown to form glassy layers along the surfaces of aluminosilicate or ash materials. Typically this reaction involves the alkali and the silica fraction of the ash material, which is considered

to lead to the evolution of chloride as HCl. Additional reactions are projected between the alkali and aluminosilicate fraction of the ash materials which lead to the formation of feldspar complexes (i.e., $\text{NaAlSi}_3\text{O}_8$ or KAlSi_3O_8).

Studies have been undertaken at Westinghouse and the Argonne National Labs to identify the potential use of aluminosilicate materials as suitable alkali gettering materials for high temperature gas cleaning. The use of these materials as fines injected directly into the gasifier or combustor could significantly influence the alkali gas phase concentration and chemistry which would ultimately result at the ceramic cross-flow filter element surface. The potential therefore exists to reduce the high temperature alkali concentration to the ppb level if alkali gettering materials as emathlite were utilized. Alternately if the alkali removal system were positioned downstream of the filters, the ceramic cross-flow filter would be exposed to the higher effluent gas alkali concentration.

TABLE 3.7

COAL ASH COMPOSITIONS, Wt%⁽⁸⁸⁾

	Illinois No. 6 Coal	Eastern Coal	Western Coal
Al	1.2	1.7	1.0
Si	2.4	2.8	1.7
Fe	2.0	1.5	0.53
Ca	0.67	0.47	1.7
Mg	0.05	0.06	0.14
Na	0.05	0.04	0.14
K	0.17	0.25	0.05
Ash	11	12	9.6
Moisture	9.4	2.7	18.0

TABLE 3.8a

ELEMENTAL REACTION IN PITTSBURGH SEAM COAL ASH DURING PROCESSING

Pittsburgh Seam Coal: 100,000 lb/hr

Oxidant: 62,970 lb/hr

Steam: 50,000 lb/hr

Temp, K (°C)	300 (27)	400 (127)	500 (227)	600 (327)	700 (427)	800 (527)	900 (627)	1000 (727)	1100 (827)	1200 (927)	1300 (1027)
MgCO ₃	✓	✓									
C	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	
CaSO ₄ ·2H ₂ O	✓										
H ₂ O	✓										
KAlSi ₃ O ₈	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
Al ₂ SiO ₅	✓	✓	✓	✓							
Al ₂ O ₃ ·TiO ₂	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
Na ₂ SO ₄	✓										
SiO ₂	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
FeS ₂	✓	✓	✓								
S	✓										
NaCl	✓	✓	✓	✓	✓						
CaCO ₃		✓	✓								
NaAlSi ₃ O ₈		✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
CaO·MgO·2SiO ₂			✓		✓	✓	✓				
CaO·Al ₂ O ₃ ·2SiO ₂				✓	✓	✓	✓	✓	✓	✓	✓
FeO·Al ₂ O ₃				✓	✓	✓	✓	✓	✓	✓	✓
MgAl ₂ O ₄				✓				✓	✓	✓	✓
FeO·TiO ₂						✓	✓	✓			
FeS										✓	✓

TABLE 3.8b

ELEMENTAL REACTION IN TEXACO COAL ASH DURING PROCESSING

System: Texaco

Gasifier Type: Entrained Bed

Pressure: 15 atm

Temp, K (°C)	300 (27)	500 (227)	700 (427)	900 (627)	1100 (827)	1300 (1027)	1500 (1227)
Compound							
CaCO ₃	✓	✓					
MgCO ₃	✓						
C	✓	✓	✓	✓	✓	✓	
CaSO ₄ ·2H ₂ O	✓						
H ₂ O	✓						
KAlSi ₃ O ₈	✓	✓	✓	✓	✓	✓	
Al ₂ SiO ₅	✓	✓			✓		
SiO ₂	✓	✓	✓	✓	✓	✓	✓
FeS ₂	✓	✓					
KCl	✓	✓					
NaCl	✓	✓	✓				
CaO·MgO·2SiO ₂		✓	✓	✓			
CaO·Al ₂ O ₃ ·2SiO ₂			✓	✓	✓	✓	✓
FeO·Al ₂ O ₃			✓	✓			
FeS			✓	✓	✓	✓	✓ (2)
NaAlSi ₃ O ₈			✓	✓	✓	✓	
MgAl ₂ O ₄					✓	✓	✓
Al ₆ Si ₂ O ₁₃						✓	✓
Na ₂ Si ₂ O ₅							✓
K ₂ SiO ₃							✓

(a) (b) (c)

Figure 3.8a - Phase Stability Diagrams for Si-O, Al-O, and Fe-O. (a) Reprinted by Permission of the American Ceramic Society from Phase Diagrams for Ceramists; (a and b) 1975 Supplement, p. 12, 5. M. K. Reser (ed.), E. M. Levin and H. F. McMurdie, Columbus, OH: American Ceramic Society, 1975. (c) Basic Volume, p. 38. M. K. Reser (ed.), E. M. Levin, C. R. Robbins, and H. F. McMurdie, Columbus, OH: American Ceramic Society, 1964.

FIG. 237.—System CaO-SiO₂.

Bert Phillips and Arne W. Muan, *J. Am. Ceram. Soc.*, 42 [9] 414 (1959).

Based mainly on data of G. A. Rankin and F. E. Wright, *Am. J. Sci.*, 46, 8 (1915) and J. W. Greig, *Am. J. Sci.*, 15, 1-44; [74] 133-54 (1927). Changes with respect to stability relations of tricalcium and dicalcium silicates based on data of D. M. Roy, *J. Am. Ceram. Soc.*, 41 [6] 283-89 (1958) and J. H. Welch and W. Gutt, *J. Am. Ceram. Soc.*, 42 [1] 11-18 (1959).

(b)

Figure 3.8b - Phase Stability Diagrams for Al₂O₃-SiO₂, CaO-SiO₂, and CaO-Al₂O₃. (a) Reprinted by Permission of the American Ceramic Society from Phase Diagrams for Ceramists; (a and c) Vol. IV, p. 116, 95. G. Smith (ed.), R. S. Roth, T. Negas, and L. P. Cook, Columbus, OH: American Ceramic Society, 1981. (b) Basic Volume, p. 104. M. K. Reser (ed.), E. M. Levin, C. R. Robbins, and H. F. McMurdie, Columbus, OH: American Ceramic Society, 1964.

Fe-Si-O

(a)

Fig. 80.—System FeO-SiO₂.

N. L. Bowen and J. F. Schaefer, *Am. J. Sci.*, 8th Ser., 24, 200 (1932).

FeO-Al₂O₃

(b)

Fig. 81.—System FeO-Al₂O₃.
K. Rusebach and J. A. Schmitz, *Arch. Eisenhüttenwes.*, 45 (1972), 843 (1974).

Ca-Fe-O

(c)

Fig. 43.—System CaO-FeO in air. Hem = hematite, Magn = magnetite, or solid solution. Curve A-A' is triangular diagram above composition of liquids at liquidus temperatures.

Bert Phillips and Arnold Meier, *J. Am. Ceram. Soc.*, 41 (1958), 468 (1959).

Fe-Mg-O

(d)

Fig. 43.—System FeO-MgO: this system has not been studied in detail, but the equilibrium diagram is believed to be as shown above if the incongruent melting of FeO is neglected.

N. L. Bowen and J. F. Schaefer, *Am. J. Sci.*, 8th Ser., 29, 163 (1935).

Figure 3.8c - Phase Stability Diagrams for Fe-Si-O, FeO-Al₂O₃, Ca-Fe-O, and Fe-Mg-O. (31) Reprinted by Permission of the American Ceramic Society from Phase Diagrams for Ceramists; (a, c, and d) Basic Volume, p. 58, 49, and 54. M. K. Reser (ed.), E. M. Levin, C. R. Robbins, and H. F. McMurdie, Columbus, OH: American Ceramic Society, 1964. (b) Vol. IV, p. 99. G. Smith (ed.), R. S. Roth, T. Negas, and L. P. Cook, Columbus, OH: American Ceramic Society, 1981.

Figure 3.8d - Phase Stability Diagrams for $\text{Na}_2\text{O}-\text{SiO}_2$, $\text{NaAlO}_2-\text{Al}_2\text{O}_3$, and $\text{SiO}_2-\text{K}_2\text{O}-\text{SiO}_2$. (a) Reprinted by Permission of the American Ceramic Society from Phase Diagrams for Ceramists; (a and b) 1969 Supplement, p. 81, 81. M. K. Reser (ed.), E. M. Levin, C. R. Robbins, and H. F. McMurdie, Columbus, OH: American Ceramic Society, 1969. (c) Basic Volume, p. 87. M. K. Reser (ed.), E. M. Levin, C. R. Robbins, and H. F. McMurdie, Columbus, OH: American Ceramic Society, 1964.

FIG. 5510. — System CaCO_3 , P - T phase relations showing the sub-solidus phase transformation aragonite — calcite and the melting curve. A. J. Irving and P. J. Wyllie, *Geochim. Cosmochim. Acta*, 39 [1] 35 (1975).

FIG. 5511. — The pure CaCO_3 - MgCO_3 at 27 kbars pressure Cc = calcite (CaCO_3), Cd = dolomite ($\text{CaMg}(\text{CO}_3)_2$), Cm = magnesite (MgCO_3). There is complete solid solution between Cc and Cd and limited solid solution between Cd and Cm . A. J. Irving and P. J. Wyllie, *Geochim. Cosmochim. Acta*, 39 [1] 35 (1975).

Figure 3.8e - Phase Stability Diagrams for CaCO_3 , MgCO_3 , and CaCO_3 - MgCO_3 . (a) Reprinted by Permission from the American Ceramic Society from *Phase Diagrams for Ceramists*, Vol. IV, G. Smith (ed.), R. S. Roth, T. Negas, and L. P. Cook, Columbus, OH: American Ceramic Society, 1981, p. 283, 287.

3.1.1.2 Ceramic Materials

A review of the ceramics literature pertaining to chemical attack or corrosion of candidate cross-flow filter element materials, as well as a review of the ceramics patent literature are presented in this Section.

Ceramics Literature

Corrosion of Refractory Oxide-Based Ceramic Materials

Limited studies have been conducted on the high temperature corrosion behavior of oxide ceramics. Although, considerable data exist for refractory oxide bricks, this information is considered proprietary by the producers and users of refractory brick.

Rigby and Hutton⁽⁶²⁾ studied the effect of alkali and alkali-vanadium oxide slags on the phase stability of $\text{Al}_2\text{O}_3 \cdot \text{SiO}_2$ compounds with the SiO_2 concentrations varying from 0 to 100 mole percent. Tests were conducted in air at temperatures ranging from 800 to 1600°C (1470 to 2910°F). Mullite, α -alumina, and α -cristobalite were reported in the unexposed samples using x-ray diffraction (XRD) techniques. Samples with varying SiO_2 concentrations were ground, mixed with anhydrous sodium carbonate, pressed into 1 inch diameter cylinders and heated to the appropriate test temperature. Samples containing α -cristobalite formed sodium silicate or sodium aluminosilicate phases which melted between 800 and 1000°C (1470 and 1830°F). Samples containing primarily mullite and alumina (40% SiO_2 -60% Al_2O_3) formed sodium aluminate and nepheline ($\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$). Sodium aluminate caused large volume expansions at temperatures in excess of 900°C (1650°F). At 1200°C (2190°F) and higher, mullite was not detected; at 1300°C (2370°F), only nepheline and Al_2O_3 were detected; and at 1400°C (2550°F) the sample melted. Nepheline was not detected in the two high Al_2O_3 (80 and 100 percent) samples at any temperature. The primary phases for the

80 percent sample were sodium aluminate and Al_2O_3 . This compound melted at 1600°C (2910°F). The 100 percent Al_2O_3 sample differed only in the formation of $\beta\text{-Al}_2\text{O}_3$ at temperatures $\geq 1300^\circ\text{C}$ ($\geq 2370^\circ\text{F}$). Similar to sodium aluminate, $\beta\text{-Al}_2\text{O}_3$ also caused large volume expansions. The primary effect of the vanadium oxide addition was to form sodium vanadate which acted as a flux and increased the total melt at any temperature.

Bunar⁽⁶³⁾ examined the effect of acidic and basic slags on the corrosion behavior of fused-cast $\alpha\text{-Al}_2\text{O}_3$ in either a $\beta\text{-Al}_2\text{O}_3$ matrix or bonded with a borocaluminate glass at 1500°C (2730°F) for up to 500 hours. Data indicated that these Al_2O_3 refractories were attacked twice as fast by the basic slags than by acidic slags. The primary reaction product for the basic slag exposure was calcium hexaluminate. Increased MgO and FeO contents resulted in the formation of spinel.

Ferber and Tennery⁽⁶⁴⁾ studied on the effect of acidic coal ash from coal-oil-mixture combustion on the corrosion behavior of high purity Al_2O_3 heat exchanger tubes at temperatures of 1230°C (2245°F) for exposure durations of 496 hours. Substantial bonding between the Al_2O_3 and the slag, and extensive cracking of the tube during cooldown were observed. The cracking was attributed to coefficient of thermal expansion mismatch between the tube and the slag. Using scanning electron microscopy (SEM), elemental x-ray analysis, and XRD techniques, the intermediate bonding phase was determined to be an aluminosilicate with a thickness of 6-12 μm .

Bianco and Jacobsen⁽⁶⁵⁾ examined the corrosion of dense cordierite by sodium sulfate (Na_2SO_4) at 1000°C (1830°F) in flowing oxygen and oxygen with 1 percent SO_2 . Thin layers of Na_2SO_4 were applied to the cordierite samples. The key component in hot corrosion of cordierite by Na_2SO_4 , was considered to be the formation of sodium oxide as shown in the following reaction:

A high partial pressure of SO_3 establishes a low Na_2O activity (acidic salt), and a low partial pressure of SO_3 establishes a high Na_2O activity (basic salt).

Sodium aluminosilicate (NaAlSiO_4) was detected after exposure of the sample for one hour in flowing oxygen. Analysis of the material after 72 hours of exposure under these conditions indicated the presence of large crystallites and only trace amounts of liquid NaAlSiO_4 . In addition, a thin surface layer of Mg_2SiO_4 was detected using x-ray elemental mapping techniques. The overall reaction which was considered to have occurred follows:

Cracks were also observed which extended through the corrosion product scale and into the cordierite matrix. No mechanism was proposed for the crack formation. Since reaction [5] depends on the partial pressure of SO_2 , the use of a flowing 1% SO_2 - O_2 system was shown to suppress the formation of NaAlSiO_4 . Conduct of burner rig tests in flowing O_2 produced results similar to that of the furnace tests, with the exception that the reaction was more severe.

Oxidation and Corrosion Behavior of Silicon Nitride

Introduction

The high temperature properties of silicon nitride (Si_3N_4) are strongly dependent on the processing formulation. Of primary interest are the properties of materials produced by means of liquid-phase

sintering or reaction-bonding. Table 3.9 shows the properties of dense (via hot-pressing or pressureless sintering techniques which utilize liquid-phase sintering) and reaction-bonded Si_3N_4 (RBSN) ceramics. The 10-30 percent porosity in RBSN is characteristic of the reaction-bonding process, and accounts for the property differences between these materials.

Because of the high degree of covalent bonding, fabrication of dense Si_3N_4 requires densification aids (i.e., MgO , Y_2O_3 , Y_2O_3 and Al_2O_3 , etc.), temperatures in excess of 1600°C (2910°F), and usually, the application of pressure. At the relative sintering temperature, the additives react with the SiO_2 layer on the Si_3N_4 powder and form a liquid phase which permits densification.

In contrast, porous RBSN materials utilize a silicon powder starting material, consolidated by either isostatic pressing, injection molding or slip-casting. The silicon compact is nitrided at 1200 to 1400°C (2190 to 2550°F) to form Si_3N_4 . Most silicon powders contain impurities (i.e., Mn, Fe, Co, Ni, or Cu) which act to accelerate the nitridation reaction. To further enhance the reaction kinetics, additional iron is typically added to the silicon powder. The role of these impurities, particularly Fe, has been investigated by many researchers⁽⁶⁶⁻⁷⁸⁾. Although many mechanisms for the improved reaction kinetics have been proposed, the exact mechanism(s) remains to be determined.

The following Sections focus on the oxidation and corrosion behavior of high-purity Si_3N_4 (i.e., as a baseline material), reaction-bonded Si_3N_4 , and MgO and/or Al_2O_3 -doped Si_3N_4 . Since the cross-flow filter element materials currently do not contain Y_2O_3 , the literature for the Y_2O_3 -doped materials is not presented. With the exception of RBSN, prior research has focused on dense materials. Conversely, the cross-flow filter element materials are anticipated to contain substantial porosity (i.e., 50 volume percent). Consequently, the

TABLE 3.9
PROPERTIES OF DENSE AND REACTION BONDED SILICON NITRIDE CERAMICS

Crystal Structure:

α -phase, hexagonal	a-axis 0.775-0.777 nm c-axis 0.516-0.569 nm c/a approximately 0.70
β -phase, hexagonal	a-axis 0.759-0.761 nm c-axis 0.271-0.292 nm c/a approximately 0.37

Decomposition Temperature, °C 1900

Theoretical Density, g/cm³:

α -phase	3.168-3.188
β -phase	3.19-3.202

Density, g/cm³:

Dense Si ₃ N ₄	90-100% Th.D.*
Reaction Bonded Si ₃ N ₄	70-80% Th.D.

Coefficient of Thermal Expansion:

20-1500°C, 10 ⁻⁶ /°C	2.9, 3.6
---------------------------------	----------

Thermal Conductivity (RT), W/mK:

Dense Si ₃ N ₄	15-50
Reaction Bonded Si ₃ N ₄	4-30

Thermal Diffusivity (RT), cm²/sec:

Dense Si ₃ N ₄	0.08, 0.29
Reaction Bonded Si ₃ N ₄	0.02, 0.22

Specific Heat, J/kg°C 700

Poisson Ratio:

Dense Si ₃ N ₄	0.22-0.24
Reaction Bonded Si ₃ N ₄	0.25-0.28

Young's Modulus (RT), GN/m²:

Dense Si ₃ N ₄	300-330
Reaction Bonded Si ₃ N ₄	120-220

Flexural Strength (RT), MN/m²:

Dense Si ₃ N ₄	400-1000
Reaction Bonded Si ₃ N ₄	150-350

Fracture Toughness, MN/m^{-3/2}:

Dense Si ₃ N ₄	3.4-8.2
Reaction Bonded Si ₃ N ₄	1.5-3.6

Thermal Stress Resistance
Parameter R = $\sigma_f(1-\nu)/\alpha E$, °C,
R' = $R\lambda$, 10⁵ W/m:

Dense Si ₃ N ₄	R = 300-780; R' = 7-32
Reaction Bonded Si ₃ N ₄	R = 220-580; R' = 0.5-10

Th.D. = Theoretical Density is dependent on the type and composition of consolidated aids (Th.D. of pure Si₃N₄ = 3.2 g/cm³).

overall oxidation and corrosion reaction kinetics of the bulk material may be affected by this large available surface area. The basic chemistry and reaction mechanisms, however, are expected to be similar to those for the dense materials.

Comprehensive reviews on the oxidation and corrosion behavior of Si_3N_4 have been published. For example, Stern⁽⁷¹⁾ reviewed the literature pertaining to the oxidation mechanisms and reactions of Si, SiC, and Si_3N_4 , emphasizing the common features among the three materials; Jacobsen⁽⁷²⁾ reviewed the literature on the molten salt corrosion (primarily Na_2SO_4) of SiC and Si_3N_4 ; and Tressler⁽⁷³⁾ identified the oxidation and molten salt corrosion reactions and kinetics of SiC and Si_3N_4 , using the results of application studies in industry.

Oxidation Reactions

Some silicon-based ceramics, such as Si_3N_4 , are inherently unstable in oxygen containing environments. As a result, two types of reactions may occur. The first is termed "passive" oxidation, in which SiO_2 forms as a protective coating on the bulk Si_3N_4 , and a weight gain is observed:

The majority of the literature which discusses the oxidation behavior of Si_3N_4 focuses on passive oxidation kinetics and mechanisms.

The second type of reaction, "active" oxidation represents the case in which gaseous SiO forms and a weight loss occurs:

Oxidation of Chemical Vapor Deposited Silicon Nitride

Single crystals of Si_3N_4 have never been grown. Consequently, fundamental oxidation studies of pure, dense Si_3N_4 have utilized chemical vapor deposited silicon nitride (CVDSN). Unfortunately, few detailed studies on the oxidation behavior of CVDSN have been conducted.

Recent efforts by Du⁽⁷⁴⁾ studied the passive oxidation behavior of α -CVDSN in flowing dry oxygen at 1 atmosphere pressure; oxygen-argon mixtures with varying oxygen partial pressures (0.05, 0.1, and 0.5 atm; and oxygen-nitrogen-argon mixtures with varying N_2 partial pressures (0.05 and 0.5 atm) and a constant O_2 partial pressure of 0.5 atm. The temperature ranges and oxidation times for the dry O_2 and the two gas mixtures were 1100-1400°C (2010-2550°F) for 60-360 minutes, and 1200-1400°C (2190-2550°F) for 60 and 480 minutes, respectively. Parabolic oxide growth kinetics were observed and activation energies of about 115 kcal/mol were calculated. The parabolic rate constant showed an increase with increasing O_2 partial pressure, but was unaffected by changes in the N_2 partial pressure. In general, the oxidation scales were amorphous. Only after exposure to 1400°C (2550°F) for a long period of time was crystallization to cristobalite detected. The prolonged amorphous nature of the oxide scale at high temperature was attributed to the dry and clean oxidizing ambient conditions, and the high viscosity of the oxide was attributed to the absence of fluxing impurities.

This work and subsequent research by Du, Tressler and Spear⁽⁷⁵⁾ indicated that in addition to SiO_2 , $\text{Si}_2\text{N}_2\text{O}$ should be formed when Si_3N_4 is oxidized. Du observed an intermediate separate phase which was identified to be silicon oxynitride ($\text{Si}_2\text{N}_2\text{O}$) through the use of ellipsometry, step-by-step etching, secondary ion mass spectroscopy (SIMS), and x-ray photoelectron spectroscopy (XPS). Raider⁽⁷⁶⁾ and Zhdan⁽⁷⁷⁾ also identified $\text{Si}_2\text{N}_2\text{O}$ on CVDSN oxidized in dry oxygen using

auger electron spectroscopy (AES) and XPS techniques. In these efforts samples were oxidized at 1070°C (1960°F) for durations as long as 420 minutes, and to 1010-1200°C (1850-2190°F) for durations of 60-360 minutes, respectively. Using AES techniques, Maguire and Augustus⁽⁷⁸⁾ observed Si₂N₂O on as-deposited amorphous CVDSN films grown at 900°C (1650°F).

Du described the formation of a duplex oxide scale as the result of the following reaction sequence:

Du, Tressler, and Spear developed a kinetic model for the passive oxidation of CVDSN in oxidizing atmospheres at high temperatures. This model showed good agreement with the experimental results generated by Du. Furthermore, they concluded that molecular oxygen diffusion in Si₂N₂O was the rate-limiting step during oxidation of CVDSN.

Oxidation Behavior of Reaction Bonded Silicon Nitride

To date limited oxidation studies, and virtually no detailed research on RBSN have been conducted. The majority of the oxidation studies were performed in static air at temperatures ranging from 1000 to 1400°C (1830 to 2550°F) for durations of up to 250 hours. Few studies have examined the oxidation behavior below 1000°C (1830°F) and/or for long exposure times.

The fundamental oxidation behavior of RBSN is similar to that of CVDSN. As expected, parabolic oxidation kinetics are observed, and oxide growth occurs not only on the surface, but also internally, as well as in the pores. This inherent porosity along with the exposure temperature are the primary variables affecting the oxidation behavior of RBSN.

Both pore size and internal pore structure significantly influence the oxidation behavior of RBSN. The pore size and pore interconnects are more important factors in determining oxidation behavior than the actual amount of porosity in the material.⁽⁷⁹⁻⁸²⁾ As the pores are frequently open ones, oxidation starts both at external and internal surfaces. Both amorphous and crystalline SiO_2 , which are formed during oxidation, have a larger volume (~80 percent larger) than Si_3N_4 . Consequently, oxidation leads to a decrease in total porosity and to a reduction in pore diameter. As the macropores are in most cases closed pores (in some cases these macropores are interconnected by micropores), the size and distribution of the micropores is the major parameter in an assessment of the Si_3N_4 oxidation behavior.⁽⁸²⁾ Small pore channels with diameters on the order of 10 nm can be closed after a relatively short time; with larger micropores present there is an increase in the extent of internal oxidation of the material.⁽⁷⁹⁾ After formation of a closed SiO_2 layer, oxygen must diffuse through the SiO_2 layer for further oxidation to occur. This strongly reduces the oxidation rate. These two types of oxidation behavior are illustrated in Figure 3.9.

In addition to the pore structure, the type and degree of oxidation is determined by temperature. At high temperatures [$\geq 1200^\circ\text{C}$ ($\geq 2190^\circ\text{F}$)], a continuous oxide surface layer is rapidly formed, open pores are closed, and further oxidation occurs slowly by diffusion. At lower temperatures [$\leq 1100^\circ\text{C}$ ($\leq 2010^\circ\text{F}$)], the open pores remain open for longer times and reaction may take place throughout the whole sample.

Figure 3.9 - RBSN Oxidation Model for Materials with (a) Small and (b) Large Pores⁽⁷⁹⁾

This results in a higher material weight gain than at higher exposure temperatures. Impurities may also play a role in forming either melts with lower softening temperatures by reaction with silica as a result of diffusion through a widened glass network, or by inducing crystallization which may lead to crack formation.⁽⁸²⁾

Cristobalite and amorphous silica are two phases that are typically reported as being present in the oxidation product. The effect of impurity diffusion in RBSN on the conversion of the amorphous layer to cristobalite or to lower viscosity phases has not been extensively studied. Although silicon oxynitride has been observed in the oxidation of CVDSN, it has not been detected by XRD in oxidation studies of RBSN.⁽⁸³⁻⁸⁵⁾

The literature contains only one study which examines the effects of very long exposure times on the passive oxidation of RBSN. Warburton⁽⁸⁶⁾ oxidized thin sheet (0.1-0.2 μm thick) RBSN in flowing air saturated with moisture (i.e., 2.5 volume percent water vapor). Samples were exposed in this environment for up to 8000 hours at 700-1100°C (1290-2010°F). Figure 3.10 shows the percent weight gain and percent conversion of RBSN to SiO_2 as a function of time and temperature. At 700-800°C (1290-1470°F) very little weight gain was observed, while at 900 and 1000°C (1650 and 1830°F), the oxidation rate increased significantly. At 1100°C (2010°F), a lower oxidation rate and a lower weight gain were observed. At 1100°C (2010°F), a high initial oxidation rate resulted with the formation of a 5-10 μm thick protective silica layer in <500 hours, and a subsequent leveling off of the oxidation rate. X-ray diffraction techniques were attempted, but were not able to determine whether the protective layer was amorphous or crystalline. No obvious cracking of the protective layer was observed on cooldown from the oxidation temperatures. If cracks would have resulted, it would have been an indication of a crystalline phase (i.e., cristobalite) undergoing a displacive phase transformation at approximately 250°C (480°F).

Figure 3.10 - Percent Weight Gain and Percent Conversion of RBSN to SiO₂ as a Function of Time and Temperature for Materials with Densities of (A) 2.10, (B) 2.31, and (C) 2.39 g/cm³

Using optical metallography techniques, data were also generated which demonstrated the occurrence of oxidation throughout the pore network when the samples were exposed to temperatures of $\geq 900^{\circ}\text{C}$ ($\geq 1650^{\circ}\text{F}$), as well as a reduction in the number of large pores by silica fill-in. The gas permeabilities of unoxidized and oxidized specimens were determined, and were shown to rapidly decrease as oxidation progressed. After 5000 hours of oxidation, the permeability reduction factors were observed to be approximately 8 and >50 after exposures at temperatures of 700 and 1100°C (1290 and 2010°F), respectively.

Several conflicting results have been reported on the effect of oxidation on room temperature bend strength of RBSN. Strength degradation, strength increases and unaffected strengths have been observed in the literature. Several factors, depending on the oxidation conditions are considered to influence these ambiguous results.⁽⁸²⁾ These include:

- Rounding off of internal flaws and pores, and crack healing effects which lead in particular to an increase in strength.
- Formation of cracks in the oxidized surface layer caused by the $\alpha \rightarrow \beta$ displacive phase transformation of cristobalite during cooling in the temperature range between 200 - 270°C (390 - 520°F) accompanied by a 5 percent volume increase. These cracks are thought to be the reason for the observed decrease in strength after cooling.
- Building up of stresses due to the large volume increase, and the changes in the coefficient of thermal expansion during the conversion of RBSN to SiO_2 .

Evans and coworkers^(87,88) conducted oxidation studies on RBSN ($\rho = 2.5 \text{ g/cm}^3$, largest pores were approximately $25 \mu\text{m}$) in static air at 1000 - 1400°C (1830 - 2550°F) for exposure durations of up to 150 hours.

Initially the fast oxidation rates were observed which subsequently began to level off after approximately 40 hours at 1000°C (1830°F), and <15 minutes at 1200 or 1400°C (2190 or 2550°F). Using XRD, the oxidized layer which formed at all test temperatures was determined to be cristobalite. Data were not presented which identified the retention of any amorphous silica. At 1000°C (1830°F) the oxidation product weight gain was 2-3 times larger than at temperatures $\geq 1200^{\circ}\text{C}$ ($\geq 2190^{\circ}\text{F}$) for equivalent exposure durations. At the higher temperatures, the rapid formation of a smooth dense oxide surface layer was observed which then limited oxidation of the internal pore surfaces. Conversely, at 1000°C (1830°F) the slower oxidation rate prevented sealing of the surfaces and allowed the internal pore surfaces to be oxidized. Thus, the larger weight gain at the lower test temperature can be attributed to the oxidation of a much larger surface area for a longer time. The room temperature strength of samples increased slightly when the materials were oxidized at 1000°C (1830°F) for 96 hours, whereas at the higher temperature, the oxidized material's strength decreased. Cracking of the oxide layer was observed after cooling from the oxidation temperature. The decrease in strength was attributed to the $\alpha \rightarrow \beta$ displacive transformation of cristobalite at approximately 250°C (480°F).

Other researchers have also reported the degradation of room temperature strength after oxidation of RBSN at temperatures $\geq 1200^{\circ}\text{C}$ ($\geq 2190^{\circ}\text{F}$) in static air.^(88, 89-95) Cracking was also observed in the cristobalite oxidation layer, and similarly the reduction in strength was attributed to the displacive transformation of cristobalite.

The effect of oxidation at 1000 and 1400°C (1830 and 2550°F) on the internal porosity of RBSN was examined by Sharp using high voltage electron microscopy (HVEM).⁽⁸⁹⁾ A thin sheath of amorphous silica was observed around the internal pores after oxidation at both temperatures. The number of oxidized regions observed to form after oxidation at 1000°C (1830°F) was greater than the number of oxidized regions formed at 1400°C (2550°F). This was consistent with the weight gain data generated in the

experiments conducted by Evans. The main effect of oxidation on strength was considered to be the rounding off of the internal pores, which increased the surface energy and therefore strength. For both temperatures, the surface oxide layer was reported to be cristobalite. Removal of this layer by grinding produced an increase in strength showing that oxidation has a greater beneficial effect on the internal surface than on the external surface.

Lindbergh⁽⁸⁰⁾ studied the oxidation behavior of four RBSN materials that were fabricated by various methods under static air conditions at 900°C (1650°F) for 10 hours. Specimens which contained 8-10 percent interconnected open porosity of $>1\text{ }\mu\text{m}$ exhibited a 20-30 percent decrease in average room temperature four-point bend strength. The strength degradation was attributed to internal oxidation. Specimens which contained 10 percent interconnected open porosity of $<1\text{ }\mu\text{m}$, or specimens which contained 2-4 percent interconnected open porosity of approximately $1\text{ }\mu\text{m}$ did not decrease in strength after exposure to 900°C (1650°F) temperatures. Improved oxidation resistance and strength of all four materials were demonstrated after samples experienced a preoxidation treatment that sealed the surfaces with an oxide layer and decreased subsurface oxidation. This sealant layer was most likely an amorphous silica which was not subjected to the displacive phase transformation, and which healed the near-surface and surface flaws.

Grathwohl⁽⁷⁹⁾ evaluated the oxidation of RBSN materials of low to medium bulk density ($2.11\text{--}2.40\text{ g/cm}^3$) at 1200-1400°C (2190-2550°F). Severe internal oxidation occurred in all the low density materials, and in all the materials with coarse porosity. The internal oxidation decreased material strength and creep resistance. The RBSN materials with very fine open porosity and a bulk density in the 2.4 g/cm^3 range exhibited less internal oxidation and property degradation.

Oxidation Behavior of Hot-Pressed and Pressureless Sintered Silicon Nitride

Hot-pressed or pressureless sintered Si_3N_4 materials always contain additives (i.e., MgO , $\text{Al}_2\text{O}_3 + \text{Y}_2\text{O}_3$, Y_2O_3 , ZrO_2) that vary widely in composition and concentration. In general, these additives aid in densification and increase mechanical strength, while lowering the oxidation resistance of the ceramic material. The literature contains information on the oxidation of primarily MgO or Y_2O_3 -doped Si_3N_4 . The discussion which follows focuses on the MgO -doped material studies.

The oxidation behavior of MgO -doped Si_3N_4 has been investigated in dry O_2 , air and water saturated air or O_2 . The experimental temperatures and exposure durations ranged from 800-1500°C (1110-2730°F) and 0.25-1000 hours, respectively. Major impurities that have been found in these materials include Fe, Al, Mn, Na, K, and Ca. (98-92)

Data (98-98) indicate that weight-gain versus time curves for all temperatures approximate classical parabolic oxidation behavior, indicating that the rate of oxidation is diffusion-controlled. Cubicciotti (98) demonstrated that the rate of oxidation is relatively unaffected by removal of the surface oxide scale, suggesting that oxygen diffusion through the oxide scale is not the rate-controlling step, as with the CVDSN and RBSN materials. On the basis of examining of the magnesium concentration below the scale, Cubicciotti concluded that the diffusion of magnesium out of the material and into the scale was the rate controlling mechanism.

Clarke and Lange (97) demonstrated depletion in the magnesium concentration immediately below the scale. Magnesium was considered to be drawn into the scale faster than its diffusion from the interior to the scale. The depletion in the magnesium concentration was consistent with the presence of a liquid phase in the scale during oxidation. Cubicciotti and Lau, (99) and Kiehle (91) reported the presence of a glass

phase in the oxide scales. Clarke and Lange also suggested that a liquid phase containing nitrogen exists within the scale, and that it would have two effects. First, the liquid nitrogen containing phase would provide a high diffusivity path for the reaction species to the oxide scale/subscale interface. Second, the liquid would accommodate the molar volume changes that accompany the formation of the reaction products in the oxide scale.

Singhal⁽⁹⁸⁾ reported the activation energies for oxidation of Si_3N_4 in wet O_2 as 488 ± 30 kJ/mol, and for dry O_2 as 375 ± 25 kJ/mol. The higher activation energy in wet O_2 was considered to result from:

- Diffusion and solution of OH^- ions through the surface oxide film.
- Change in viscosity of the surface oxide, which could alter the rates at which additives and impurities diffuse through the oxide layer.

Unfortunately, additional studies of the effects of moisture on the oxidation behavior of hot-pressed or sintered Si_3N_4 have not been conducted.

Alternate studies have shown that the exact phase composition in multiphase oxide scales is dependent on the oxidation temperature. Kiehle⁽⁹¹⁾ demonstrated that oxidation begins as low as 700°C (1290°F) in air, with an amorphous SiO_2 scale being formed after 24 hours at 750°C (1380°F). The simultaneous formation of cristobalite with increasing exposure time and/or temperature was also observed. According to Kiehle, the occurrence of cristobalite at a temperature as low as 750°C (1380°F) suggested that cations (i.e., Na and Mg) reduce the viscosity of the glassy layer. Below 1000°C (1830°F) crystalline and amorphous SiO_2 remain the primary components of the oxide scale.

Above 1000°C (1830°F) the silicate reaction products have been identified as enstatite (MgSiO_3), akermanite ($\text{Ca}_2\text{MgSi}_2\text{O}_7$), forsterite (Mg_2SiO_4), and diopside ($\text{CaMgSi}_2\text{O}_6$).⁽⁹⁸⁻⁹²⁾ Akermanite and forsterite are the first silicates to form. Enstatite and diopside do not form until 1350°C (2460°F). Singhal's analysis⁽⁹²⁾ of the oxide scale formed at 1100-1400°C (2010-2550°F) also revealed the presence of Mg, Al, Ca, Fe, Mn, Na, and K in the scale.

The effect of oxidation in air at 1000°C (1830°F) for 10 minutes and 50 hours has been reported by Jakus and coworkers.^(99,100) Initially oxidation was considered to create a glassy phase that tends to smooth out the preexisting flaws, and consequently, increases the strength of the material. After increased oxidation, surface pits form in Si_3N_4 under the oxide layer. Surface pit formation was attributed to the production of gaseous oxidation products. These pits became the strength-controlling flaw population and led to a reduction in room temperature strength.

Freiman and coworkers^(101,102) reported a >50 percent decrease in strength of Si_3N_4 upon oxidation at 1000-1400°C (1830-2550°F) for exposure durations of 100 to 400 hours. The strength-limiting flaws were also determined to be surface pits on the Si_3N_4 .

Besides surface pits, bubbles and holes on the oxide surface, and pores at the oxide scale and subscale interface have been reported for oxidation temperatures $\geq 1000^\circ\text{C}$ ($\geq 1830^\circ\text{F}$).^(98,91,93) Cubicciotti⁽⁹³⁾ attributed the bubbles to trapped N_2 gas, and the holes to burst bubbles. Pits were considered to occur at sites of higher-than-average magnesium concentrations, which enhance the ability of the oxide scale to dissolve Si_3N_4 . This leads to accelerated penetration of the oxide scale into the bulk Si_3N_4 at the same sites, and eventually to the formation of pits.

The effect of water-saturated flowing air on the time-dependent failure in four-point bending of RBSN and hot-pressed Si_3N_4 was examined at temperatures up to 900°C (1650°F) by Gulden and Metcalfe.⁽¹⁰³⁾ For test durations up to 1000 hours, data indicate that the RBSN material had an approximate 10 percent decrease in strength, and that the hot-pressed material was unaffected by the low-to-moderate temperature, moist air environment.

Corrosion Behavior of Silicon Nitride

Heat engine development has driven the majority of the research on silicon nitride corrosion behavior. These studies have primarily focused on sodium sulfate (Na_2SO_4) induced corrosion.

Brooks and Meadowcroft⁽¹⁰⁴⁾ investigated the corrosion resistance of RBSN in a simulated fuel oil fired environment containing sodium, vanadium, and sulfur at 900, 1100, and 1400°C (1650 , 2010 , and 2550°F). Severe corrosion of reaction bonded silicon nitride (RBSN) was observed within 225 hours at 900 and 1100°C (1650 and 2010°F). Corrosion was attributed to the formation of sodium silicates which are molten above 800°C (1470°F). Sodium sulfate attack of Si_3N_4 at 1100°C (2010°F) was considered to result from the reaction of the molten salt with the passive silica film, forming sulfur trioxide gas as shown by the following reaction:

The liquid sodium silicate film permits rapid transport of reactants and products, and accelerated attack of the Si_3N_4 . At 1400°C (2550°F) where Na_2SO_4 deposition did not occur, high temperature oxidation was observed to be the principal mode of attack.

Fox and Jacobsen^(185,186) examined the corrosion effects of sodium carbonate (Na_2CO_3) and sodium sulfate thin films on various types of Si_3N_4 which included CVDSN; hot-isostatically-pressed (HIP) RBSN; and MgO-doped, Y_2O_3 -doped, and $\text{Y}_2\text{O}_3 + \text{Al}_2\text{O}_3$ -doped Si_3N_4 . Sodium carbonate was shown to readily attack Si_3N_4 when exposed to temperatures of 1000°C (1830°F) in air for durations of up to 200 hours.⁽¹⁸⁵⁾ The corrosion was reported to occur in the following three stages:

- Decomposition of the carbonate, and formation of a non-protective, liquid $\text{Na}_2\text{O} \cdot x(\text{SiO}_2)$ layer on the surface of the material.
- Enhanced oxidation continues with formation of a porous oxide layer between the sodium silicate and Si_3N_4 .
- The SiO_2 layer becomes dense and protective, slowing the corrosion rate of the material.

Parabolic reaction kinetics were observed for all materials.

For similar studies with Na_2SO_4 , Jacobsen and Fox⁽¹⁸⁶⁾ reported that for each of the various Si_3N_4 materials, a slow weight loss occurred for the first 40-50 hours which was the result of both Na_2SO_4 vaporization and dissolution. With extended exposure all materials except MgO-doped Si_3N_4 , began to show a slight weight gain caused by continued oxidation. The MgO-doped Si_3N_4 continued to show a weight loss for the duration of the 160 hour test.

For both salts, the $\text{Y}_2\text{O}_3 + \text{Al}_2\text{O}_3$ -doped Si_3N_4 experienced the greatest amount of oxidation, whereas, oxidation of the Y_2O_3 -doped Si_3N_4 material was much lower. This implies that alumina decreases the oxidation/corrosion resistance of Si_3N_4 . Data indicate that for both salts, attack of the Si_3N_4 materials occurred primarily at the grain boundaries.

A number of other studies have been conducted on sodium-based molten salt corrosion of Si_3N_4 . Mayer and Riley⁽¹⁰⁷⁾ studied the corrosion effects of sodium carbonate thin films on RBSN at temperatures of 1100-1300°C (2010-2370°F) in air. Although the Mayer and Riley data are similar to those generated by Fox and Jacobsen, an increase in the corrosion reaction kinetics was observed with temperature.

Tressler⁽¹⁰⁸⁾ indicated that up to 40 percent dissolution of RBSN and hot-pressed, MgO-doped Si_3N_4 samples could occur when the materials are immersed in molten Na_2SO_4 at 1000°C (1830°F). Conversely, the weight of these materials did not change when immersed in pure NaCl at 1000°C (1830°F). Electron microprobe examination has shown substantial penetration of elemental sodium and sulfur along the amorphous oxide grain boundary phase in MgO-doped Si_3N_4 . Further studies by Bourne and Tressler⁽¹⁰⁹⁾ demonstrated that after exposure to molten NaCl and molten NaCl- Na_2SO_4 eutectic salts for 144 hours at 1000°C (1830°F), both Si_3N_4 materials experienced significant reductions in strength from room temperature to 1200°C (2190°F).

Mayer and Riley⁽¹¹⁰⁾ examined the oxidation of RBSN in the presence of NaCl and Na_2SO_4 vapors over the temperature ranges of 800-950°C (1470-1740°F) and 1100-1300°C (2010-2370°F), respectively. Enhanced oxidation rates were observed and attributed to the formation of liquid sodium silicate which provides rapid diffusion paths for O_2 inward and N_2 outward.

Cavallotti⁽¹¹¹⁾ studied the corrosion of hot-pressed $\text{Y}_2\text{O}_3 + \text{MgO}$ -doped Si_3N_4 , RBSN, $\text{Y}_2\text{O}_3 + \text{MgO}$ -doped sintered RBSN, and pressureless-sintered $\text{Y}_2\text{O}_3 + \text{MgO}$ -doped Si_3N_4 . These materials were coated with thin films of Na_2SO_4 , NaCl, and $\text{Na}_2\text{SO}_4 + 10\% \text{NaCl}$, and heated to temperatures of 900°C (1650°F) in air. Materials exposed to Na_2SO_4 corroded four times as fast as those exposed to NaCl. The porous RBSN corroded approximately 10 times faster than the other materials. For an

unidentified material which was similarly coated with Na_2SO_4 , Li_2SO_4 , or K_2SO_4 , and subsequently exposed to still air at 900°C (1650°F), corrosion rates were identified as $\text{K} > \text{Li} > \text{Na}$.

Richerson and Yonushonis⁽¹¹²⁾ exposed RBSN in a burner rig to high-velocity oxidizing gases seeded with sea salt. The test conditions consisted of 25 cycles at 900°C (1650°F)/1.5 hour to 1120°C (2050°F)/0.5 hr to an air quench/5 min. A heavy buildup of glassy material was observed on the RBSN surface. Subsequent mechanical testing demonstrated a 45 percent strength reduction of the corroded material.

Henager and Jones⁽¹¹³⁾ demonstrated that the presence of Na_2SO_4 enhanced slow crack growth in hot-pressed Y_2O_3 -doped Si_3N_4 at 1200°C (2190°F) in air. Sodium ion penetration of the SiO_2 -based film at the Si_3N_4 grain boundaries was considered to lower the melting point and viscosity of the film, and increase the film deformation rate and material transport along grain boundaries.

Sato⁽¹¹⁴⁾ examined the corrosion behavior of pressureless sintered $\text{Y}_2\text{O}_3 + \text{Al}_2\text{O}_3$ -doped Si_3N_4 immersed in various molten alkali (i.e., Li, Na, K) sulfates and carbonates exposed to air and nitrogen at 900 – 1200°C (1650 – 2190°F) and 700 – 1013°C (1290 – 1855°F), respectively. The corrosion rates of Si_3N_4 in potassium sulfate and potassium carbonate melts exposed to N_2 were shown to be much faster than those exposed to air. The apparent activation energies for the corrosion of Si_3N_4 in molten alkali sulfate and carbonate melts exposed to N_2 at 900 – 1200°C (1650 – 2190°F) and 700 – 1000°C (1290 – 1830°F) were 430 and 106 kJ/mol, respectively, and were shown to be independent of the alkali metal ion species.

Becher⁽¹¹⁵⁾ exposed MgO -doped and Y_2O_3 -doped Si_3N_4 ceramics to basic and acidic slags at 1200°C (2190°F). Materials which were exposed for 240 hours to the basic slag experienced very accelerated corrosive

attack and a rapid material loss. In the 350 and 500 hour acidic slag exposures, these materials were shown to be more resistant to material loss, with the overall surface recession rates being at least two orders of magnitude lower than for the basic slags. Irregardless of the type of slag, these materials were reported to have significant reductions in strength.

Patent Literature

The patent literature was reviewed emphasizing the formulation and/or fabrication of candidate cross-flow filter materials. These include alumina, aluminosilicates, cordierite, cordierite-silicon nitride, silicon nitride, and silicon carbide. The following Sections contain excerpts which have been taken directly from the patent literature for each material.

Alumina

1. M. J. Fenerty, and D. L. Mustoe, Composite Seal Ring and Assembly, U. S. Patent No. 3,926,443, December 16, 1975. (116)

Sintered alumina ceramics typically contain at least 85 percent aluminum oxide with the remainder being fluxing agents, glass-formers or crystal growth inhibitors. Examples of alumina ceramics include:

- 100% aluminum oxide
- 98% aluminum oxide and 2% magnesium oxide
- 90% aluminum oxide, 6% silica, and 4% calcium oxide
- 85% aluminum oxide, 10% silica, and 5% magnesium oxide.

A density of at least 80 percent theoretical can be achieved during sintering of aluminum ceramics. The resulting alumina ceramics are essentially non-porous and almost impermeable. Maximum mechanical

strength and wear resistance can be obtained by starting with aluminum crystals which are $\leq 20 \mu\text{m}$. Hardnesses of greater than 7 on the Mohs scale can be obtained with these ceramics, as well as with ceramics containing a sintered magnesia-alumina spinel.

2. L. B. Starling, J. E. Stephen, and R. D. Stroud, Shrink-Free Ceramic and Method and Raw Batch for the Manufacture Thereof, U. S. Patent No. 4,265,669, May 5, 1981.⁽¹¹⁷⁾

Typically aluminum ceramics are formed with particulates (i.e., aluminum oxide) plus a binder. The mixture is then molded or formed into a compact body, and fired. Firing sinters or vitrifies the compact body, causing the ceramic to shrink by 10-20 percent.

If high pressure is used to mold or otherwise form the compact, the resulting body is typically less than its theoretical density value due to porosity. Similarly if the ceramic ingredients undergo chemical or crystalline transformation during firing, the resulting ceramic body is of greater density or lesser volume than the raw ingredients, and shrinks when fired.

The formation of a shrink-free, high strength material can be achieved with a mixture of 50 percent aluminum oxide, 5 percent magnesium oxide, 5-25 percent glass frit, and 10-15 percent silicone resin. The SiO content is at least 50 percent of the silicone concentration, and an aluminum oxide content is at least twice that stoichiometrically required to react with all the magnesium oxide to form the magnesium aluminate spinel. The ceramic body is formed by molding, with the silicone resin functioning as a binder, providing good green strength. When the compact is fired into a dense (2.7 g/cm^3), hard, monolithic body, shrinkage does not occur.

During firing, all of the magnesium oxide which is present in the mixture reacts with some of the aluminum oxide to form the magnesium aluminate spinel. The frit and the silica from the silicone resin react to form a glassy aluminosilicate phase. Approximately 3-5 percent kaolin can be added to improve flow characteristics.

The resulting fired ceramic body contains 70-95 percent crystalline material, with the remainder consisting of an interstitial glass phase. The crystalline material consists of 70 percent aluminum oxide and magnesium aluminate spinel, with secondary phases of crystalline aluminum silicate. The glass and crystalline material include alkaline earth aluminosilicates. The ceramic body which results is non-porous, has high hardness and wear resistance, and has high flexural and compressive strength.

The desired reaction between magnesium oxide and aluminum oxide which forms the spinel, and the reaction which forms the glass phase are both optimally achieved by firing the ceramic mixture to temperatures of 1300°C (2370°F). Firing of the ceramic body is optimized by using both oxidizing conditions to temperatures of least 650°C (1200°F), and with a gradual firing schedule as shown below:

- Firing from room temperature to 500°C (930°F) at a rate of 160°C/hour
- Holding the ceramic body at 500°C (930°F) for 16 hours
- Continued firing from 500 to 650°C (930 to 1200°F) at a rate of 150°C/hour
- Holding the ceramic body at 650°C (1200°F) for 8 hours
- Increasing temperature from 650 to 1315°C (1200 to 2400°F) at a rate of 420°C/hour.

Firing is complete when temperatures of 1315°C (2400°F) are achieved.

A specific ceramic formulation is presented which illustrates several of the reactions which occur during the formation of the non-shrinking, high temperature compact body. A typical ceramic mixture consists of seven parts aluminum oxide, one part magnesium oxide, 1.5 parts barium aluminum silicate glass frit, and 1.5 parts silicone resin. All of the constituents with the exception of the silicone resin are placed in a ball mill, and the mixture is dry milled for about five minutes. The silicone resin which is dissolved in 70 ml of an organic solvent such as Chlorothene Nu (1,1,1 trichloroethane) is then added to the dry mixture from the ball milling operation, and mixed until a homogeneous slurry is formed. The slurry is then sprayed dried at room temperature.

The compact body which is formed is fired under oxidizing conditions and temperatures of 650°C (1200°F). At 650°C (1200°F) SiO is converted to SiO₂. During this low temperature firing stage there is burn out or vaporization of the organics in the organic lubricant, as well as burn out from the organic portion of the silicone resin. If the ceramic body were rapidly fired, a substantial portion of the SiO groups would also be volatilized. The purpose of the silicone in the mixture is to provide excellent binding properties and moldability prior to firing, while contributing little, if any, to the effective porosity of the compact body. When exposed to a gradual firing schedule with hold periods at specified temperatures, conversion of SiO to SiO₂ is optimized. Silicon dioxide is very reactive and results within a crystalline or an amorphous glass alkaline earth aluminosilicate phase.

At temperatures of 700°C (1290°F), magnesium oxide reacts with aluminum oxide. Simultaneously the highly reactive SiO₂ derived from the silicone resin reacts with the glass frit, as well as with the kaolin, with some of the aluminum oxide, and with some of the magnesium oxide to generate siliceous glass, forming a continuous interstitial phase. It is speculated that during cooling, a portion of the glass

phase crystallizes out as a crystalline aluminum silicate phase (i.e., possibly as the alkaline earth aluminosilicate, osumulite $[\text{BaMg}_2\text{Al}_3(\text{Si}_2\text{Al}_3\text{O}_{18})]$).

The resulting fired monolithic body contains approximately 90 percent crystalline material, with the remainder being an interstitial alkaline earth aluminosilicate glass phase. The crystalline material consists of 40 percent α -alumina, and 20 percent barium osumulite.

3. D. W. Roy and K. J. Stermole, Method for Manufacturing a Transparent Ceramic Body, U. S. Patent No. 3,974,249, August 10, 1976.⁽¹¹⁸⁾

Several attractive features of the sintered ceramic magnesia-alumina spinel (MgAl_2O_4) include high temperature resistance, high mechanical strength, high resistance to thermal shock, and good light transparency.

Transparent bodies of the magnesia-alumina spinel can be formed by cold pressing and then sintering a mixture containing approximately equal quantities of magnesia and alumina in the presence of lithium fluoride. Initially magnesia, alumina, and lithium fluoride are dry milled together for about 3 hours. The body is formed by cold pressing at about 15,000 psi prior to calcining the compact. The mixture is calcined at ambient pressure and temperatures of 800 to 1050°C (1470 to 1920°F) for 1/2 to 5 hours. The magnesia and alumina which are present in the precalcined mixture react completely during the sintering operation, forming the spinel. Optimum conditions for this reaction are temperatures of 900 and 950°C (1650 and 1740°F), in a reducing environment. A final firing is then conducted in a wet reducing atmosphere (i.e., wet hydrogen) at temperatures of at least 1600 to 1900°C (2910 to 3450°F) with a substantial soak period.

The addition of lithium fluoride to the mixture apparently prevents complete reaction between the magnesia and the alumina. Magnesium salts (i.e., sulfates or carbonates) can also be used, as well as aluminum sulfate.

4. R. A. Langman, D. R. Glovanini, and M. P. Letzig, Method of Manufacturing Ceramic Substrate for Fine-Line Electrical Circuitry, U.S. Patent No. 4,631,160, December 23, 1986. (119)

A sintered, monolithic, ceramic substrate has been developed which consists of a base plate layer containing at least 90 percent crystalline alumina or beryllia, and a thin upper layer which contains at least 90 percent by weight of the same crystalline material. The base plate layer additionally contains a glassy phase.

The method for making the plates is comprised of

- Mixing the raw batch of materials in the form of an aqueous slurry in the presence of a small amount of wax or organic binder
- Spray drying the batch
- Dry pressing the batch into desired plates
- Firing the plates to simultaneously burn out the organic binder and to sinter the ceramic.

The base plate layer is typically an alumina ceramic. Beryllium oxide can be substituted for aluminum oxide, if beryllia is desired. If the substrate composite is required to contain a glassy phase, a small amount of silica and an alkaline earth oxide or talc is added.

The technique for fabricating the base plate consists of mixing together and ball milling 96.6 percent alumina, 2.3 percent silica, and 0.8 percent magnesia. An aqueous slurry is then formed containing a

small amount of wax or similar organic binders. The slurry is then sprayed dried as in a conventional spray drying operation. Plates are formed by dry pressing the spray dried batch in matched metal dies. The pressure which is applied varies from 10,000 to 15,000 lbs/in². Subsequent firing causes vaporization of the binder and sintering of the ceramic. Shrinkage of approximately 15 percent results in the compact body.

Firing is typically conducted between temperatures of 1575 to 1675°C (2870 and 3050°F) under ambient, oxidizing atmospheres. For the alumina-silica-magnesia ceramic, temperatures of 1640°C (2985°F) are desirable, with a five hour soak at temperature. During the latter stages of firing, when the ceramic sinters, there is an interaction between the silica, magnesia, and a small amount of alumina which leads to the formation of a glassy phase. In addition to the chemical reaction and glass phase formation, some growth in the crystalline alumina grains occurs.

Typically the upper or coating layer consists of at least 90-95 percent alumina, with the remainder as silica and/or glass formers such as talc or earth oxides. The talc or earth oxides react with silica at temperature to form a glass phase. The glass serves to bond the base and top layers together.

Preparation of the top layer consists of mixing and ball milling alumina, silica, magnesia, and oxides, prior to forming a slurry. Although water can be used as the liquid for slurring, the preferred liquid is an organic vehicle containing a small amount of dissolved organic resin which provides good adherence to the plate. A mixture of 40 percent butyl carbitol, 40 percent methyl ethyl ketone and 20 percent alpha terpinol is an example of the preferred composition of the organic vehicle. If water is used, a small amount of binder is added as polyvinyl alcohol or a water emulsifiable wax. The slurry is spray dried or otherwise coated on the surface of the plates.

After the base plates are coated, they are fired to burn out or vaporize any organic binder present, and to sinter the resulting thin upper layer into a monolithic structure with the base layer. Firing is usually done under ambient, oxidizing atmospheres. During the final stages of firing, the upper layer forms a monolithic structure with the base layer, and fills in all surface irregularities. The upper surface layer is relatively free of surface defects.

Aluminosilicates

1. J. E. Cartwright, Refractory Heat-Insulating Materials, U.S. Patent No. 4,041,199, August 9, 1977. (125)

Refractory heat insulating materials can be formed which contain 45-75 percent refractory aluminosilicate fibers; 2-16 percent binding agent consisting of starch and colloidal silica; and 1-20 percent particulates of aluminum, magnesium, and/or silicon. The density of the resulting heat insulating materials range between 0.25-0.4 g/cm³.

The aluminosilicate fibers consist of 42-57 percent Al₂O₃, 45-57 percent SiO₂, and 1-8 percent TiO₂. The binding agent which is used to bond the fibers and/or particulates into a coherent form consists of a combination of starch and colloidal silica. This combination provides unexpectedly higher material transverse strength and handleability, in comparison to materials which are formed with either colloidal silica or starch alone. The particulate metals which are used are small enough to pass through a 0.053 mm opening mesh.

In the formation of the refractory heat insulating material an aqueous water slurry is pulled through a mesh former. The slurry is deposited along the mesh former, which is then subsequently dried. The slurry suspension may require the addition of a suitable suspension complex as aluminum sulfate/colloidal silica sol to maintain appropriate suspension properties. For example, a 1 percent solids content aqueous slurry consists of:

53% Aluminosilicate fibers
7% Aluminum
15% Colloidal silica sol
7% Starch
17% Alumina
1% Aluminum sulfate.

Cordierite

1. C. W. Fritsch, S. T. Buljan, Low Thermal Expansion Coefficient Synthetic Cordierite-Containing Ceramic Bodies and Method for Producing the Same, U.S. Patent No. 3,979,216, September 7, 1976. (121)

Synthetic cordierite ($2\text{MgO} \cdot 2\text{Al}_2\text{O}_3 \cdot 5\text{SiO}_2$) ceramic bodies which exhibit low thermal expansion are characterized by a microstructure which contains <10 percent by volume glass and by microcracks of a certain size and frequency. The synthetic cordierite ceramic bodies can be produced by

- Initially dry ball milling talc, ball clay, and alpha alumina
- Consolidating the mixture to form a green body
- heating the green body at a rate of 150°C/hr to temperatures of $1350\text{--}1425^\circ\text{C}$ ($2460\text{--}2600^\circ\text{F}$)
- Holding the body at temperature for $1/2\text{--}10$ hours
- Cooling the body to below 1000°C (1830°F) at a rate of 150°C/hour .

When formed under these conditions, the cordierite ceramic bodies have good to excellent thermal shock resistance, and chemical durability.

In order to form low thermal expansion cordierite-containing bodies, the starting materials are critical. Materials which are

typically used include talc, ball clay, and a reactive form of alumina (i.e., alpha alumina, or aluminum hydroxide which will be converted to a reactive form of alumina at sintering temperatures). The presence of impurities in the starting materials is detrimental to the formation of the low thermal expansion body in that the impurities

- Tend to lower the melting point of the resulting product
- Stabilize the formation of contained glass phases
- Impede crystallization.

Particularly detrimental is calcium. Impurities which should be kept at concentrations below 300 ppm include alkaline earths, calcium, strontium, and barium. Similarly alkali metals as lithium, sodium, and potassium should be kept at concentrations below 3000 ppm, while iron and titanium should be maintained at concentrations below 0.5 weight percent. Details of a cordierite formulation procedure are described below.

The starting materials (13-18 percent MgO; 30-36 percent Al_2O_3 ; 49-54 percent SiO_2) are mixed and ball milled. The ball milled mixture is combined with binders or plasticizers, and formed into a desired shaped by pressing, extruding, casting, etc. The consolidated green ceramic is fired at a rate of 150-350°C/hr to 1325-1425°C (2415-2600°F). Heating at a faster rate would result in mechanical failure. The body is maintained at 1350°C (2460°F) for 6-10 hours to obtain optimum properties. The body is then heated to 1425°C (2600°F) and maintained at temperature for 1/2 to 1 hour. Preferably the body is heated to 1375-1400°C (2505-2550°F) for about 3 to 5 hours. Cooling should be carried out at a rate of 30-150°C/hr until temperatures of 1000 or 500°C (1830 or 930°F) are achieved, followed by air quenching to cool the unit to room temperature. The melting temperature of cordierite ranges between 1415 and 1430°C (2580 and 2605°F).

2. J. J. Cleveland, Method for Producing High Strength Low Expansion Cordierite Bodies, U.S. Patent No. 4,275,855, November 25, 1980. (122)

Synthetic cordierite ceramic bodies can be produced by

- Pelletizing talc, clay and alumina
- Sintering the pellets to form cordierite
- Milling the pellets to 1-10 μm particles
- Consolidating the particles
- Sintering the polycrystalline body.

Conventional organic binders, plasticizers or other forming aids which are added prior to pelleting and/or formation of the green body, volatilize at or before sintering temperatures. Some of these materials include:

Carbowax - polyethleneglycol - binder
Methocel - methylcellulose - binder
Gelvatcl - polyvinylalcohol - binder
TEG - triethyleneglycol - plasticizer
Ethyleneglycol - plasticizer
Glycerine - plasticizer
Darvan C - dispersant
Darvan 7 - dispersant
Dispex A-40 - dispersant.

The starting material typically includes 13-16 percent MgO , 30-36 percent Al_2O_3 , and 49-54 percent SiO_2 . These materials are mixed in a Waring blender with water being slowly added until pellets are formed. The pellets are converted to cordierite by sintering at temperatures about 1350-1450°C (2460-2640°F for 1/2 to 6 hours in air. The pellets are then milled for 10-48 hours. The milled material is then consolidated into a final shape with a binder or plasticizer, and

dry pressed, extruded, slip cast, isostatically pressed, or injected molded. This is then followed by sintering at 1350-1450°C (2460-2640°F) for 1/2 to 6 hours in air. Sintering within this temperature range leads to the formation of a crystalline or polycrystalline synthetic cordierite body which is essentially free of glassy material.

3. C. W. Fritsch, R. W. Wolfe, Method for Producing Low Expansion Ceramics, U.S. Patent No. 4,142,879, March 6, 1979. (123)

Low thermal expansion ceramics consisting of essentially a 100 percent cordierite solid solution are prepared by the devitrification of a glass frit compact having the nominal composition of 16 percent MgO, 30 percent Al₂O₃, and 54 percent SiO₂.

The raw materials which are used to form the glass may be oxides or materials which convert to oxides upon heating. The raw materials are mixed and precalcined at temperatures between 800 to 1000°C (1470 to 1830°F) for 1 to 4 hours. The mixture is then melted at temperatures of 1490 to 1600°C (2715 to 2910°F) for 4 to 24 hours. The resulting melt is air or water quenched. The glass is reduced to finely divided particles by grinding. The particles are then dry pressed to form a green compact. The compact is heated to temperatures between 1350 and 1425°C (2460 and 2600°F) for 2 to 10 hours to sufficiently induce devitrification and sintering, ultimately forming a structurally integrated ceramic body. ZrO₂ and Si are sometimes added as nucleating agents.

Cordierite-Silicon Nitride

1. A. E. Pasto, Silicon Nitride-Cordierite Ceramic Article, and Process of Manufacture Thereof, U.S. Patent 4,542,109, September 17, 1985. (124)

Silicon nitride (Si_3N_4) ceramics have high strength, excellent thermal shock resistance, and good oxidation resistance. Fabrication of high density silicon nitride is difficult because of the covalent nature of the bonding and low diffusivity of the material. The most satisfactory way to accomplish densification is through liquid phase sintering.

Cordierite-silicon nitride structures can be fabricated. Silicon nitride in the structure imparts high mechanical strength, while cordierite contributes to low thermal conductivity in the material, making the composition extremely useful for internal diesel engine parts. The mechanical strength can be increased by crystallizing the continuous cordierite glassy phase. Crystallization is accomplished by the addition of a nucleating agent such as zirconium dioxide in the formulation, and a subsequent reheating step after densification.

The approximate formula is $(\text{Si}_3\text{N}_4)_{(1-x)}(2\text{MgO} \cdot 2\text{Al}_2\text{O}_3 \cdot 5\text{SiO}_2)_x$ where $x = 0.05-0.75$. Processing consists of blending silicon nitride, magnesium oxide, silicon dioxide, aluminum sesquioxide, and a nucleating agent to form a powder mixture. The mixture is pressed to form the structure, and then sintered at an effective temperature in an inert atmosphere to form a densified particle. The densified structure consists of a first phase of silicon nitride, and a continuous second phase of cordierite and a nucleating agent. The densified article is reheated to an effective temperature to crystallize the second continuous phase of cordierite.

The first phase of silicon nitride is a dispersed phase within the continuous cordierite phase. Depending on the composition of the mixture and sintering temperature, phases of α - and β - Si_3N_4 can be formed, as well as Si_2ON_2 , and an amorphous unidentified phase.

Silicon Nitride

1. Eldon W. Hauck, Ceramic Turbine Wheel, U.S. Patent 3,881,845, May 6, 1975. (125)

In the formation of reaction bonded silicon nitride (RBSN), the reaction of nitrogen with silicon occurs at depths of roughly 1/8 inch into the surface of the material. At greater depths the reaction becomes unreliable forming low density silicon nitride, or even unreacted silicon. In these areas the strength of the material is either low or zero. A process has been demonstrated to eliminate these low density or unreacted regions.

The process utilizes finely powdered silicon which has a maximum particle size of 10 μm , with an average particle size of $\leq 2 \mu\text{m}$. The fine silicon powder is isostatically pressed to a green density of 1.5 grams/cm³, and then sintered under an argon atmosphere at temperatures of 1100°C (2010°F). Analyses indicate that sintering has occurred along the grains, which is an important step in making a continuous silicon structure. The resulting material has sufficient strength to be machined. The unit is initially machined, and subsequently exposure to a nitrogen atmosphere at temperature.

Silicon Nitride/Silicon Carbide

1. Ramakrishna T. Bhatt, Fiber Reinforced Ceramic Material, U. S. Patent 4,781,993, November 1, 1988. (126)

Ceramic materials have been considered for use in high performance, advanced gas turbine and diesel engines. The use of these materials is limited because of their inherent flaw sensitivity and brittle behavior. Similarly the use of reaction bonded silicon nitride (RBSN) materials for structural applications is limited because of the low strength and brittle behavior of the material. The reinforcement

of ceramics by high strength, high modulus, continuous length ceramic fibers is expected to yield stronger, tougher materials. Glass matrix composites reinforced by silicon carbide (SiC) fibers have clearly demonstrated the feasibility of obtaining stronger, tougher materials. The composites are, however, limited in temperature capability by matrix properties, interfacial reactions, and by thermal instability of the fibers at temperatures above 1000°C (1830°F). A strong and tough SiC/RBSN composite material can be fabricated by combining silicon fibers with a reaction bonded silicon nitride (RBSN) matrix. When formed, the composite material may be used at temperatures of up to at least 1400°C (2550°F).

In the past, SiC fiber reinforced RBSN composites were prepared by slip casting or plasma spraying. In slip casting, a slurry consisting of silicon powder, fugitive polymer binder, and a dispersing medium is poured into a mold which contains a cavity filled with ceramic fibers oriented in the desired direction. The mold is agitated ultrasonically to remove entrapped molecules between the fibers and slurry, and to distribute the fibers in the slurry. The slurry and the fibers are heated in an oven at a controlled rate to drive off the fugitive polymer binders and the dispersing medium. The resulting preform is further densified by conventional ceramic processing methods.

In the plasma spray method, composite preforms are prepared by spraying molten silicon onto an array of fibers. These preforms are further treated in a nitrogen atmosphere at an elevated temperature to convert the silicon to a silicon nitride matrix.

A silicon carbide fiber/reaction bonded silicon nitride matrix composite material is produced by hot pressing alternate layers of mats of specially coated SiC fibers and silicon monotapes. The resulting silicon carbide/silicon preforms are nitrified at elevated temperature in N_2 or N_2/H_2 to form a composite material which consists of SiC fibers and a RBSN matrix.

The formulation of the SiC fiber/RBSN composite involves milling high purity silicon powder for 7 to 24 hours with nickel oxide and heptane solvent. Although NiO serves as the preferred nitriding aid, other materials as Fe_3O_4 , MgO, and Al_2O_3 may be used for this purpose. After milling, the powder is oven dried to evaporate the milling medium. The dried powder is used for the silicon monotape.

Silicon carbide fibers are produced by chemical vapor deposition from methyltrichlorosilane onto a heated carbon monofilament which is continuously drawn through a conventional deposition reactor. Different surface coatings are deposited onto the silicon carbon fiber by introducing hydrocarbon gas or a mixture of hydrocarbon gas and silane vapor near the exit port of the reactor. The fiber consists of a silicon carbide sheath surrounding a pyrolytic graphite coated carbon core. The silicon carbide sheath has an outer diameter of 142 μm , while the graphite coated carbon core has a diameter of 37 μm . The silicon carbide sheath consists entirely of columnar beta-silicon carbide grown radially with a preferred {111} orientation.

The fiber has a surface coating consisting of an overlayer with a high silicon/carbon ratio on top of an amorphous carbon layer. The average room temperature tensile strength of the starting fiber is >3.8 GPa.

The silicon carbide mat is prepared by winding the silicon carbide fiber on a metal drum. The fiber is then coated with a polymer slurry which consists of a low glass transition temperature polymer and a solvent. The silicon monotapes are produced by mixing the previously milled silicon powder, NiO, a fugitive polymer binder as polybutylmethacralate or polytetrafluoroethylene (Teflon), and a standard solvent. The mixture is blender for 15 minutes, and filtered to remove the excess solvent. The resulting slurry is poured onto a hot skillet to drive off the remaining solvent, forming a dough.

Alternate layers of the silicon carbide fiber mat and the monotape are stacked, and hot pressed in two stages. The first step involves heating the die to 600°C (1110°F) in a vacuum furnace, which is maintained for 1/2 hour to remove the fugitive binder. In the second stage, the die temperature is raised to 1000°C (1830°F) and pressed at 35 to 138 MPa for 15 minutes. The die is then returned to room temperature under vacuum. The composite preform is then removed and placed in a horizontal nitridation furnace. A nitriding gas of N₂, or N₂ and 4 percent H₂ is passed through the furnace at 1100 to 1400°C (2010 to 2550°F) for 30 to 70 hours.

Silicon Carbide

1. R. A. Clyde, Ceramic Sponge Heat Exchanger Member, U.S. Patent No. 4,222,434, September 16, 1980. (127)

Recuperator tubes are generally made of mullite or silicon carbide. Although SiC conducts heat better than mullite, SiC is brittle and expensive, and has to be encapsulated with an oxygen protective layer when the tubes are used in an oxidizing environment.

In fabricating the recuperator tubes, polyurethane foam is cut to the desired shape, and soaked in a slurry of the ceramic precursor. Excess slurry material is removed by squeezing the foam. An area is cut, and a silicon carbide rod is inserted. The sponge is then dried to the maturing temperature of the ceramic material. If a metallic glass is used as an insert, it is added after heating to the maturing temperature. The thermal expansion of SiC and mullite is 4.7×10^{-6} cm/cm/°C, and 6×10^{-6} cm/cm/°C, respectively. Silicon carbide is known to be attacked by chlorine.

2. W. G. Brown, Method for Manufacturing Silicon Carbide Bodies, U.S. Patent No. 4,154,787, May 15, 1979. (128)

Silicon carbide is used as seal rings in rotating shafts of slurry pumps due primarily to the inherent hardness of the material, and hence greater wear resistance, high thermal conductivity, and high thermal shock resistance.

One method of fabricating SiC rings, is to form a compact of SiC and C, and then permeate the structure with Si either in a vapor or liquid form. Silicon reacts with the carbon and forms in situ SiC. These bodies are referred to as reaction bonded SiC structures. Achieving a non-porous structure is difficult, as well as finishing due to the extreme hardness of SiC.

Alpha silicon carbide with a grain size ranging from 0.5 to 25 μm is used for processing the reaction bonded SiC structures. Carbon which is used in the formulation is either amorphous carbon or graphite with a particle size of 0.01 to 1 μm . Commercial grade silicon which is used consists of particles ranging from 100 to 325 mesh. An organic binder is added to ensure good green strength, and handleability of the material. During heating the organic binder decomposes to form elemental carbon, in excess of the initial concentrations. Organic binders which may be used include acrylic resins, polyvinyl butyral, cellulose acetate, methyl cellulose, or polyethylene glycol. The organic binder should be water soluble.

Mixture typically consist of 75-95 parts by weight silicon carbide-carbon, 5-25 parts by weight elemental carbon, and 5-15 parts by weight organic binder. Alternately mixtures can consist of 80 parts SiC, 20 parts carbon black, 10 parts polyethylene glycol, and 100 parts water.

In forming the mixture, water, polyethylene glycol and carbon are first mixed to form a slurry. Silicon carbide is then added. The water is evaporated and the SiC particles contain a coating of the binder and carbon mixture. The coated particles are then pressed to

form a compact. When polyethylene glycol is used, heating is not required during pressing to form a good green strength compact body. Typically the compact which is formed has a bulk density of 1.8 g/cm³, and a porosity of 20-50 percent by volume which results from voids present between the coated SiC grains.

The silicon-carbon layer is made from 94 parts by weight silicon, 6 parts by weight carbon black or graphite, 5 parts polyethylene glycol, and 100 parts water.

The seal ring is fabricated from a ring of silicon carbide-carbon as the bottom layer, with a silicon-carbon layer placed on top, followed by another silicon carbide-carbon layer. The unit is pressed, and then heated to a temperature which decomposes the binder. Although the heating step can be performed in air, a non-oxidizing atmosphere as 85 percent N₂/15 percent H₂ by volume is preferred.

Heating to temperatures of 300-450°C (570-840°F) decomposes the organic binder, leaving behind carbon, and evolving gaseous or volatile hydrogen and/or oxygen. Heating to temperatures of 375°C (705°F) for one hour in N₂/H₂ is satisfactory when polyethylene glycol is used as the binder.

After the binder has been decomposed, the assembly is heated to temperatures to melt the silicon either under an inert atmosphere, or under vacuum. If heated in an inert atmosphere, the temperature should be higher to ensure flow of the silicon through the silicon carbide-carbon structure. The preferred temperature and time for heating the assembly under vacuum are 1450 to 1650°C (2640 to 3000°F), for 1/2 to six hours depending on the thickness and final porosity of the body being made. In general, the greater the thickness and the lower the porosity, the higher the temperature and the longer the heating time are used. For a 1/2 inch body, heating the silicon carbide-carbon body with

a bulk density of 1.8 g/cm³ under vacuum would require temperatures of 1500°C (2730°F) for two hours. If, however, the same body were heated in an inert atmosphere, temperatures of 2000°C (3630°F) may be desirable to obtain optimum infiltration of silicon within a short period of time.

During heating, the silicon becomes molten and reacts with the carbon in the silicon-carbon mixture, forming silicon carbide. The resulting silicon carbon is a highly porous, friable matrix, which serves to guide the flow of the remaining silicon into the porous silicon carbide-carbon compact. The molten silicon reacts with the carbon in the carbide-carbon unit. Unreacted silicon then flows into the pores and fills the voids as elemental silicon. The resulting body has high strength, and is a unitary structure. The reaction bonded SiC contains pores that are filled with silicon which ultimately results in a substantially non-porous structure. After infiltration is complete, the resulting body is removed and cooled. Excess silicon on the surface of the body is also removed.

Summary

Significant effort has been invested in the formulation and fabrication of high strength, thermally stable, and wear resistant ceramic materials. Multi-step fabrication procedures are required to produce such materials with the desired properties. For most ceramics, the final firing temperatures which are used in the formulation processes exceed the process temperature which the cross-flow filter elements will experience during particulate removal in either the gasification or combustion systems.

With the exception of crystallization, the principal composition of the initial materials is not expected to undergo further chemical change during exposure to particulate filtration temperatures. During the final firing step, impurities that are contained in the ceramic may have achieved an equilibrium state, forming localized defects within the

matrix material. The stability of the ceramic materials is therefore expected to be affected by

- Possible crystallization of phases as a result of thermal or gas phase exposure
- Reactions of the ceramic matrix with either the process gas or with char or ash fines
- Reactions of trace impurities within the matrix with either the process gas or with char or ash fines
- Volatilization of the ceramic matrix at process conditions
- The formation of microcracks and separation along grain boundaries.

The influence of each of the above will be explored in Section 3.2.

3.1.2 Materials Characterisation

Several ceramic materials which possess excellent mechanical properties along with good thermal shock and corrosion resistance are being considered for fabrication of particulate filter elements which will be used in aggressive, high temperature, coal process environments. Five materials that were selected for evaluation include both oxide and non-oxide ceramics. The compositions range from a relatively high alumina-containing silica, to an oxide-nonoxide composite, to silicon nitride. The materials include:

- Alumina/Mullite
- Cordierite
- Cordierite-Silicon Nitride
- Aluminosilicate Foam
- Reaction Bonded Silicon Nitride.

Samples of each ceramic material were procured and subjected to chemical and physical characterization in an attempt to:

- Identify major and minor phase constituents
- Identify inclusion of trace and minor elements which could interact with the ceramic matrix, or with the process gases or fines
- Identify material strength, porosity, and density.

Characterization techniques include:

- Atomic absorption analysis to quantitatively determine the concentration of the major elemental constituents (i.e., silicon as SiO_2 , alumina as Al_2O_3 , etc.), and emission spectroscopy for qualitative elemental concentration determination of trace and minor constituents.

- X-ray diffraction analysis for identification of the various phases or compounds present in the ceramic materials.
- Scanning electron microscopy/energy dispersive x-ray analysis (SEM/EDAX) for phase morphology identification of both the ceramic filter surfaces and cross-sections, and qualitative elemental concentration determination within selected regions of the cross-flow filter material.
- Four-point bend strength analysis, porosity, and density determinations for identification of the physical characteristics of the starting filter material.

Chemical reactions of entrained fines with the cross-flow filter element materials have been proposed at filter process conditions. Fines that are tentatively planned for use in Phase II (Task 4) were selected on the basis of their expected chemical composition, as well as on the criteria that the fines had previously been generated in sub-pilot scale process systems. In order to demonstrate the influence of process environment and coal composition on the resulting entrained fines, process chars and ashes were procured from the Kellogg Rust-Westinghouse fluid-bed gasifier, the Texaco entrained-bed gasifier, and the New York University pressurized fluidized-bed combustor. Each material was subjected to chemical and physical analysis using the following techniques:

- X-ray diffraction for determination of the phases or compounds present in the various char or ash fines.
- Atomic absorption and emission spectroscopy for quantitative and qualitative determination of the major, minor, and trace element concentrations present in each material.

- Scanning electron microscopy and energy dispersive x-ray analysis identifying the surface morphology of the char or ash fines, and qualitative elemental concentration determination.
- X-ray sedimentation or coulter counter analysis for particle size distribution analysis.
- Melt/fusion temperature and ultimate analysis to further characterize the chemical and physical properties of the char or ash materials.

The following Section discusses the chemical and physical data generated for both the ceramic cross-flow filter materials and char and ash fines.

3.1.2.1 Cross-Flow Filter Materials

Variation in the techniques which are used in fabricating the ceramic materials into structural components (i.e., reaction sintering, conventional sintering, or hot-pressing) leads to differences in the resulting physical properties as porosity, microstructure, mechanical strength, and oxidation-resistance. Reaction-sintered materials are generally porous and weaker in comparison to hot-pressed materials which are denser, stronger, and exhibit a greater resistance to thermal shock. The resulting physical properties of the ceramic filter is therefore characteristic of the supplier's process.

The candidate cross-flow filter materials selected in this study include alumina/mullite, cordierite, aluminosilicate foam, cordierite-silicon nitride, and reaction bonded silicon nitride. All of the materials either contain SiO_2 or have an inherent SiO_2 surface layer (Table 3.10). Additionally, these materials, as expected, will have significantly lower strengths and elastic moduli as a result of the

TABLE 3.10a
CROSS-FLOW FILTER MATERIAL
CHARACTERIZATION

	Alumina/ Mullite	Cordierite	Cordierite- Si ₃ N ₄	Alumino- Silicate Foam	Reaction Bonded Si ₃ N ₄
Atomic Absorption Analysis, Wt%					
Al ₂ O ₃	52.29	(a)	(a)	54.18	(a)
SiO ₂	39.64			46.86	
Fe ₂ O ₃	0.46			0.04	
CaO	4.79			0.03	
MgO	2.60			0.02	
K ₂ O	0.31			0.02	
Na ₂ O	0.18			0.16	
X-Ray Diffraction Analysis,					
Major Phases:	Mullite	Cordierite	β-Si ₃ N ₄	Mullite	β-Si ₃ N ₄
Minor Phases:	Corundum	Amorphous	Si ₂ ON ₂	Amorphous	α-Si ₃ N ₄
	Anorthite (b)		α-Cordierite		Amorphous
	Amorphous (b)		Amorphous		
Four-Point Bend Strength, psi	8,995±738 (c)	1,967±125	48,459± 15,632	(d)	(e)
Density, g/cm³					
True	3.087	2.678	(e)	2.928	(e)
Bulk	2.26±0.02	1.42±0.01	2.85	0.447	
Percent	73.1±0.5	53.1±0.5		15.3	
Porosity, %					
Open	18.8±1.7	43.2	(e)	83.1	(e)
Closed	8.1±1.3	3.8±0.6		1.6	

(a) Since variation in chemical composition was demonstrated between the alumina fabrication lots, rigorous atomic absorption analyses were not conducted for cordierite, cordierite-silicon nitride, and reaction bonded silicon nitride.

(b) X-ray analysis demonstrated variation in phase composition of the alumina material in the various fabrication lots. Materials are reported to range from 95% mullite/5% corundum to 70% mullite/17% anorthite/12% corundum/amorphous.

Table 3.10a (continued)

- (c) MOR parallel to short filter channel: $8,995 \pm 38$ for 8 samples.
MOR perpendicular to short filter channel: $8,425 \pm 1196$ for 8 samples.

Variation in MOR, density, and porosity data was demonstrated for the various filter fabrication lots.

- (d) Foam was determined to lack strength during handling and testing. Demonstration of adequate material strength at service conditions is required.

- (e) Both cordierite-silicon nitride and reaction bonded silicon nitride are undergoing further development to increase porosity in each material.

TABLE 3.10b
CROSS-FLOW FILTER MATERIAL
CHARACTERIZATION

	Alumina/ Mullite	Cordierite	Cordierite- Si ₃ N ₄	Alumino- Silicate Foam	Reaction Bonded Si ₃ N ₄
Emission Spectroscopy, Wt%					
Al	>10	>10	3	>10	0.05
Ag	<0.001	<0.001	<0.001	<0.001	<0.001
B	0.02	0.01	0.1	<0.002	0.02
Ba	0.03	0.004	0.003	<0.02	<0.003
Be	<0.001	<0.001	<0.001	<0.001	<0.001
Bi	<0.003	<0.003	<0.003	<0.003	<0.003
Ca	3	0.4	0.08	0.03	0.01
Cd	<0.03	<0.03	<0.03	<0.03	<0.3
Co	<0.003	<0.005	<0.005	<0.003	<0.005
Cr	0.01	0.009	0.003	<0.01	0.009
Cu	0.003	0.02	<0.005	<0.003	0.02
Fe	0.3	0.8	0.2	0.4	0.8
Ga	<0.03	<0.01	<0.01	<0.03	<0.01
Ge	<0.03	<0.01	<0.01	<0.03	<0.01
K	0.2	0.3	0.01	<0.005	<0.005
Li	0.006	0.008	<0.001	<0.002	<0.001
Mg	1	>5	2	0.02	0.01
Mn	<0.01	0.04	<0.01	<0.01	0.02
Mo	<0.01	<0.003	0.03	<0.01	<0.003
Na	0.1	0.5	0.004	0.1	<0.003
Nb	<0.03	<0.01	<0.01	<0.03	<0.01
Ni	<0.01	0.008	0.01	<0.01	0.005
Pb	<0.02	<0.005	<0.005	<0.02	<0.005
Sb	<0.03	0.07	<0.03	<0.03	<0.03
Si	>10	>10	>10	>10	>10
Sn	<0.01	<0.005	<0.005	<0.01	<0.005
Sr	0.01	0.006	<0.003	<0.003	<0.003
Ti	0.03	0.2	0.03	0.02	0.002
V	0.01	0.005	<0.003	<0.01	<0.003
Zn	<0.02	<0.03	<0.03	<0.02	<0.03
Zr	0.02	0.03	0.01	0.07	0.01

large amount of porosity required for effective gas cleaning operations. This decrease in mechanical properties may or may not affect the thermal shock resistance (TSR) of these materials. High thermal shock resistance requires high strength, low coefficient of thermal expansion (CTE) and low elastic modulus. If the porosity causes a material's modulus to decrease more than the strength, then the TSR may actually increase. The converse will cause a decrease in the TSR. All the materials being considered for the cross-flow filter should have good to excellent thermal shock resistance properties.

Alumina/Mullite

The alumina/mullite material is formed in the green (unfired) state from alumina, silica, and pore formers, and when fired, generally contains mullite rods surrounded by a grain boundary "glassy" or amorphous phase. Samples were removed from a porous, mid-ribbed alumina/mullite cross-flow filter element which was part of the fabrication lot intended for use in the New York University combustor filter tests conducted in October 1988. The samples were subjected to chemical and physical characterization using atomic absorption analysis, emission spectroscopy, scanning electron microscopy (SEM), energy dispersive x-ray analysis (EDAX), x-ray diffraction (XRD) analysis, four-point bend strength testing, and porosity and density determinations.

Atomic absorption analysis of the alumina/mullite material indicates the presence of 52.29 wt% Al_2O_3 , 39.64 wt% SiO_2 , 0.46 wt% Fe_2O_3 , 4.79 wt% CaO , 2.60 wt% MgO , 0.31 wt% K_2O , and 0.18 wt% Na_2O (Table 3.10). The emission spectroscopy analysis indicates the relatively low concentration of additional trace elements present in the material.

Mid-rib cross-section and gas channel surface samples were removed from the alumina/mullite cross-flow filter element and were prepared for SEM/EDAX characterization by initially applying a thin carbon coating (Figure 3.11). The surface morphology of the mid-ribbed cross-section is shown in Figure 3.12a. The pores within the alumina/mullite filter are relatively evenly dispersed. Using higher magnification (Figure 3.12b), the areas surrounding the pores appear to contain both a "smooth" or "melt" phase, and mullite rods. The internal surface of the pore appears to contain discrete mullite rods. EDAX analysis of the "smooth" or "melt" areas indicates that this phase is predominantly silicon, with nearly equivalent concentrations of alumina and calcium, and minor phases of magnesium, potassium, titanium, and iron (Figure 3.12d, Spot 1; Figure 3.12e, Spot 5). The composition of the rods are predominantly aluminum, with secondary concentrations of silicon (Figure 3.12d, Spot 2; Figure 3.12e, Spot 6).

Figure 3.13a illustrates the surface morphology of the channel area of the alumina/mullite filter which would be in direct contact with the process gases. For this particular filter, the channel is shown to consist of ridges and grooves. The composition of the material in the grooved areas consist predominantly of a silicon-rich, high alumina phase, with minor contributions of calcium, magnesium, potassium, and titanium (Figure 3.13b, Spot 1). The small particles which align the ridges of the channel are identified as predominantly an aluminum phase (similar to Figure 3.13b, Spot 2).

The surface shown in Figure 3.14a is adjacent to the grooved channel region in the alumina/mullite filter, and illustrates the fracture surface at the base of a previously attached rib. The pores are more apparent in this fractured region than along the ridged channel area. A higher magnification of the fractured surface illustrates a similar morphology to that previously described for the mid-ribbed cross-section. The "smooth" or "melt" areas contain predominantly silicon and high aluminum concentrations, with additional calcium,

Areas that were analyzed included:

- (1) Mid-Ribbed Cross Section
- (2) Gas Channel Surface
- (3) Adjoining Surface where Rib was Previously Attached.

Figure 3.11 - Sections Removed from a Mid-Ribbed Alumina/Mullite Cross-Flow Filter

Figure 3.12a - Scanning Electron Micrographs Showing Fractured Surface of an Alumina/Mullite Cross-Flow Filter Mid-Ribbed Area

Figure 3.12b - Higher Magnification Scanning Electron Micrographs
Showing the Fractured Surface of the Alumina/Mullite
Mid-Ribbed Area

Figure 3.12c - Scanning Electron Micrograph Showing Internal Surface
of a Pore in the Alumina/Mullite Mid-Ribbed Area

ALUMINA Z=00
 PR= S 42SEC 0 INT
 U=2048 H=10KEV 1:10 AQ=10KEV 10

ALUMINA Z=00
 PR= S 11SEC 0 INT
 U=2048 H=10KEV 1:10 AQ=10KEV 10

Figure 3.12d - SEM/EDAX Analysis Characterizing the Various Phases in the Alumina/Mullite Mid-Ribbed Area

ALUMINA

PR= S 10SEC

0 INT

ALUMINA

PR= S 14SEC

0 INT

U=1024 H=10KEV 1:10 AQ=10KEV 10 U=1024 H=10KEV 1:10 AQ=10KEV 10

Figure 3.12e - SEM/EDAX Analysis Characterizing the Fractured Mid-Ribbed Surface of the Alumina/Mullite Filter

Figure 3.13a - Scanning Electron Micrographs Showing the Gas Flow Channel Surface of an Alumina/Mullite Mid-Ribbed Filter

ALUMINA CHANNEL

PR= S 16SEC

0 INT

ALUMINA CHANNEL

PR= S 13SEC

0 INT

U=1024 H=10KEV 1:10 AQ=10KEV 10 U=1024 H=10KEV 1:10 AQ=10KEV 10

Figure 3.13b - SEM/EDAX Analysis Characterizing the Gas Flow Channel Surface of an Alumina/Mullite Mid-Ribbed Filter

Figure 3.14a - Scanning Electron Micrographs Showing the Fractured Surface Beneath the Mid-Rib Area in an Alumina/Mullite Filter

magnesium, and potassium phases (Figure 3.14b, Spot 3), while the mullite or rod-like phase is principally aluminum, with secondary and minor contributions of silicon and calcium, respectively (Figure 3.14b, Spot 4).

X-ray diffraction analysis of the mid-ribbed alumina/mullite filter element sample indicated that the material consisted primarily of mullite, with a secondary corundum (Al_2O_3) phase.

Four-point bend strength tests were performed on sections that were removed parallel and perpendicular to the dirty gas channel in the mid-ribbed alumina/mullite filter element. Typically the samples were cut and the ground to dimensions of 0.13-0.19 cm x 0.5-0.8 cm x 2-3.2 cm. Load and strength data are presented in Table 3.11. These data indicate that the strength of the mid-ribbed alumina/mullite material along the gas flow channel is similar to material that is removed from sections that are perpendicular to the dirty gas channel.

Characterization of the density and porosity of the mid-ribbed alumina/mullite filter indicates that the material is approximately 73 percent dense, and has an open porosity of approximately 19 percent (Table 3.10a).

Cordierite

Cordierite is produced from a mixture of talcs (magnesium silicates), alumina, and clay (hydrated aluminosilicates). The talcs and the clay are potential sources of trace impurities. This material has a coefficient of thermal expansion (CTE) on the order of $1.85\text{--}2.2 \times 10^{-6}/^\circ\text{C}$. Porosity in this material decreases the modulus more than the strength. Additionally, this material microcracks upon cooling, a follow-up anneal blunts these cracks. Microcracking has been shown to be an effective method of increasing the TSR by decreasing the elastic modulus. This material should have very good thermal shock resistance characteristics.

ALUMINA

PR= S 13SEC

0 INT

ALUMINA

PR= S 8SEC

0 INT

U=2048 H=10KEV 1:10 AQ=10KEV 10

U=2048 H=10KEV 1:10 AQ=10KEV 10

U=2048 H=10KEV 1:10 AQ=10KEV 10

U=2048 H=10KEV 1:10 AQ=10KEV 10

Figure 3.14b - SEM/EDAX Analysis Characterizing the Fractured Surface
Beneath the Mid-Rib Area in an Alumina/Mullite Filter

TABLE 3.11

FOUR-POINT BEND STRENGTH TEST DATA
FOR THE ALUMINA/MULLITE CROSS-FLOW FILTER MATERIAL

Sample Location	Dimensions, cm			Load, kg	Stress, psi
	Height	Width	Span*		
Mid-Ribbed Alumina/Mullite					
• Parallel to Gas Flow Channel	0.169	0.535	0.635	5.30	9,386
	0.135	0.537	0.635	3.50	9,676
	0.153	0.541	0.635	3.70	7,894
	0.150	0.536	0.635	3.80	8,509
	0.162	0.646	0.635	5.60	8,925
	0.193	0.646	0.635	8.20	9,219
	0.172	0.824	0.635	8.95	9,939
	0.135	0.820	0.635	4.45	8,092
Mid-Ribbed Alumina/Mullite					
• Perpendicular to Gas Flow Channel	0.171	0.708	0.635	6.35	8,312
	0.193	0.709	0.635	7.35	7,544
	0.189	0.706	0.635	8.70	9,354
	0.182	0.710	0.635	5.40	6,226
	0.190	0.707	0.635	9.55	10,147
	0.171	0.708	0.635	6.15	8,050
	0.172	0.707	0.635	6.85	8,880
	0.174	0.709	0.635	7.05	8,884

* Inner Span; Outer Span of 1.9 cm.

Samples were removed from a thin, 5x5 cm cordierite plate, and were subjected to emission spectroscopy analysis, scanning electron microscopy and energy dispersive x-ray analysis (SEM/EDAX), x-ray diffraction analysis, four-point bend strength testing, and porosity and density determinations.

Qualitative emission spectroscopy analysis of the cordierite sample indicates that the material principally contains aluminum, silicon, magnesium, iron, sodium, calcium, potassium, and titanium. Additional trace elements are present at concentrations comparable to those present in the alumina/mullite matrix.

The scanning electron micrographs shown in Figure 3.15a illustrate the cordierite surface morphology. Higher magnification of the porous surface illustrates that the material consists of what appears to be a smooth, "melt" phase which contains numerous smaller particles. The smaller fines can also be found as protrusions along the edges of the pores (Figures 3.15b-3.15e).

An energy dispersive x-ray analysis (EDAX) area scan of the cordierite surface indicates that the material consists principally of aluminum and silicon, with magnesium present as a secondary constituent. Traces of iron, potassium, and titanium are also present within the smooth or "melt" phase of the material (Figure 3.15d). Iron concentrations are identified to range between 0.5 and 1.3 weight percent, while potassium concentrations are generally between 0.4 and 0.7 weight percent. The smaller particles which are embedded within the smooth substrate phase randomly contain high concentrations of chlorine (1.80 weight percent).

X-ray diffraction analysis indicates that although cordierite is the principal phase present in the sample, an amorphous phase is also present. The amorphous phase may be indicative of the smooth or "melt" phase that was detected by SEM.

Figure 3.15a - Scanning Electron Micrographs of the Cordierite Plate Surface

Figure 3.15b - High Magnification Scanning Electron Micrographs
of the Cordierite Plate Surface

Figure 3.15c - Higher Magnification Scanning Electron Micrographs
of the Cordierite Plate Surface

Figure 3.15d - Area Scan of the Cordierite Plate Surface Using Energy Dispersive X-Ray Analysis

Figure 3.15e - Localized Energy Dispersive X-Ray Analysis Along the Cordierite Plate Surface

Samples were cut from the cordierite plate, and were ground to dimensions of 0.13-0.19 cm x 0.5-0.8 cm x 2-3.2 cm for four-point bend testing. An average strength of the cordierite material is approximately 2,000 psi (Table 3.12). The cordierite sample has a density of approximately 53 percent, and an open porosity of approximately 43 percent (Table 3.10a).

Aluminosilicate Foam

The third material considered for use as a candidate cross-flow filter material is an aluminosilicate foam. This material consists of glass fibers which are coated and held together by mullite (aluminosilicate). Uncoated fibers are susceptible to devitrification in the presence of sodium resulting in fiber shrinkage and cracking. Mullite which coats the fibers is expected to prevent this from occurring.

Samples of the aluminosilicate foam were subjected to chemical and physical characterization using the following techniques: atomic absorption and emission spectroscopy analyses, x-ray diffraction analysis, and density and porosity determinations. Four-point bend strength testing was attempted, however, due to the inherently low strength of the material, strength data could not be generated.

Atomic absorption analysis of the aluminosilicate foam indicates the presence of 54.18 wt% Al_2O_3 , 46.86 wt% SiO_2 , 0.04 wt% Fe_2O_3 , 0.03 wt% CaO , 0.02 wt% MgO , 0.02 wt% K_2O , and 0.16 wt% Na_2O . Emission spectroscopy analysis supports the atomic absorption data in that the foam consists principally of an aluminum- and silicon-containing phase, which is virtually free of secondary elements, but contains only trace concentrations of iron, calcium, magnesium, potassium, and sodium.

A sample of the aluminosilicate foam was removed and initially coated with carbon prior to SEM/EDAX characterization. Due to the highly porous nature of the aluminosilicate foam, which enhanced the

TABLE 3.12

FOUR-POINT BEND TEST DATA
FOR THE CORDIERITE CROSS-FLOW FILTER MATERIAL

Dimensions, cm			Load, kg	Stress, psi
Height	Width	Span*		
0.125	0.586	0.635	NA	NA
0.126	0.581	0.635	0.60	1,767
0.126	0.587	0.635	0.65	1,894
0.125	0.582	0.635	0.65	1,935
0.125	0.583	0.635	0.70	2,084
0.126	0.581	0.635	0.70	2,062
0.126	0.578	0.635	0.70	2,062

NA = Not Available.

* Inner Span; Outer Span of 1.9 cm.

charging characteristics of the material during analysis, the sample was recoated with gold. The gold peak generated in the EDAX analysis is therefore an artifact of sample preparation.

The scanning electron micrograph shown in Figure 3.16 indicates that the aluminosilicate foam consists of fibers ranging from 1-10 μm . The array of fibers have either:

- A smooth surface which consists of a high alumina, and a secondary silicon phase
- Small particles attached along the surface of the fibers which appear to be compositionally identical to the smooth surface of the fibers
- Clusters or masses of particles which adjoin adjacent fibers, and which consist of a higher aluminum to silicon ratio than the individual fibers.

Although the aluminosilicate foam pore size distribution was not determined, a variable pore size range is expected to result in the material due to the random orientation of the fibers and small particle clusters.

X-ray diffraction analysis indicates that although mullite is the principal phase present in the aluminosilicate foam, an amorphous phase is also present. The aluminosilicate foam is identified to be approximately 15 percent dense, and has an open porosity of approximately 83 percent (Table 3.10a).

Cordierite-Silicon Nitride

The cordierite/silicon nitride (CSN) material is initially formed from a mixture of 25 weight percent cordierite and silicon nitride. The role of cordierite is to enhance the densification of the

Figure 3.16a - Scanning Electron Micrographs of the Aluminosilicate Foam Cross-Flow Filter Material

Figure 3.16b - High Magnification Scanning Electron Micrographs of the Aluminosilicate Foam Cross-Flow Filter Material

Figure 3.16c - Higher Magnification Scanning Electron Micrographs of the Aluminosilicate Foam Cross-Flow Filter Material

ALUMINOSILICATE FOAM

PR= 60S 10SEC 0 INT

U=512 H=10KEV 1:1Q AQ=10KEV 1Q

ALUMINOSILICATE FOAM

PR= 60S 16SEC 0 INT

U=512 H=10KEV 1:1Q AQ=10KEV 1Q

ALUMINOSILICATE FOAM

PR= 60S 8SEC 0 INT

U=512 H=10KEV 1:1Q AQ=10KEV 1Q

Figure 3.16d - Energy Dispersive X-Ray Analyses of Various Phases Present in the Aluminosilicate Foam

Si_3N_4 via liquid phase sintering. Additionally, the low melting characteristics and large volume fraction of the cordierite significantly decreases the sintering temperature of the Si_3N_4 to the 1400-1550°C (2550-2820°F) range. Typically, Si_3N_4 is sintered or hot-pressed at 1700-2100°C (3090-3810°F) with the addition of 2-10 weight percent sintering additives. Since production of porous CSN for the cross-flow filter applications is currently under development, mechanical property data are not available. The high temperature mechanical properties of the porous material should, however follow those of the dense material. At 1100 and 1200°C (2010 and 2190°F) the dense material retains 90 and 50 percent, respectively, of its room temperature strength. The oxidation resistance of the CSN is enhanced by a silicon oxynitride (Si_2ON_2) phase, which acts as an intermediate bonding layer between the composite and the inherent SiO_2 surface layer.

Preliminary characterization of a 5x5 cm thin plate of CSN included emission spectroscopy analysis, scanning and back-scattering electron microscopy and energy dispersive x-ray analysis (SEM/BSE/EDAX), x-ray diffraction analysis, density, and four-point bend strength testing.

Emission spectroscopy data indicate that the CSN material contains principally silicon phases, with secondary phases of aluminum, magnesium, and iron (Table 3.10b).

The scanning electron micrographs shown in Figure 3.17 illustrate the morphology along the dense CSN surface. Several pores are evident, and are typically less than 10 μm in diameter. An EDAX area scan shows that the surface is extremely rich in silicon, with minor aluminum concentrations, and trace magnesium concentrations. Since the surface is nearly smooth, BSE can be used to identify phase variation within the material. The BSEs in Figures 3.17b and 3.17d indicate the possibility that two phases co-exist in the material. EDAX analysis of the "rod-like" grey areas illustrates the similarity of the

Figure 3.17a - Scanning Electron Micrographs of the Cordierite-Silicon Nitride Plate Surface

Figure 3.17b - Scanning Electron and Back-Scattering Electron
Micrographs of the Cordierite-Silicon Nitride
Plate Surface

Figure 3.17c - High Magnification Scanning Electron and Back-Scattering Electron Micrographs of the Cordierite-Silicon Nitride Plate Surface

Figure 3.17d - Higher Magnification Scanning Electron and Back-Scattering Electron Micrographs of the Cordierite-Silicon Nitride Plate Surface

Figure 3.17e - Energy Dispersive X-Ray Analysis of the Cordierite-Silicon Nitride Surface

silicon:aluminum:magnesium ratio to that detected in the overall area scan. Alternately, the white areas indicate that the phase which is present consists of a higher silicon content in relationship to the aluminum. Magnesium is not evident in this phase.

X-ray diffraction analysis indicates that the CSN material consists principally of β -silicon nitride, with secondary contributions of silicon oxynitride (Si_2ON_2), and traces of α -cordierite. The ratio of β - Si_3N_4 to Si_2ON_2 is estimated at 79:21 percent. A bulk density of 2.85 g/cm³ was determined for this material. Four-point bend strength tests indicate that strength varies significantly with location along the plate, ranging from 32,827 to 64,091 psi. Table 3.13 illustrates the positions sampled along the bowed sample plate, and the resulting strength data.

Reaction Bonded Silicon Nitride

The fifth potential cross-flow filter material is reaction bonded silicon nitride (RBSN). This material is produced by nitriding silicon powder at approximately 1400°C (2550°F). Iron is added to the silicon powder to remove the SiO_2 layer present on the silicon, thus, allowing the nitriding reaction to occur. Typically, 1-3 weight percent iron oxide is expected to be present in RBSN bodies. This material does not have a grain boundary phase. RBSN materials are weaker than other Si_3N_4 bodies made by other methods. This lowered strength is a result of the approximate 15 percent porosity which occurs as a result of the RBSN production process. This material has not been produced with the full porosity necessary for gas filtering applications. As such, the material's properties for the porous material are not available.

Preliminary characterization of a 10x10 cm thin plate of reaction bonded silicon nitride included emission spectroscopy analysis, surface analysis using scanning electron microscopy and energy

TABLE 3.13

FOUR-POINT BEND STRENGTH TEST DATA FOR
THE CORDIERITE-SILICON NITRIDE MATERIAL

Position	Dimensions, cm			Load, kg	Stress, psi
	Height	Width	Span		
Cordierite-Silicon Nitride					
1	0.091	0.600	0.635	8.8	47,688
1a	0.090	0.604	0.635	9.5	52,532
2	0.092	0.588	0.635	8.5	46,062
2a	0.092	0.590	0.635	11.2	60,693
3	0.094	0.594	0.635	6.3	32,827
3a	0.093	0.598	0.635	12.3	64,091
4	0.096	0.593	0.635	8.9	43,844
5	0.098	0.591	0.635	*	*
6	0.098	0.591	0.635	9.3	44,208
7	0.095	0.597	0.635	9.4	47,166
8	0.098	0.600	0.635	9.7	45,314
9	0.098	0.602	0.635	11.1	51,856

* Sample broke during handling.

9	3	2	1
8			
7			
6	3a	2a	1a
5			
4			

dispersive x-ray analysis (SEM/EDAX), as well as x-ray diffraction (XRD) analysis. Four-point bend tests, density and porosity determinations were not performed on this sample due to the lack of obvious surface porosity as seen by SEM.

Emission spectroscopy analysis of the RBSN plate indicates that the material principally contains a silicon phase, with secondary contributions of iron (Table 3.10b).

Figure 3.18 illustrates the surface morphology of the RBSN plate using SEM techniques. Low magnification of the surface structure indicates that a very dense packing of particles results with randomly interdispersed cracks (Figure 3.18a). Higher magnification of the 1-20 μm densely packed particles indicates whisker-type formations not only on the surface of the particles, but also between adjoining particles. A significant portion of the densely packed particles have straight sides and sharp corners, and appear to have "melted" with adjacent particles (Figures 3.18b and 3.18c).

Within the cracked regions are whisker-type strands which form a matted appearance. Generally within these regions large particles are absent, and pores (5-15 μm) are more evident (Figures 3.18c and 3.18e).

EDAX characterization of the surface indicates that the large particles are silicon-rich, with minor contributions of iron (Figure 3.18f). In the dense whisker regions, EDAX indicates a similar composition.

A portion of the material was removed from the 4x4 inch plate and ground for x-ray diffraction (XRD) analysis. Data indicate that the material consists of hexagonal β -silicon nitride and α -silicon nitride as major phases, with minor contributions of α -iron. A somewhat broadened diffraction pattern results between the two-theta angles of 10 and 24, possibly indicating the presence of an amorphous phase.

Figure 3.18a - Scanning Electron Micrographs of the Reaction Bonded Silicon Nitride Plate (RBSN) Surface

Figure 3.18b - Scanning Electron Micrographs of the Dense Particle Formations Along the RBSN Surface

Figure 3.18c - Scanning Electron Micrographs of the Whisker Formations in Both the Dense Particle and Cracked Regions Along the RBSN Surface

Figure 3.18d - Higher Magnification Scanning Electron Micrographs of the Whisker Formations in the Cracked Areas of the RBSN Surface

Figure 3.18e - Higher Magnification Scanning Electron Micrographs of the Whisker Formations in Both the Dense Particle and Cracked Regions Along the RBSN Surface

RBSN

PR= 100S 42SEC 0 INT
U=256 H=10KEV 1:30 AQ=10KEV 10

RBSN

PR= 100S 41SEC 0 INT
U=256 H=10KEV 1:30 AQ=10KEV 10

Figure 3.18f - Energy Dispersive X-Ray Analysis of RBSN
Particles and Whiskers

Figure 3.18g - Scanning Electron Micrograph and Energy Dispersive X-Ray Analysis of the RBSN Whiskers

Summary

All of the ceramic cross-flow filter materials which have been subjected to chemical and physical characterization in this study have been shown to contain silicon. Silicon is present as either

- The major base constituent (i.e., aluminosilicate foam; cordierite)
- A secondary constituent (i.e., alumina/mullite)
- A resulting protective surface layer (i.e., oxidation of the CSN or RBSN materials).

Typical chemical reactions which occur with the oxide silicon-based constituents during exposure to oxidizing (combustion) or reducing (gasification) environments include:

Eutectic or glass phase formations, as well as crystalline changes are also likely to occur within the silicon oxide-based materials during exposure to high temperature gasification or combustion gases containing volatile alkali. Examples of possible reactions which can occur within the silica lattice include:

Similar reactions are expected to occur for the non-oxide silicon-based materials as silicon nitride and silicon carbide. The affinity for release of volatiles from these substrates is dependent on

the localized oxygen partial pressure. Typical of "active" oxidation (low oxygen partial pressures), the non-oxide silicon-based ceramics release gaseous silicon monoxide (Reaction 17 and 18), while under "passive" oxidation conditions (high oxygen partial pressures as in combustion systems), oxidation of the substrate results (Reactions 19 and 20).

Table 3.14 presents an abbreviated summary of pertinent chemical reactions which have been reported in the literature with regard to the influence of volatile alkali, sulfur, and halides, as well as condensates (i.e., alkali sulfates) and ash/slag on the stability of alumina, silica, mullite, and silicon nitride. Silicon carbide is included in this table to illustrate the similarities between the nonoxide silicon-based matrices.

TABLE 3.14

CHEMICAL REACTIVITY OF ALUMINA, SILICA, MULLITE,
SILICON NITRIDE, AND SILICON CARBIDE

- ALUMINA -

- With the exception of high purity Vistal, alumina is fluxed by alkali oxides, forming a glass phase.
- Reaction of alumina with alkali results in the formation of NaAlO_2 in the grain boundaries which (1) weakens the grain boundaries; (2) collapses the crystal structure; and (3) creates broad cracks.
- Alumina reacts with calcium to form glassy phases.
- Alumina reacts with iron and zinc to form spinels.
- Alumina is nearly unaffected by halide attack.
- Alumina is not as resistant to acidic ash attack as silicon carbide (SiC).

- SILICA -

- Silica as a substrate outer surface layer, or silica along the grain boundaries is subject to salt attack causing etching and destruction of the protective layer.
- Silica (low cristobalite and alpha-quartz) and silica-based materials react with alkali oxides to form glassy silicate phases. The ceramic gradually restructures as a glassy phase, has a lower melt temperatures, and is more susceptible to further fluxing by alkali oxides. The formation of the liquid phase as a result of reaction with Na_2O or K_2O leads to a loss of structural integrity.
- Extensive corrosion of silica results with alkali and iron oxide.
- Silica reacts with calcium to form glassy phases.
- Silica reacts with halides causing volatile silicon halides to form.
- Silica dissolves in slag.

TABLE 3.14 (continued)

- MULLITE -

- At high temperature, mullite ($3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$) which typically contains SiO_2 forms corundum (Al_2O_3) which dissolves in the glassy SiO_2 portion of the mullite structure.
- Mullite is fluxed by alkali oxides, forming glass phases. The reaction of mullite with Na_2O and K_2O leads to the formation of liquid phases and loss of structural integrity, similar to alumina.
- Mullite reacts with iron to form spinels.
- Mullite is almost unaffected by halide attack.
- Mullite reacts with slag, leading to the formation of corundum crystals.

- SILICON NITRIDE -

Oxidation Characteristics

- Hot pressed Si_3N_4 experiences oxidation between 1000 and 1400°C (1832 and 2552°F). Silica and silicates form on the surface, with impurities influencing the surface layer composition. Mg, Ca, Fe, and Al diffuse outwardly, and react or dissolve in the surface silica.
- Typical oxidation of Si_3N_4 indicates a weight gain, through the following reaction

No significant weight gain is observed below 1100°C (2012°F). At higher temperatures during initial oxidation, a compact oxide layer is formed on the surface which grows inward by the diffusion of oxygen, resulting in a parabolic oxidation rate.

TABLE 3.14 (continued)

The oxidation rate is unaffected by the partial pressure of O_2 , but is governed by the impurity content in the material, porosity, and humidity.

Nitrogen forms at the surface, bursting through the oxide film, forming pores and fissures. The oxide forms by gas diffusion of O_2 along the cracks and pores.

- Passive oxidation of hot-pressed Si_3N_4 with 1 wt% MgO in the 1000-1400°C (1832-2552°F) range leads to the formation of an oxide film which is predominantly $MgSiO_3$ with minor amounts of cristobalite and glass. The outward diffusion of Mg^{+2} from the grain boundary glass phase through the oxide appears to be the rate controlling step.

In pure O_2 at 982°C (1800°F) after 300 hours, the oxide which is formed is completely glassy and cracked.

At 1093°C (2000°F), long needle-like crystalline phases are formed which are inferred to consist of enstatite ($MgSiO_3$).

At 1370°C (2498°F) the entire surface is covered by needle-like SiO_2 .

SiO_2 begins to appear at 982°C (1800°F). The concentration levels off at temperatures $>1205^\circ C$ ($>2201^\circ F$). $MgSiO_3$ appears in the oxidized samples at 1205°C (2201°F).

Higher temperatures and higher oxygen partial pressures lead to the formation of the SiO_2 film.

Si_2ON_2 may form as an internal phase.

TABLE 3.14 (continued)

Alkali

- Sodium assisted oxidation of Si_3N_4 proceeds at a high rate. Molten Na_2SO_4 and NaCl reduces strength and fracture toughness of Si_3N_4 . Molten Na_2SO_4 produces severe corrosion. Molten sea salt and NaCl produces very mild corrosion.

The following reactions occur at 800-900°C (1472-1652°F) in air/ Na_2SO_4 :

In the absence of oxygen, elemental sulfur results on the surface.

The rate of molten salt corrosion is dependent on the concentration of free oxide ions in the $\text{NaCl}/\text{Na}_2\text{SO}_4$ melt.

Loss of mechanical strength is apparent for these materials during exposure to Na_2SO_4 and/or NaCl due to reaction with contained magnesium and silica. MgSiO_3 , Mg_2SiO_4 , MgSiN_2 forms at the grain boundaries.

The structure of the oxide layer is the main factor in influencing mechanical properties of the material. In salt free oxidation, the oxide layer assumes a smooth, glassy film with pores located at iron impurities. In the presence of molten salt, an uneven oxide layer forms with numerous pores. The pores in the oxide are stress concentrators and cracks develop from them as a result of a difference in thermal expansion of the glass and the substrate.

TABLE 3.14 (continued)

Si_3N_4 and NaCl forms a glassy phase with low viscosity which permeates the pore structure and/or grain boundaries, allowing considerable slow crack growth. $\text{Na}_2\text{SO}_4/\text{NaCl}$ is more oxidizing and causes greater flaws.

For hot pressed Si_3N_4 at room temperature, preferential oxidation results, significantly reducing the material's strength. At room temperature, NaCl forms a glassy layer which also reduces the material's strength. At 1200°C (2192°F) $\text{NaCl}/\text{Na}_2\text{SO}_4$ causes a more drastic increase in flaw severity than NaCl.

Oxidation at 1400°C (2552°F) improves the high temperature strength of reaction sintered Si_3N_4 .

- At room temperature, $\text{Na}_2\text{SO}_4/\text{NaCl}$ reduces the strength of reaction sintered Si_3N_4 by 50%, but has little effect on fracture toughness.
- Oxide grain boundaries in hot pressed materials were significantly affected by contaminant penetration than were grain boundaries of reaction-sintered materials which do not have the oxide phase.
- Si_3N_4 forms low melting eutectic ($\text{Si}_3\text{N}_4\text{-Mg}_2\text{SiO}_4\text{-MgO}$). Surface pits develop during oxidation due to iron type inclusions.
- Change in strength is linked to cavitation creep. Cavitation creep dominates when mixtures that are compositionally similar to the eutectic are formed. Cavitation creep dominates with higher stress.
- The volume content of the glassy phase is linked to composition. Diffusional creep which results with lower stress dominates for compositions furthest from the eutectic.

TABLE 3.14 (continued)

- SILICON CARBIDE -

Oxidation Characteristics

- Silicon carbide under oxidizing conditions leads to the formation of SiO_2 and CO (g), indicative of a weight gain. SiO_2 rapidly grows along the surface initially to a limiting thickness. The reaction which occurs is as follows:

- SiC is oxidized by CO_2 and steam.
- SiC exhibits both active and passive oxidation characteristics depending on the oxygen partial pressure.

High O_2 partial pressures lead to passive oxidation which forms the protective SiO_2 film.

Low O_2 partial pressures lead to severe active oxidation.

- Oxidation reactions:

At 1093°C (2000°F) for 30 hours, limited oxide formation results.

At $1205\text{--}1280^\circ\text{C}$ ($2201\text{--}2300^\circ\text{F}$), a layer of cristobalite and a glassy phase is formed with particles of aluminosilicate.

At $1315\text{--}1370^\circ\text{C}$ ($2399\text{--}2498^\circ\text{F}$), a uniform smooth liquid oxide results with no discrete alumina particles present. The surface layer is highly viscous containing silicates and cristobalite formations.

TABLE 3.14 (continued)

The surface layer is porous due to the escape of gas at the SiC/SiO₂ interface.

- Hot pressed SiC oxidation in 1000-1400°C (1832-2552°F) follows a parabolic rate law, forming surface silica and silicates.
- Highly oxidizing environment as the gas turbine causes a thin layer of SiO₂, and various silicates to result which contains impurities along the surface of the material.
- Contaminants present in SiC diffuse out to the surface of the material during oxidation and concentrate in the outer surface of the oxide layer. Contaminants generally include Na, K, Al, and W.

Alkali

- Reaction of alkali with the protective SiO₂ film along the SiC surface lowers the viscosity of the film.
- Contact of SiC with molten soda salt and NaCl produces very mild corrosion at moderate temperatures. Molten Na₂SO₄ produces severe corrosion under similar conditions.

At 950°C (1742°F), the surface of the SiC which is in contact with molten Na₂SO₄ is fully etched.

At 800-900°C (1472-1652°F) in air/Na₂SO₄ the following reactions occur:

TABLE 3.14 (continued)

Loss of mechanical strength is apparent due to $\text{Na}_2\text{SO}_4/\text{NaCl}$ reactions with magnesium. Phases which are formed include MgSiO_3 , Mg_2SiO_4 , MgSiN_2 at the grain boundaries.

In a salt-free environment, the surface layer forms a smooth glassy film containing occasional pores which appear to be related to the location of iron and other impurities. With molten salt, a knobby oxide layer forms resulting with numerous pores. The pores are stress concentrators with cracks developing from them. The material in which the cracks are formed has a different thermal expansion coefficient than the glassy phases.

SiC dissolves slowly in K_2CO_3 , but proceeds quantitatively in K_2SO_4 .

- SiC has a higher rate of dissolution with alkali in comparison to Si_3N_4 .

Halides

- SiC is attacked by halides.

Slag

- SiC has the potential to be unstable in the presence of incompletely combusted coal gas or complex fused slags.
- Little change is exhibited in SiC after 200 hours at $1000\text{--}1300^\circ\text{C}$ ($1832\text{--}2372^\circ\text{F}$). No change is observed with slag at 1000°C (1832°F). At $1250\text{--}1300^\circ\text{C}$ ($2282\text{--}2372^\circ\text{F}$) with slag, loss of mechanical properties and surface recession resulted due to slag/ SiC interactions, and possible evolution of CO .

TABLE 3.14 (continued)

Reactions depends on the slag composition. Iron and nickel silicides can be detected in the slag/ceramic interface. At temperature $>1000^{\circ}\text{C}$ ($>1832^{\circ}\text{F}$), SiC can reduce oxides of iron, calcium, and magnesium in the slag, and form low melting eutectics.

At 1000°C (1832°F), acidic slag is not very reactive.

At 1300°C (2372°F), slag forms a glassy appearance.

$\text{Fe}_2\text{O}_3 + 3\text{SiC} \rightarrow 2\text{Fe} + 3\text{Si} + 3\text{CO}$ - This reaction occurs with iron in pockets of subsurface SiC pores and forms the Fe/Si alloy. Part of the SiC is oxidized to SiO_2 and C is converted to CO via

$\text{Fe}_2\text{O}_3 + 2\text{SiC} \rightarrow \text{Fe}_2\text{Si} + \text{SiO}_2 + 2\text{CO}$.

Basic slag reacts with SiC forming iron rich pockets in the pores of the material. CaO and MgO do not react with SiC but contribute by lowering the viscosity of the slag, and allowing for diffusion of reactants and products across the coating.

- A 15% decrease in strength of SiC is detected in the absence of ash or with acidic ash. A larger reduction in strength is observed with basic ash.

General

- SiC is stable up to maximum temperatures of 1200°C (2192°F). Use of SiC above these temperatures is foreseeable by only with low iron content materials as basic coals.

TABLE 3.14 (continued)

- Hot pressed combustion gases at 1100°C (2012°F) with simultaneous corrosion/ erosion causes an average of 2.3 microns net erosion after 250 hours. Strength of the material is not affected by exposure in these environments.
- Typical SiC sintering aids include lattice soluble nitrogen and insoluble phosphorus materials (nitrides, carbides, phosphides, borides). The most successful of these include metallic boron and phenolic resins.

3.1.2.2 Process Char and Ash

Sintering has been demonstrated when char fines deposit along candle material surfaces in gasification environments.⁽¹²⁹⁾ Similarly discoloration of the alumina candle fibers results due to the presence of iron in the deposited fines. The interaction of the ash constituents with the alumina fiber and binder was suggested to promote the formation of lower temperature melts or eutectic phases.

In combustion environments, ash fines containing calcium based sulfur sorbents have been shown to sinter strongly to aluminosilicate fibers, as well as to the clay binder phase of ceramic candles. The deposit appeared as droplets of anhydrite that fuse to the fiber and surrounding constituent phases. Similar to the low melting temperature phases of the iron and silicates or aluminosilicates, calcium present in the ash matrix also has the potential to produce low melting temperature eutectic phases.

Since the chemistry of the entrained fines is largely dependent on the process, the potential exists for various reactions to occur at the ceramic filter material surface. For this reason, the following chars and ashes were selected as possible materials for use in the bench-scale testing in Task 4, Phase II of this contract.

- PFBC ash generated at New York University (Pittsburgh Coal and dolomite; cross-flow filter element fines catch)
- Gasifier char/ash generated at KRW (West Virginia Coal; candle filter element fines catch)
- Gasifier char/ash generated at KRW (Pittsburgh Coal, Ireland Seam; candle filter element fines catch)
- Gasifier char/ash generated at KRW (Pittsburgh Coal, Aloe Seam)
- Gasifier char/ash generated at KRW (Wyoming Coal; Rosebud Seam)
- Gasifier char/ash generated at Texaco (Pittsburgh No. 8 coal).

Chemical and physical analyses of the char and ash samples are presented in the following sections. Analytical techniques which were used to characterize these materials include atomic absorption and emission spectroscopy analysis, x-ray diffraction (XRD), scanning electron microscopy (SEM), ultimate analysis, melt/fusion temperature, and particle size distribution. A brief description of the combustor or gasifier process conditions, and identification of the feed materials are also presented.

Chemical Analysis of Processed Char and Ash Fines

Both the gasifier chars and combustor ash were ashed to remove residual carbon prior to being chemically analyzed using atomic absorption and emission spectroscopy techniques. Table 3.15 summarizes the atomic absorption data, and identifies the major elements (Al, Si, Fe, Ca, Mg, Na, and K) present in the ash as oxides. These values reflect the composition of the solids which result in the various process streams. The processed solids may contain sulfur sorbent materials in addition to the feed coal (See discussion in Section titled Physical Characterization of Processed Char/Ash Fines). Irrespective of the feed sources, fines from the various process streams may impact and stick to the ceramic cross-flow filter, and are classified as acidic [$\text{Fe}_2\text{O}_3 > (\text{CaO} + \text{MgO})$] for the:

- KRW Pittsburgh, Ireland seam char fines
- KRW Pittsburgh, Aloe seam char fines
- KRW Wyoming char fines
- Texaco Pittsburgh No. 8 char fines,

and as basic [$\text{Fe}_2\text{O}_3 < (\text{CaO} + \text{MgO})$] for the:

- NYU Pittsburgh ash fines
- KRW West Virginia char fines.

TABLE 3.15a
CHARACTERIZATION OF PROCESS CHAR AND ASH FINES

Process:	NYU PFBC	KRW	KRW	KRW	KRW	Texaco
		: <----- Gasification -----> :				
Coal:	Kittanning	Ireland	West Virginia	Aloe	Wyoming	Pittsburgh
<hr/>						
Atomic Absorption Analysis, Wt% Ash						
Al ₂ O ₃	19.09	15.93	18.76	18.16	15.23	23.15
SiO ₂	35.54	23.05	34.03	38.90	38.48	45.51
Fe ₂ O ₃	5.05	21.50	9.18	21.25	13.74	22.41
CaO	16.98	15.89	24.45	4.89	8.36	5.64
MgO	7.43	4.28	4.88	0.40	3.84	0.94
Na ₂ O	1.45	0.28	0.68	0.21	0.11	1.57
K ₂ O	0.88	1.88	1.04	2.14	1.80	2.65
Ash, Wt%	99.67	17.64	16.33	64.91	86.00	73.74
Moisture, Wt%	0.05	0.33	0.19	0.19	0.09	0.28
Powder Density, g/cm ³	2.88	2.46	2.73	2.68	2.49	3.04
50 Percent Mass Point, microns	4	3.4	5.2	52	70	23
X-Ray Diffraction Analysis,						
Major Phases:	CaSO ₄ , SiO ₂	Amorphous	Amorphous	NA	NA	NA
Possible Minor Phases:	Fe ₂ O ₃ , CaSO ₄		CaSO ₄ , FeS, Fe ₂ O ₃	NA	NA	NA

NA: Not Analyzed.

TABLE 3-15b

CHARACTERIZATION OF PROCESS CHAR AND ASH FINES

Process:	NYU PFBC	KRW : <-----	KRW Gasification	KRW ----->:	KRW	Texaco
Coal:	Kittanning	Ireland	West Virginia	Aloe	Wyoming	Pittsburgh
Emission Spectroscopy, Wt% Ash						
Al	≥10	≥10	≥10	≥10	≥10	≥10
Ag	<0.001	0.001	<0.001	<0.001	<0.001	<0.001
B	0.04	0.01	0.1	0.2	0.02	0.2
Ba	0.05	0.05	0.2	<0.02	0.2	0.05
Be	0.001	0.0007	0.001	0.0006	<0.0005	0.0006
Bi	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Ca	>5	>5	>5	5	>5	4
Cd	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03
Co	0.01	0.07	0.03	0.01	<0.01	0.01
Cr	0.04	0.4	0.1	0.05	0.04	0.05
Cu	0.03	0.2	0.03	0.03	0.03	0.04
Fe	7	>10	10	>10	10	>10
Ga	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
Ge	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
K	0.4	1	1	0.3	0.3	0.4
Li	0.9	0.03	0.03	0.02	0.02	0.02
Mg	2	1	1	0.3	1	0.3
Mn	0.2	0.2	0.1	0.04	0.05	0.1
Mo	<0.01	0.02	0.01	0.02	0.01	0.03
Na	0.4	0.2	0.3	0.1	0.08	0.4
Nb	0.04	0.1	0.04	<0.03	<0.03	0.03
Ni	0.1	0.8	0.2	0.2	0.1	0.05
Pb	0.02	0.1	0.1	0.1	<0.02	<0.02
Sb	<0.05	0.1	<0.05	<0.05	<0.05	<0.05
Si	>10	>10	>10	>10	>10	>10
Sn	<0.01	0.03	0.01	<0.01	<0.01	<0.01
Sr	0.1	0.1	0.2	0.04	0.1	0.1
Ti	1	2	1	0.3	0.4	1
V	0.03	0.08	0.04	0.02	0.02	0.03
Zn	0.02	0.3	0.1	<0.02	<0.02	0.03
Zr	0.06	0.08	0.1	0.03	0.03	0.06

With the exception of the ash fines generated at the New York University combustor, the potassium concentration in the ash is greater than the sodium concentration. Both alkalis are considered to be associated within the aluminosilicate lattice of the ash. Due to the pre-ashing step used in the preparation of the fines prior to chemical characterization, a portion of the alkali, if initially present as a water soluble chloride, hydroxide, or sulfate, would have been expected to volatilize.

Review of the emission spectroscopy data (Table 3.15b) illustrates the concentrations of trace elements present in the various ashes. The emission spectroscopy data indicate that titanium is present as a secondary or minor element, similar perhaps to the alkali or magnesium concentration as detected by atomic absorption techniques.

Table 3.15a also demonstrates the wide range in the ash content for the original materials. The KRW Pittsburgh (Ireland seam) and KRW West Virginia gasifier chars have a relatively low ash content (<20 percent), while the ash content of the NYU Pittsburgh fines approaches 100 percent.

X-ray diffraction analyses were performed on the NYU Pittsburgh ash, and on the KRW Pittsburgh (Ireland seam) and West Virginia chars. The principal phases that were detected in the NYU Pittsburgh ash included CaSO_4 and SiO_2 , with possible minor phases of Fe_2O_3 . Conversely, a principal phase could not be detected in the KRW chars, and a possible minor phase of either CaSO_4 , or CaSO_4 , FeS , Fe_2O_3 was considered to be present in the amorphous char structure.

Physical Characterization of Processed Char/Ash Fines

Scanning electron micrographs detailing the physical morphology of the combustor or gasifier ash and char fines are presented in Figures 3.19 through 3.24. A brief description of the history which the fines experienced is presented in the following discussion.

Major Ash Composition
Reported as Oxides, Wt%

19.09	Al ₂ O ₃
35.54	SiO ₂
5.05	Fe ₂ O ₃
18.98	CaO
7.43	MgO
1.45	Na ₂ O
0.88	K ₂ O

Basic: [Fe₂O₃] < [CaO + MgO]

Figure 3.19a - Scanning Electron Micrograph and Major Ash Composition
of the NYU Combustor Pittsburgh Ash Fines

Figure 3.19b - Scanning Electron Micrographs of the NYU Combustor
Pittsburgh Ash Fines

Figure 3.19c - High Magnification Scanning Electron Micrographs of the NYU Combustor Pittsburgh Ash Fines

Figure 3.19d - Higher Magnification Scanning Electron Micrographs
of the NYU Combustor Pittsburgh Ash Fines

Major Ash Composition
Reported as Oxides, Wt%

18.76	Al_2O_3
34.03	SiO_2
9.18	Fe_2O_3
24.45	CaO
4.88	MgO
0.68	Na_2O
1.04	K_2O

Basic: $[\text{Fe}_2\text{O}_3] < [\text{CaO} + \text{MgO}]$

Figure 3.20a - Scanning Electron Micrograph and Major Ash Composition
of the KRW Gasifier West Virginia Char Fines

Figure 3.20b - Scanning Electron Micrographs of the KRW
Gasifier West Virginia Char Fines

Figure 3.20c - High Magnification Scanning Electron Micrograph of the
KRW Gasifier West Virginia Char Fines

Major Ash Composition
Reported as Oxides, Wt%

15.93	Al_2O_3
23.05	SiO_2
21.50	Fe_2O_3
15.89	CaO
4.28	MgO
0.28	Na_2O
1.88	K_2O

Acidic: $[\text{Fe}_2\text{O}_3] > [\text{CaO} + \text{MgO}]$

Figure 3.21a - Scanning Electron Micrograph and Major Ash Composition
of the KRW Gasifier Pittsburgh, Ireland Seam Char Fines

Figure 3.21b - Scanning Electron Micrographs of the KRW Gasifier
Pittsburgh, Ireland Seam Char Fines

Figure 3.21c - High Magnification Scanning Electron Micrographs of the
KRW Gasifier Pittsburgh, Ireland Seam Char Fines

Major Ash Composition
Reported as Oxides, Wt%

18.16	Al_2O_3
38.90	SiO_2
21.25	Fe_2O_3
4.89	CaO
0.40	MgO
0.21	Na_2O
2.14	K_2O

Acidic: $[\text{Fe}_2\text{O}_3] > [\text{CaO} + \text{MgO}]$

Figure 3.22a - Scanning Electron Micrograph and Major Ash Composition
of the KRW Gasifier, Pittsburgh Aloe Seam Char Fines

Figure 3.22b - Scanning Electron Micrographs of the KRW Gasifier,
Pittsburgh Aloe Seam Char Fines

Figure 3.22c - Scanning Electron Micrographs of the KRW Gasifier,
Pittsburgh Aloe Seam Char Fines

Major Ash Composition
Reported as Oxides, Wt%

15.23	Al ₂ O ₃
38.48	SiO ₂
13.74	Fe ₂ O ₃
8.36	CaO
3.84	MgO
0.11	Na ₂ O
1.80	K ₂ O

Acidic: [Fe₂O₃] > [CaO + MgO]

Figure 3.23a - Scanning Electron Micrograph and Major Ash Composition
of the KRW Gasifier Wyoming Char Fines

Figure 3.23b - Scanning Electron Micrographs of the KRW Gasifier
Wyoming Char Fines

Major Ash Composition
Reported as Oxides, Wt%

23.15	Al_2O_3
45.51	SiO_2
22.41	Fe_2O_3
5.48	CaO
0.94	MgO
1.57	Na_2O
2.65	K_2O

Acidic: $[\text{Fe}_2\text{O}_3] > [\text{CaO} + \text{MgO}]$

Figure 3.24a - Scanning Electron Micrograph and Major Ash Composition
of the Texaco Gasifier Pittsburgh No. 8 Char Fines

Figure 3.24b - Scanning Electron Micrographs of the Texaco Gasifier
Pittsburgh No. 8 Char Fines

Figure 3.24c - Scanning Electron Micrographs of the Texaco Gasifier
Pittsburgh No. 8 Char Fines

An eastern bituminous Kittanning coal was combusted with Ohio lime dolomite injection at temperatures of 925°C (1700°F) and pressures of 100 psig at the New York University pressurized fluidized-bed combustor. The NYU combustor ash fines shown in Figure 3.19 were collected on the array of fifteen 12x12x4 inch alumina/mullite cross-flow filters in a 90 hour test conducted in October 1988. Filter collection temperatures during this test ranged from 800 to 815°C (1470 to 1500°F). The micrographs shown in Figure 3.19 indicate what appears to be an agglomerate of molten fine particles. Typically fines which are 1-2 μm in diameter are firmly attached to larger particles. Interdispersed throughout the sample are cenospheres which are approximately 10 μm in diameter, and appear to contain the 1-2 μm fines.

The entrained char fines generated from the gasification of a West Virginia coal at KRW are shown in Figure 3.20. The char fines are representative of the candle filter catch during operation of the pressurized fluidized-bed gasifier in May 1988. Typically the larger (40-150 μm) fines generated by the KRW gasifier appear to be somewhat more discrete and less molten in appearance than NYU combustor ash fines. The particles do, however, seem to consist of numerous small fine particles attached to the external surface of the larger particles.

Char fines generated at KRW during the gasification of an Ireland Seam Pittsburgh coal are shown in Figure 3.21. Similar to the West Virginia char fines, the Pittsburgh, Ireland seam char fines represent material captured by candle filter elements during operation of the gasifier in December 1987. The gasifier product gas outlet temperatures were reported at 925-982°C (1700-1800°F) with operating pressures of 200 psig. Operating conditions at the ceramic candle ranged from 426-538°C (800-1000°F), and 180-220 psig. Similar to the West Virginia char fines, the Pittsburgh, Ireland seam char fines consist of numerous smaller particles attached to what appears to be a molten underlying surface.

Scanning electron micrographs of the KRW Pittsburgh, Aloe seam and Wyoming chars shown in Figures 3.22 and 3.23 illustrate the morphology of char fines after sieving the gasifier withdrawal ash material through 100 mesh screens. Consideration was given to these materials since discussions with KRW personnel indicated that the Pittsburgh, Aloe seam char was acidic, and that the Wyoming char was basic in nature.

The Pittsburgh Aloe seam fines shown in Figure 3.22 illustrate that after gasification at 975°C (1790°F) and pressures of 200 psig in December 1986, a molten particle surface appearance results. Irregularity in the shapes of the -100 mesh particles is evident. The SEMs of the 10-15 μm fine particle shown in Figure 3.22c, illustrate the lack of attached smaller fines to the molten particle surface. Typical product gas analysis on a dry basis resulting from the gasification of the Pittsburgh Aloe seam coal was identified as 16.04% CO, 6.67% CO₂, 0.68% CH₄, 64.16% N₂, 12.29% H₂, 305 ppm COS, and 1473 ppm H₂S. The moisture content of the product gas was identified at 8.55%.

The KRW Wyoming char fines shown in Figure 3.23 also illustrate the relatively molten appearance of the fines generated during gasification. The gasifier which operated in November 1985 produced a product gas consisting of 14.91% CO, 7.8% CO₂, 1.26% CH₄, 56.65% N₂, 13.15% H₂, 800 ppm COS, and 2300 ppm H₂S. The moisture content of the product gas was identified at 5.9%. The gasifier product gas outlet temperature was reported at 890°C (1635°F), with the unit operating at 200 psig.

Figure 3.24 illustrates the char material generated from the gasification of Pittsburgh No. 8 coal at the Texaco gasifier. The char material represents fines collected in the cross-over duct between the radiant and convection syngas coolers. Operational temperatures of the gasifier were identified at 1205-1540°C (2200-2800°F), with system pressures of 350 psig. The large fines generated in this collection

sample appear to have relatively smooth, molten outer surfaces. The smaller 10 μm fines are almost spherical in appearance. Even smaller fines are attached to what may have been a sticky molten outer surface, or contained particles which could be released from the larger particles during further processing. The spherical nature of the 10 μm Texaco fines is similar to that of the 10 μm fines generated at the New York combustor unit.

Particle Size Distribution of Processed Char and Ash

Particle size distribution of the chars and ashes are shown in Figure 3.25. With the exception of the KRW West Virginia and Pittsburgh, Ireland seam chars, the particle size distribution were determined using a Micromeritics x-ray sedimentation unit. Due to the relatively high carbon content of the KRW West Virginia and Pittsburgh, Ireland seam chars, a coulter counter was used to determine the particle size distribution.

The KRW Pittsburgh, Aloe seam and Wyoming chars were initially sieved through 100 mesh nylon screens. The resulting KRW Pittsburgh, Aloe seam and Wyoming sample fines contained particles which had approximately 10 and 30 percent of the resulting fines $>90 \mu\text{m}$. The 50 percent mass point of these materials is 54 and 70 μm , respectively.

The Texaco Pittsburgh No. 8 char contained approximately 2 percent of the fines with particle diameters that are greater than 80 μm . The 50 percent mass point for the Texaco fines is 24 μm .

A relatively evenly dispersed particle size distribution results for the NYU Pittsburgh ash. The maximum particle size of the ash material is approximately 50 μm . The NYU fines have a 50 percent mass point of 4.2 μm .

Curve 756770-8

Figure 3.25 - Char and Ash Particle Size Distribution

The KRW Pittsburgh, Ireland seam and West Virginia char fines are predominantly less than 20 μm in diameter. The 50 percent mass point of the KRW Pittsburgh, Ireland seam and West Virginia char fines is 3.4 and 5.4 μm , respectively.

The NYU Pittsburgh ash, and the KRW Pittsburgh, Ireland seam and West Virginia chars are representative (i.e., chemically and particle size) of the fines which are expected to impact the cross-flow filter surface. Grinding the KRW Pittsburgh, Aloe seam, and Wyoming chars, or the Texaco Pittsburgh No. 8 materials may accomplish reduction in the overall size of the particles, however, during processing the fine present in the effluent gas may not be chemically similar to that of the ground material.

Material Selection

Based on the chemical and particle size distribution analyses, the basic NYU Pittsburgh ash, the acidic KRW Pittsburgh, Ireland seam char, and the basic KRW Wet Virginia char are recommended for consideration and use in the bench-scale tests of Phase II (Task 4). This selection is based on the criteria that testing would be performed with:

- Gasification and combustion materials
- Acidic and basic ash materials
- Materials that have a representative filter catch size distribution.

Ultimate analyses were performed on these materials, as well as determination of the melt/fusion temperature. Table 3.16 summarizes these data. During preparation and analysis of the New York combustor ash and the KRW Pittsburgh Ireland seam char, sulfur was noted to be retained within the residual ash. A definitive sulfur and oxygen content is therefore not identified for these materials. The New York

TABLE 3.16

ULTIMATE ANALYSIS AND MELT FUSION
TEMPERATURES OF COMBUSTOR AND GASIFIER FINES

Material	NYU Combustor Fines		KRW Pittsburgh Ireland Char		KRW West Virginia Char	
Ultimate Analysis:						
H	0.12	(0.10)*	0.61	(0.51)	1.07	(1.02)
C	0.27	(0.27)	80.97	(81.72)	81.51	(81.97)
N	0.06	(0.06)	0.41	(0.41)	0.40	(0.40)
S	5.14	(5.15)	1.23	(1.24)	0.34	(0.34)
Ash	98.75	(98.95)	16.83	(16.99)	15.11	(15.20)
Moisture	0.20	--	0.92	--	0.56	--
Ash Fusion Temperatures, °C(°F):						
Initial						
Deformation	1149	(2100)	1138	(2080)	1166	(2130)
Softening	1154	(2110)	1160	(2120)	1177	(2150)
Hemisphere	1166	(2130)	1188	(2170)	1193	(2180)
Fluid	1243	(2270)	1254	(2290)	1254	(2290)

*As-Received Basis (Dry Basis).

combustor fines are reported to consist of 98.75 percent ash on an as-received basis, with 0.2 percent moisture, and a minimum of 5.14 percent sulfur. The KRW Pittsburgh, Ireland seam char is reported to consist of 16.83 percent ash on an as-received basis, with 0.92 percent moisture, while the KRW West Virginia char fines consist of 15.11 percent ash on an as-received basis, with 0.56 percent moisture. Sulfur is identified at approximately 1.23 and 0.34 weight percent for the KRW Pittsburgh, Ireland seam and West Virginia chars, respectively.

Ash fusion temperatures were determined for each of these materials under a reducing gas environment of CO/CO_2 . Ash deformation temperatures are seen to range from 1138 to 1166°C (2080 to 2130°F); softening temperatures from 1154 to 1177°C (2110 to 2150°F); hemisphere formation between 1166 and 1193°C (2130 and 2180°F); and become fluid at 1243 to 1254°C (2270 to 2290°F). The deformation through fluid temperatures for the fines all exceed the projected operating filter temperature for fixed-bed, fluid-bed, and entrained bed gasification processes, as well as for pressurized fluidized bed combustion, and for current direct coal fired turbine operations [1010°C (1850°F)]. If the combustor or gasifier operates at higher temperatures as in the advanced direct coal fired turbine concept [1370°C (2500°F)], and fines carryover to the filter is rapid, there exists the potential for deformed, and/or even softened fines to impact the filter surface.

3.1.3 Phase Stability Assessment

Using the chemical analysis data discussed in Section 3.1.2, the phase stability of the char and ash constituents can be assessed on the basis of thermodynamic equilibrium calculations, as well as the potential for reaction of the char or ash fines with the various ceramic cross-flow filter materials. In Appendix A, thermodynamic projections which have previously been generated at Westinghouse are presented illustrating the composition of the effluent gas stream, and char or ash fines released in fluid-bed gasification and direct coal-fired turbine systems. This approach was extended during the course of this contract to projecting similar effluent gas and fines compositions simulating a fixed-bed gasification system, the entrained-bed Texaco gasifier, and the New York University pressurized fluidized-bed combustor.

Since the composition of the effluent gases is largely dependent on the feed material compositions used during processing, a parametric approach was developed to identify the phase and composition of alkali that would potentially be experienced at the ceramic cross-flow filter surface. In addition, calculations were performed which attempt to illustrate the interaction of the entrained char or ash fines with the volatile alkali. A final series of calculations was performed simulating the thermal stability of the various ceramic cross-flow filter material phases at process conditions, as well as possible interaction with volatile alkali, and char or ash fines. These calculations were generated at Westinghouse using the NASA CET86 thermodynamic equilibrium program. The results of these calculations are discussed in the following Sections.

3.1.3.1 Projected Process Effluent Gas and Fines Interactions

The public domain NASA CET86 thermodynamic equilibrium computer program⁽¹³⁸⁾ was used in Phase I to project the possible reaction of process gas alkali and entrained fines, as well as to project the

stability of ceramic materials at filter process gas conditions. The NASA program is written in FORTRAN IV, and has been adapted for use on a mainframe VAX computer at Westinghouse. The program uses a free energy minimization technique to calculate the chemical equilibrium for the following assigned thermodynamic states:

- Temperature and pressure (T,P)
- Enthalpy and pressure (H,P)
- Entropy and pressure (S,P)
- Temperature and volume (or density) (T,V)
- Internal energy and volume (or density) (U,V)
- Entropy and volume (or density) (S,V).

Condensed species, as well as gas phase species are considered.

The NASA equilibrium calculations are based on the assumption that condensed phases are pure. The possibility therefore exists for encountering phase transitions between a solid and liquid (melting points) or between two stable solid phases. Such transitions constitute triple points since three phases of the same species coexist, one gaseous and two condensed phases. Such triple points are characterized by a definite vapor pressure and temperature, independent of the relative proportions of each phase. The NASA program can obtain one or two condensed phases of a species with or without the corresponding gas phase.

Thermodynamic data are included in the NASA program for 1300 compounds (solid, liquid, and gas species are counted as individual species). With few exceptions, thermodynamic data are taken from the JANAF tables.

Effluent Gas Stream Alkali Condensation

Gaseous alkali species that are released during coal gasification or combustion have the potential to:

- Remain as a volatile species in the effluent gas stream
- Form as a condensed phase, retaining the original species' identity [i.e., $\text{NaCl (g)} \rightarrow \text{NaCl (s)}$]
- React and form an alternate condensed phase
[i.e., $2\text{NaCl (g)} + \text{SO}_2 \text{ (g)} + \text{H}_2\text{O (g)} + 1/2\text{O}_2 \text{ (g)} \rightarrow \text{Na}_2\text{SO}_4 \text{ (c)} + 2\text{HCl (g)}$]
- Adsorb or condense along the surface of entrained fines
- React with the ash matrix of the entrained fines.

If alkali remains as a volatile species in the effluent gas stream, the projected gasifier or combustor emissions concentrations represent an upper estimate of the alkali concentration that may be experienced at the ceramic cross-flow filter surface. If the temperature of the effluent gas stream cools as the gas approaches the ceramic cross-flow filter, or the alkali species is converted into an alternate stable, condensable phase, then a reduction in the total gas phase alkali species concentration is expected at the filter surface. The ceramic filter could also experience a reduction in the effluent gas phase alkali concentration if alkali either adsorbs along the surface of the entrained char or ash fines, or reacts and is retained within the ash matrix of the entrained fines. For most process systems, the short residence time between when gas is released at either the gasifier or combustor outlet and when it arrives at the ceramic cross-flow filter surface is considered to be inadequate for an equilibrium state to be attained in which a substantial concentration of volatile alkali reacts with and is driven into the ash structure. If, however, char or ash is retained along the ceramic cross-flow filter surface, or is adherent to phases within the filter pores after pulse jet cleaning, the potential exists for reaction with alkali after long-term, high temperature filter operation.

Since variation exists in process design, operating temperatures and pressures, and feed material composition, a parametric series of calculations was performed to demonstrate the composition and concentration of alkali that could be expected to reach the ceramic cross-flow filter as a function of the alkali content initially released into the effluent streams. In this series of calculations, a representative bulk gas chemistry (Table 3.1) is utilized for each process system, and the total alkali concentration is permitted to vary between 2 ppb and 20 ppm. The concentration of sodium is equivalent to the potassium concentration (i.e., 2 ppb total = 1 ppb Na + 1 ppb K) in each calculation. The gasifier or combustor effluent stream containing the various alkali concentrations is permitted to equilibrate as the gas cools and approaches the operating filter temperature and pressure (Figures 3.26 through 3.30, Tables 3.17 through 3.21).

In the fixed-bed gasification system (Figure 3.26), alkali has the potential to be distributed between volatile species and the NaCl, KCl, and Na₂CO₃ condensed phases (Table 3.17). Condensation of NaCl, KCl, and Na₂CO₃ at a mole fraction of $<10^{-12}$ (combined gas and solid phases) will not occur at the temperatures and pressures indicated above each line in Figure 3.26. Conversely, at temperatures and pressures below each line, condensation of the respective species is expected at a mole fraction of $>10^{-12}$. The filter operating temperature and pressure in each process system is identified by an asterisk (*). For example, if the fixed-bed gasifier emitted a concentration of 20 ppb total alkali, condensation of the alkali as either NaCl, KCl, or Na₂CO₃ is not expected to occur at the ceramic cross-flow filter surface (i.e., with or without adherent char fines). At an emitted concentration of 200 ppb total alkali, condensation/deposition of sodium as Na₂CO₃ has the potential to occur at the filter. At concentrations of 2 to 20 ppm total alkali, condensation of NaCl, KCl, and Na₂CO₃ is expected at the filter.

KCl (s)

Na₂CO₃ (s)

NaCl (s)

Figure 3.26 - Condensed Alkali Phases Projected in Fixed-Bed Gasification Systems

KCl (s)

Na₂CO₃ (s)

NaCl (S)

Figure 3.27 - Condensed Alkali Phases Projected in Fluid-Bed Gasification Systems

KCl(s)

NaCl(s)

Na₂CO₃(s)

Figure 3.28 - Condensed Alkali Phases Projected in Entrained-Bed Gasification Systems

Figure 3.29 - Condensed Alkali Phases Projected in Direct Coal Fired Turbine Systems

Figure 3.30 - Condensed Alkali Phases Projected in Pressurized Fluidized-Bed Combustion Systems

TABLE 3.17

PROJECTED MOLE FRACTIONS OF ALKALI SPECIES
FORMED IN FIXED-BED GASIFICATION PROCESSES

PRESSURE: 20 atm

Temp., K	Total Alkali	
	20 ppm	20 ppb
	NaCl(g)	
1800	8.536-8	1.058-13
1500	1.730-7	2.860-13
1400	3.272-7	7.434-13
1300	5.465-7	2.289-12
1200	7.964-7	7.496-12
1100	1.030-6	2.618-11
1000	9.296-7	1.033-10
900	1.658-7	4.021-10
800	4.219-9	5.362-10
700	3.590-11	3.591-11
600	5.896-14	5.896-14

Temp., K	Total Alkali	
	20 ppm	20 ppb
	NaOH(g)	
1800	2.033-7	2.204-10
1500	2.325-7	2.759-10
1400	2.575-7	3.845-10
1300	2.751-7	5.262-10
1200	2.713-7	7.910-10
1100	2.202-7	1.083-9
1000	7.421-8	1.237-9
900	5.099-9	1.038-9
800	2.140-10	2.140-10
700	2.695-15	3.470-12
600	1.310-20	9.950-15

Temp., K	Total Alkali	
	20 ppm	20 ppb
	NaH(g)	
1800	1.898-8	2.058-11
1500	1.501-8	1.781-11
1400	1.028-8	1.456-11
1300	5.513-9	1.055-11
1200	2.076-9	6.052-12
1100	5.258-10	2.586-12
1000	5.306-11	8.841-13
900	1.179-12	2.401-13
800	1.418-14	1.418-14
700	3.578-20	4.607-17
600	1.986-20	1.508-20

Temp., K	Total Alkali	
	20 ppm	20 ppb
	NaCN(g)	
1800	2.616-9	2.837-12
1500	4.568-9	5.419-12
1400	7.200-9	1.019-11
1300	8.398-9	1.606-11
1200	5.858-9	1.708-11
1100	2.197-9	1.081-11
1000	2.232-10	3.720-12
900	2.698-12	5.493-13
800	1.085-14	1.085-14
700	5.264-21	6.777-18
600	1.826-28	1.387-22

TABLE 3.17 (Continued)

PROJECTED MOLE FRACTIONS OF ALKALI SPECIES
FORMED IN FIXED-BED GASIFICATION PROCESSES

PRESSURE: 20 atm

Temp., K	Total Alkali	
	20 ppm	20 ppb
	NaCl(s)	
1600	---	---
1500	---	---
1400	---	---
1300	---	---
1200	---	---
1100	---	---
1000	---	---
900	1.057-8	---
800	1.480-8	---
700	1.478-8	1.171-9
600	1.477-8	1.474-9

Temp., K	Total Alkali	
	20 ppm	20 ppb
	Na ₂ CO ₃ (s)	
1600	---	---
1500	---	---
1400	---	---
1300	---	---
1200	---	---
1100	---	---
1000	9.917-8	---
900	7.111-8	---
800	4.60-9	3.480-10
700	---	1.281-10
600	---	---

Temp., K	Total Alkali	
	20 ppm	20 ppb
	KCl(g)	
1600	1.595-7	2.240-13
1500	2.784-7	5.285-13
1400	4.220-7	1.311-12
1300	5.637-7	3.314-12
1200	6.975-7	8.430-12
1100	8.434-7	2.408-11
1000	9.359-7	8.504-11
900	3.965-7	3.134-10
800	1.153-8	7.973-10
700	1.183-10	1.183-10
600	2.392-13	2.392-13

Temp., K	Total Alkali	
	20 ppm	20 ppb
	KOH(g)	
1600	3.547-7	4.358-10
1500	3.500-7	5.143-10
1400	3.160-7	6.115-10
1300	2.732-7	7.333-10
1200	2.319-7	8.681-10
1100	1.788-7	9.872-10
1000	7.552-8	1.028-9
900	1.262-8	8.372-10
800	6.229-10	3.389-10
700	9.647-15	1.242-11
600	6.167-20	4.684-14

TABLE 3.17 (Continued)

PROJECTED MOLE FRACTIONS OF ALKALI SPECIES
FORMED IN FIXED-BED GASIFICATION PROCESSES

PRESSURE: 20 atm

Temp., K	Total Alkali		Temp., K	Total Alkali	
	20 ppm	20 ppb		20 ppm	20 ppb
	KH(g)			KCN(g)	
1600	3.482-9	4.276-12	1600	1.287-9	1.580-12
1500	2.001-9	2.940-12	1500	1.751-9	2.573-12
1400	9.190-10	1.778-12	1400	2.004-9	3.878-12
1300	3.180-10	8.538-13	1300	1.654-9	4.441-12
1200	7.920-11	2.965-13	1200	8.498-10	3.181-12
1100	1.397-11	7.710-14	1100	2.518-10	1.390-12
1000	1.216-12	1.656-14	1000	2.570-11	3.499-13
900	4.169-14	2.767-15	900	5.762-13	3.823-14
800	3.340-16	1.818-16	800	1.944-15	1.058-15
700	4.999-22	6.435-19	700	7.518-22	9.679-19
600	1.382-28	1.049-22	600	1.924-29	1.461-23

Temp., K	Total Alkali	
	20 ppm	20 ppb
	KCl(s)	
1600	---	---
1500	---	---
1400	---	---
1300	---	---
1200	---	---
1100	---	---
1000	---	---
900	5.145-7	---
800	1.140-8	---
700	1.157-8	1.006-9
600	1.158-8	1.158-9

TABLE 3.18

PROJECTED MOLE FRACTIONS OF ALKALI SPECIES
FORMED IN FLUID-BED GASIFICATION PROCESSES

PRESSURE: 20 atm

Temp., K	Total Alkali	
	20 ppm	20 ppb
	NaCl(g)	
1600	7.046-8	8.582-14
1500	1.450-7	2.165-13
1400	2.798-7	6.080-13
1300	4.763-7	1.884-12
1200	7.018-7	6.209-12
1100	9.088-7	2.185-11
1000	9.073-7	8.804-11
900	1.658-7	3.473-10
800	4.219-9	6.895-10
700	3.590-11	3.591-11
600	5.896-14	5.896-14

Temp., K	Total Alkali	
	20 ppm	20 ppb
	NaOH(g)	
1600	1.777-7	1.913-10
1500	2.054-7	2.404-10
1400	2.306-7	3.196-10
1300	2.497-7	4.843-10
1200	2.476-7	6.994-10
1100	1.990-7	9.503-10
1000	1.038-7	1.065-9
900	7.871-9	8.828-10
800	3.349-10	3.349-10
700	4.482-12	4.482-12
600	9.759-15	9.759-15

Temp., K	Total Alkali	
	20 ppm	20 ppb
	NaH(g)	
1600	1.767-8	1.903-11
1500	1.411-8	1.652-11
1400	9.801-9	1.359-11
1300	5.348-9	9.943-12
1200	2.055-9	5.804-12
1100	5.383-10	2.571-12
1000	9.261-11	9.500-13
900	2.440-12	2.736-13
800	3.003-14	3.003-14
700	8.070-17	8.070-17
600	2.009-20	2.009-20

Temp., K	Total Alkali	
	20 ppm	20 ppb
	NaCN(g)	
1600	1.109-9	1.194-12
1500	1.946-9	2.279-12
1400	3.085-9	4.277-12
1300	3.599-9	6.691-12
1200	2.462-9	6.953-12
1100	8.698-10	4.154-12
1000	1.245-10	1.278-12
900	1.494-12	1.676-13
800	5.185-15	5.185-15
700	1.893-18	1.893-18
600	2.303-23	2.303-23

TABLE 3.18 (Continued)

PROJECTED MOLE FRACTIONS OF ALKALI SPECIES
FORMED IN FLUID-BED GASIFICATION PROCESSES

PRESSURE: 20 atm

Temp., K	Total Alkali	
	20 ppm	20 ppb
	NaCl(s)	
1800	---	---
1500	---	---
1400	---	---
1300	---	---
1200	---	---
1100	---	---
1000	---	---
900	9.277-7	---
800	1.253-8	---
700	1.284-8	1.058-9
600	1.284-8	1.281-9

Temp., K	Total Alkali	
	20 ppm	20 ppb
	Na ₂ CO ₃ (s)	
1800	---	---
1500	---	---
1400	---	---
1300	---	---
1200	---	---
1100	---	---
1000	5.439-9	---
900	2.979-8	---
800	2.140-9	9.181-11
700	---	---
600	---	---

Temp., K	Total Alkali	
	20 ppm	20 ppb
	KCl(g)	
1800	1.348-7	1.844-13
1500	2.375-7	4.354-13
1400	3.890-7	1.089-12
1300	4.984-7	2.765-12
1200	6.187-7	7.057-12
1100	7.450-7	2.028-11
1000	8.011-7	7.308-11
900	3.965-7	2.719-10
800	1.153-8	6.442-10
700	1.163-10	1.163-10
600	2.392-13	2.392-13

Temp., K	Total Alkali	
	20 ppm	20 ppb
	KOH(g)	
1800	3.170-7	3.837-10
1500	3.188-7	4.555-10
1400	2.894-7	5.447-10
1300	2.516-7	6.559-10
1200	2.130-7	7.758-10
1100	1.617-7	8.744-10
1000	9.263-8	8.933-10
900	1.948-8	7.150-10
800	9.748-10	3.333-10
700	1.804-11	1.804-11
600	4.594-14	4.594-14

TABLE 3.18 (Continued)

PROJECTED MOLE FRACTIONS OF ALKALI SPECIES
FORMED IN FLUID-BED GASIFICATION PROCESSES

PRESSURE: 20 atm

Temp., K	Total Alkali		Temp., K	Total Alkali	
	20 ppm	20 ppb		20 ppm	20 ppb
KH(g)			KCN(g)		
1600	3.315-9	4.012-12	1600	5.577-10	6.750-13
1500	1.928-9	2.771-12	1500	7.646-10	1.099-12
1400	8.957-10	1.686-12	1400	8.781-10	1.653-12
1300	3.130-10	8.160-13	1300	7.192-10	1.875-12
1200	7.893-11	2.874-13	1200	3.594-10	1.309-12
1100	1.431-11	7.737-14	1100	9.978-11	5.394-13
1000	1.862-12	1.796-14	1000	1.257-11	1.212-13
900	8.626-14	3.167-15	900	3.191-13	1.171-14
800	7.075-16	2.419-16	800	9.292-16	3.177-16
700	1.127-18	1.127-18	700	2.704-19	2.704-19
600	1.398-22	1.398-22	600	2.426-24	2.426-24

Temp., K	Total Alkali	
	20 ppm	20 ppb
KCl(s)		
1600	---	---
1500	---	---
1400	---	---
1300	---	---
1200	---	---
1100	---	---
1000	---	---
900	3.441-7	---
800	9.739-7	---
700	9.907-7	8.357-10
600	9.909-7	9.909-10

TABLE 3.19

PROJECTED MOLE FRACTIONS OF ALKALI SPECIES
FORMED IN ENTRAINED-BED GASIFICATION PROCESSES

PRESSURE: 30 atm

Temp.,K	Total Alkali		Temp.,K	Total Alkali	
	20 ppm	20 ppb		20 ppm	20 ppb
	NaCl(g)			NaOH(g)	
1600	8.248-8	1.006-13	1600	3.294-7	3.571-10
1500	1.641-7	2.433-13	1500	3.613-7	4.271-10
1400	3.059-7	6.473-13	1400	3.758-7	5.247-10
1300	5.071-7	1.883-12	1300	3.664-7	6.756-10
1200	7.398-7	5.902-12	1200	3.247-7	8.867-10
1100	9.471-7	2.065-11	1100	2.365-7	1.087-9
1000	8.496-7	8.520-11	1000	9.318-8	1.155-9
900	1.105-7	3.452-10	900	7.373-9	9.495-10
800	2.812-9	6.380-10	800	3.141-10	3.141-10
700	2.394-11	2.394-11	700	4.079-12	4.079-12
600	3.931-14	3.931-14	600	8.886-15	9.263-21

Temp.,K	Total Alkali		Temp.,K	Total Alkali	
	20 ppm	20 ppb		20 ppm	20 ppb
	NaH(g)			NaCN(g)	
1600	1.848-8	2.004-11	1600	2.835-9	2.856-12
1500	1.411-8	1.668-11	1500	4.446-9	5.255-12
1400	9.293-9	1.298-11	1400	6.786-9	9.476-12
1300	4.805-9	8.859-12	1300	7.689-9	1.418-11
1200	1.785-9	4.874-12	1200	5.096-9	1.391-11
1100	4.691-10	2.156-12	1100	1.702-9	7.820-12
1000	6.757-11	8.373-13	1000	1.843-10	2.283-12
900	1.926-12	2.480-13	900	2.393-12	3.081-13
800	2.376-14	2.376-14	800	9.496-15	9.496-15
700	6.176-17	3.176-17	700	4.488-18	4.488-18
600	1.535-20	1.600-26	600	6.555-23	6.833-29

TABLE 3.19 (Continued)

PROJECTED MOLE FRACTIONS OF ALKALI SPECIES
FORMED IN ENTRAINED-BED GASIFICATION PROCESSES

PRESSURE: 30 atm

Temp., K	Total Alkali	
	20 ppm	20 ppb
	NaCl(s)	
1800	---	---
1500	---	---
1400	---	---
1300	---	---
1200	---	---
1100	---	---
1000	---	---
900	1.083-8	---
800	1.314-8	---
700	1.324-8	1.159-9
600	1.325-8	1.325-9

Temp., K	Total Alkali	
	20 ppm	20 ppb
	Na ₂ CO ₃ (s)	
1800	---	---
1500	---	---
1400	---	---
1300	---	---
1200	---	---
1100	---	---
1000	3.977-8	---
900	2.308-8	---
800	1.534-9	1.513-10
700	---	---
600	---	---

Temp., K	Total Alkali	
	20 ppm	20 ppb
	KCl(g)	
1800	1.275-7	1.693-13
1500	2.214-7	3.778-13
1400	3.482-7	8.979-13
1300	4.878-7	2.239-12
1200	6.313-7	5.914-12
1100	7.735-7	1.816-11
1000	8.112-7	6.934-11
900	2.643-7	2.686-10
800	7.687-9	6.652-10
700	7.755-11	7.755-11
600	1.595-13	1.595-13

Temp., K	Total Alkali	
	20 ppm	20 ppb
	KOH(g)	
1800	4.755-7	5.615-10
1500	4.591-7	6.245-10
1400	4.072-7	6.927-10
1300	3.394-7	7.736-10
1200	2.704-7	8.672-10
1100	1.915-7	9.477-10
1000	8.992-8	9.499-10
900	1.825-8	7.641-10
800	9.140-10	3.498-10
700	1.460-11	1.460-11
600	4.183-14	4.381-20

TABLE 3.19 (Continued)

PROJECTED MOLE FRACTIONS OF ALKALI SPECIES
FORMED IN ENTRAINED-BED GASIFICATION PROCESSES

PRESSURE: 30 atm

Temp., K	Total Alkali		Temp., K	Total Alkali	
	20 ppm	20 ppb		20 ppm	20 ppb
	KH(g)			KCN(g)	
1600	2.805-9	3.312-12	1600	1.072-9	1.266-12
1500	1.588-9	2.160-12	1500	1.438-9	1.957-12
1400	7.331-10	1.247-12	1400	1.667-9	2.836-12
1300	2.585-10	5.893-13	1300	1.413-9	3.221-12
1200	6.636-11	2.128-13	1200	7.201-10	2.309-12
1100	1.243-11	6.149-14	1100	1.945-10	9.622-13
1000	1.469-12	1.552-14	1000	2.011-11	2.125-13
900	6.809-14	2.851-15	900	5.111-13	2.140-14
800	5.598-16	2.142-16	800	1.702-15	6.513-16
700	8.627-19	8.627-19	700	6.410-19	6.410-19
600	1.068-22	1.113-28	600	6.904-24	7.197-30

Temp., K	Total Alkali	
	20 ppm	20 ppb
	KCl(s)	
1800	---	---
1500	---	---
1400	---	---
1300	---	---
1200	---	---
1100	---	---
1000	---	---
900	5.991-7	---
800	1.025-8	---
700	1.038-8	9.305-10
600	1.039-8	1.039-9

TABLE 3.20

PROJECTED MOLE FRACTIONS OF ALKALI SPECIES
FORMED IN DIRECT COAL FIRED TURBINE PROCESSES

PRESSURE: 10 atm

Temp., K	Total Alkali	
	20 ppm	20 ppb
	NaCl(g)	
1800	1.941-8	5.483-12
1500	2.488-8	1.128-11
1400	2.894-8	2.528-11
1300	8.088-7	5.710-11
1200	1.368-7	5.122-11
1100	1.090-8	1.084-11
1000	5.051-10	4.928-13
900	1.317-11	1.285-14
800	1.502-13	1.488-16
700	5.418-16	5.291-19
600	5.310-19	6.701-20

Temp., K	Total Alkali	
	20 ppm	20 ppb
	NaOH(g)	
1800	2.881-8	4.819-9
1500	2.300-8	4.824-9
1400	1.215-8	4.799-9
1300	9.273-8	4.284-9
1200	3.635-9	1.297-9
1100	7.847-11	7.459-11
1000	7.690-13	7.500-13
900	3.150-15	3.072-15
800	3.595-18	3.508-18
700	6.840-22	6.671-22
600	1.384-26	1.330-26

Temp., K	Total Alkali	
	20 ppm	20 ppb
	Na ₂ SO ₄ (g)	
1800	5.661-9	1.584-14
1500	5.970-8	2.797-13
1400	4.647-7	7.307-12
1300	1.135-7	2.497-10
1200	1.308-8	1.746-9
1100	8.571-10	8.571-10
1000	2.755-11	2.755-11
900	3.852-13	3.852-13
800	1.714-15	1.714-15
700	1.482-18	1.482-18
600	1.089-22	1.089-22

Temp., K	Total Alkali	
	20 ppm	20 ppb
	NaO(g)	
1800	2.040-9	3.412-12
1500	7.277-10	1.574-12
1400	1.632-10	2.528-11
1300	4.480-12	2.060-13
1200	5.257-14	1.876-14
1100	---	---
1000	---	---
900	---	---
800	---	---
700	---	---
600	---	---

TABLE 3.20 (Continued)

PROJECTED MOLE FRACTIONS OF ALKALI SPECIES
FORMED IN DIRECT COAL FIRED TURBINE PROCESSES

PRESSURE: 10 atm

Temp., K	Total Alkali	
	20 ppm	20 ppb
	$\text{Na}_2\text{SO}_4(\text{c})$	
1600	---	---
1500	---	---
1400	---	---
1300	1.858-8	---
1200	2.337-8	---
1100	2.415-8	1.521-9
1000	2.420-8	2.393-9
900	2.420-8	2.420-9
800	2.420-8	2.420-9
700	2.420-8	2.420-9
600	2.420-8	2.420-9

Temp., K	Total Alkali	
	20 ppm	20 ppb
	$\text{KCl}(\text{g})$	
1600	1.588-8	4.619-12
1500	2.028-8	9.377-12
1400	2.320-8	2.083-11
1300	2.247-8	4.854-11
1200	3.678-7	5.357-11
1100	2.990-8	2.006-11
1000	1.498-9	1.461-12
900	4.314-11	4.209-14
800	5.351-13	5.221-16
700	2.051-15	2.003-18
600	2.168-18	2.733-19

Temp., K	Total Alkali	
	20 ppm	20 ppb
	$\text{KOH}(\text{g})$	
1600	2.201-8	3.791-9
1500	1.711-8	3.785-9
1400	9.955-7	3.767-9
1300	2.481-7	3.506-9
1200	9.540-9	1.324-9
1100	2.080-10	1.394-10
1000	2.306-12	2.249-12
900	1.067-14	1.041-14
800	1.364-17	1.330-17
700	2.860-21	2.790-21
600	6.451-26	6.292-26

TABLE 3.20 (Continued)

PROJECTED MOLE FRACTIONS OF ALKALI SPECIES
FORMED IN DIRECT COAL FIRED TURBINE PROCESSES

PRESSURE: 10 atm

Temp., °C	Total Alkali		Temp., K	Total Alkali	
	20 ppm	20 ppb		20 ppm	20 ppb
	$K_2SO_4(g)$			$KO(g)$	
1600	2.818-9	8.361-15	1600	3.383-10	---
1500	2.851-8	1.397-13	1500	1.082-10	---
1400	2.391-7	3.450-12	1400	2.278-11	---
1300	5.829-7	1.200-10	1300	1.751-12	2.474-14
1200	5.987-8	1.208-9	1200	---	2.361-15
1100	3.849-9	1.818-9	1100	---	---
1000	1.349-10	1.349-10	1000	---	---
900	2.110-12	2.110-12	900	---	---
800	9.974-15	9.974-15	800	---	---
700	8.489-18	8.489-18	700	---	---
600	6.040-22	6.040-22	600	---	---

Temp., K	Total Alkali	
	20 ppm	20 ppb
	$K_2SO_4(s)$	
1600	---	---
1500	---	---
1400	---	---
1300	6.660-8	---
1200	1.649-6	---
1100	1.897-6	---
1000	1.897-6	1.762-9
900	1.897-6	1.895-9
800	1.897-6	1.897-9
700	1.897-6	1.897-9
600	1.897-6	1.897-9

TABLE 3.21

PROJECTED MOLE FRACTIONS OF ALKALI SPECIES
FORMED IN PRESSURIZED FLUIDIZED-BED COMBUSTION PROCESSES

PRESSURE: 10 atm

Temp., K	Total Alkali	
	20 ppm	20 ppb
	NaCl (g)	
1800	1.850-6	5.012-12
1500	2.207-6	1.027-11
1400	1.568-6	2.260-11
1300	3.399-7	3.588-11
1200	4.370-8	1.804-11
1100	3.151-9	3.148-12
1000	1.394-10	1.322-13
900	3.150-12	3.146-15
800	4.441-14	3.437-17
700	1.248-16	1.247-19
600	1.261-19	1.861-20

Temp., K	Total Alkali	
	20 ppm	20 ppb
	NaOH (g)	
1800	2.920-6	4.842-9
1500	1.963-8	4.844-9
1400	5.393-7	4.733-9
1300	3.263-8	2.959-9
1200	1.231-9	5.010-10
1100	2.436-11	2.433-11
1000	2.229-13	2.226-13
900	6.326-16	8.313-16
800	9.096-19	9.082-19
700	1.733-22	1.730-22
600	3.527-27	3.522-27

Temp., K	Total Alkali	
	20 ppm	20 ppb
	Na ₂ SO ₄ (g)	
1800	---	1.189-13
1500	---	2.116-12
1400	7.025-7	5.419-11
1300	1.135-7	9.360-10
1200	1.308-8	2.174-9
1100	8.571-10	8.571-10
1000	2.755-11	2.755-11
900	3.852-13	3.852-13
800	1.714-15	1.714-15
700	1.482-18	1.482-18
600	1.089-22	1.089-22

Temp., K	Total Alkali	
	20 ppm	20 ppb
	NaO (g)	
1800	1.354-9	2.245-12
1500	4.197-10	1.036-12
1400	4.749-11	4.168-13
1300	1.029-12	9.329-14
1200	1.166-14	4.748-15
1100	---	---
1000	---	---
900	---	---
800	---	---
700	---	---
600	---	---

TABLE 3.21 (Continued)

PROJECTED MOLE FRACTIONS OF ALKALI SPECIES
FORMED IN PRESSURIZED FLUIDIZED-BED COMBUSTION PROCESSES

PRESSURE: 10 atm

Temp., K	Total Alkali	
	20 ppm	20 ppb
	$\text{Na}_2\text{SO}_4(\text{c})$	
1800	---	---
1500	---	---
1400	6.767-7	---
1300	2.134-6	---
1200	2.399-6	---
1100	2.431-6	1.563-9
1000	2.434-6	2.407-9
900	2.435-6	2.435-9
800	2.435-6	2.435-9
700	2.437-6	2.437-9
600	2.438-6	2.439-9

Temp., K	Total Alkali	
	20 ppm	20 ppb
	$\text{KCl}(\text{g})$	
1800	1.525-6	4.221-12
1500	1.878-6	8.556-12
1400	1.851-6	1.879-11
1300	9.444-7	3.375-11
1200	1.175-7	1.965-11
1100	8.644-9	6.039-12
1000	3.929-10	3.923-13
900	1.032-11	1.030-14
800	1.226-13	1.224-16
700	4.724-16	4.720-19
600	5.143-19	7.591-20

Temp., K	Total Alkali	
	20 ppm	20 ppb
	$\text{KOH}(\text{g})$	
1800	2.247-6	3.807-9
1500	1.574-6	3.803-9
1400	6.057-7	3.744-9
1300	8.729-8	2.680-9
1200	3.229-9	5.324-10
1100	6.627-11	4.627-11
1000	6.684-13	6.674-13
900	2.821-15	2.817-15
800	3.450-18	3.445-18
700	7.247-22	7.236-22
600	1.669-26	1.666-26

TABLE 3.21 (Continued)

PROJECTED MOLE FRACTIONS OF ALKALI SPECIES
FORMED IN PRESSURIZED FLUIDIZED-BED COMBUSTION PROCESSES

PRESSURE: 10 atm

Temp., K	Total Alkali		Temp., K	Total Alkali	
	20 ppm	20 ppb		20 ppm	20 ppb
	$K_2SO_4(g)$			$KO(g)$	
1600	2.182-8	6.268-14	1600	2.262-10	---
1500	1.811-7	1.058-12	1500	6.524-11	---
1400	6.791-7	2.599-11	1400	9.085-12	---
1300	5.829-7	5.508-10	1300	4.038-13	---
1200	5.987-8	1.632-9	1200	3.774-15	---
1100	3.849-9	1.882-9	1100	---	---
1000	1.349-10	1.349-10	1000	---	---
900	2.110-12	2.110-12	900	---	---
800	9.974-15	9.974-15	800	---	---
700	8.489-18	8.489-18	700	---	---
600	6.040-22	6.040-22	600	---	---

Temp., K	Total Alkali	
	20 ppm	20 ppb
	$K_2SO_4(c)$	
1600	---	---
1500	---	---
1400	---	---
1300	8.088-7	---
1200	1.788-6	---
1100	1.899-6	---
1000	1.908-6	---
900	1.909-6	---
800	1.909-6	1.909-9
700	1.910-6	1.910-9
600	1.912-6	1.912-9

In the fluid-bed gasification system (Figure 3.27), alkali which is released at concentrations of 20 ppb to 2 ppm at the gasifier outlet is projected to remain as gas phase species at the ceramic cross-flow filter surface (i.e., with or without adherent char fines). With 20 ppm total alkali released into the effluent gas stream, the potential exists for condensation of sodium as Na_2CO_3 , thus reducing the concentration of volatile alkali which reaches and reacts at the ceramic cross-flow filter surface.

In the entrained-bed gasification system (Figure 3.28), alkali which is released into the effluent stream at concentrations between 2 ppb and 20 ppm is not projected to condense prior to contacting the ceramic cross-flow filter surface (i.e., with or without adherent char fines).

In the direct coal fired turbine system (Figure 3.29), alkali is released as a volatile chloride, hydroxide, or sulfate, and has the potential to further react with SO_2 to condense as Na_2SO_4 or K_2SO_4 along the ceramic cross-flow filter surface (i.e., with or without adherent ash fines). Condensation of Na_2SO_4 or K_2SO_4 is expected in direct coal fired turbine effluent streams containing >2 ppm total alkali. Under these conditions, not only will the ceramic cross-flow filter experience a reduced gaseous alkali phase concentration, but will also have the potential to experience deposition and reaction with molten Na_2SO_4 . Potassium sulfate is projected to remain as a solid when impacting the filter, since the direct coal fired turbine filter temperatures are below the K_2SO_4 phase melt temperature.

As in the direct coal fired turbine system, Na_2SO_4 and K_2SO_4 are projected to condense in the pressurized fluidized-bed combustion (PFBC) system (Figure 3.30). With 20 ppb total alkali released into the PFBC effluent stream, deposition of liquid Na_2SO_4 is projected to occur. At alkali concentrations between 200 ppb and 20 ppm, both liquid Na_2SO_4 and solid K_2SO_4 are likely. As in the direct coal fired turbine system, alkali condensation reduces the total gas phase alkali concentration which reaches the filter surface (i.e., with or without adherent ash fines).

Projected Char or Ash Phase Compositions and
Reactions with Volatile Alkali

Char fines which were generated at the KRW fluid-bed gasifier and which were removed as part of the candle filter inlet catch were subjected to chemical analysis using atomic absorption and x-ray diffraction techniques (Section 3.1.2.2). Using the atomic absorption concentrations generated for each of the major elements in the char fines, a thermodynamic equilibrium product distribution was projected at 700°C (1290°F) and 20 atm, in a reducing gas environment which simulated the KRW fluid-bed gasifier process gases. The char fines were projected to consist of the following equilibrium phases:

Compound	Projected Normalized Ash Concentration, Wt%	XRD Analysis
C	72.11	-
Al ₂ SiO ₅	7.10	-
FeS	6.84	-
CaCO ₃	6.21	-
MgSiO ₃	3.07	-
SiO ₂	2.20	-
CaS	1.45	-
K ₂ CO ₃	0.80	-
NaAlO ₂	0.22	-
Amorphous	--	Major
CaSO ₄	--	Possible Minor

In the calculated equilibrium product composition, calcium carbonate or sulfide were projected as stable solid phases, and were not projected to be converted into the sulfate phase which was

identified by x-ray diffraction analysis. If the calculations considered a lower gas phase sulfur concentration and/or overall lower oxygen partial pressure in comparison to that actually experienced at process test conditions, conversion into the calcium sulfate phase would not be expected.

Similarly, ash fines which were generated at the New York University combustor and which were removed at the cross-flow filter inlet, were subjected to chemical analysis using atomic absorption and x-ray diffraction techniques (Section 3.1.2.2). Using the atomic absorption concentrations, an equilibrium product ash composition was generated at 870°C (1600°F) and 20 atm, simulating exposure of the New York University fines to PFBC process gases. Volatile alkali and chloride phases were not included in these calculations. The following compounds are projected to be thermodynamically stable at PFBC process conditions:

Compound	Projected Normalized Ash Concentration, Wt%	XRD Analysis
CaSO_4	36.88	Major Phase
MgSiO_3	22.73	--
Al_2SiO_5	19.75	--
SiO_2	12.25	Major Phase
Fe_3O_4	3.90	Minor Phase
$\text{Na}_2\text{Al}_2\text{Si}_6\text{O}_{16}$	2.88	--
K_2SO_4	1.15	--
$\text{CaAl}_2\text{Si}_2\text{O}_8$	0.45	--

Relatively good agreement is shown between the thermodynamically projected phases and the XRD analysis of the process ash.

A series of equilibrium calculations was performed in an attempt to simulate the possible reaction of gaseous alkali with the ash particles as the fines are carried from the combustor outlet to the ceramic cross-flow filter surface. A particle load of 1000 ppm is assumed. Table 3.22 identifies the mole percent of each projected ash phase based on achieving an equilibrium state for 0-20 ppb to 20 ppm total alkali in the presence and absence of chlorine in the effluent gas stream. As shown in Table 3.22, the presence of gas phase chloride (i.e., HCl) promotes volatilization of alkali from the condensed ash phases. A relatively insignificant increase in the alkali concentration of the ash is identified when the effluent gas contains low alkali concentrations (<2 ppm). At 20 ppm total alkali in the gas phase, a 1.3 mole percent increase in $\text{Na}_2\text{Al}_2\text{Si}_6\text{O}_{18}$, and a 1 mole percent increase in the K_2SO_4 concentrations is projected. Although thermodynamic equilibrium calculations have projected homogeneous gas phase alkali reactions with ash fines, the question which remains to be resolved is whether the reaction kinetics will permit this to occur within the relatively short residence time that the gas and ash experience as both travel from the combustor outlet to the ceramic cross-flow filter.

3.1.3.2 Projected Thermal Stability of Ceramic Cross-Flow Material Phases and Potential Reactions with Process Gases

In order to demonstrate the thermal stability of the ceramic cross-flow filter materials, individual ceramic phases were equilibrated with nitrogen at process temperatures and pressures. The equilibrium results which are projected represent thermal changes that could occur at process conditions.

In a second series of calculations, the process gas chemistries (Table 3.1) for the fixed-bed, fluid-bed, and entrained-bed gasification, direct coal fired turbine, and the pressurized fluidized-bed combustion systems reflect the broad range of oxygen partial pressures that the ceramic filter materials could experience. In subsequent calculations, the concentration of sulfur is varied, but is maintained at identical levels for each of the ceramic systems.

TABLE 3.22

THERMODYNAMICALLY PROJECTED NYU ASH COMPOSITION, MOL%

HCl Concentration: 0.03 Wt%

Phase	:----- Total Alkali -----:				
	0	20 ppb	200 ppb	2 ppm	20 ppm
$\text{Na}_2\text{Al}_2\text{Si}_2\text{O}_{10}$	2.816	2.817	2.828	2.946	4.174
K_2SO_4	0.954	0.955	0.964	1.049	1.949
Fe_2O_3	3.863	3.863	3.865	3.882	4.061
SiO_2	12.794	12.788	12.742	12.276	7.378
Al_2SiO_5	20.055	20.058	20.057	20.041	19.873
MgSiO_3	22.523	22.520	22.534	22.634	23.678
CaSO_4	38.991	38.992	37.009	37.172	38.887

HCl Concentration: 0 Wt%

Phase	:----- Total Alkali -----:			
	20 ppb	200 ppb	2 ppm	20 ppm
$\text{Na}_2\text{Al}_2\text{Si}_2\text{O}_{10}$	4.219	2.988	2.871	2.859
K_2SO_4	2.139	1.231	1.145	1.136
Fe_2O_3	4.063	3.883	3.866	3.865
SiO_2	7.162	12.071	12.538	12.585
Al_2SiO_5	19.835	20.005	20.021	20.022
MgSiO_3	23.684	22.639	22.540	22.531
CaSO_4	38.897	37.182	37.018	37.002

At process conditions, an operating ceramic filter will experience effluent gases which continually carry alkali, sulfur, and/or fines passed or through the filter matrix. Modeling of the potential filter and gas phase contaminant reactions for processes which operate for thousands of hours would require a large process gas to solid ceramic volume ratio (i.e., 1:>100). In order to model possible reactions which may result at the particle surface, a more realistic gas phase to solid volume ratio of 1-2 is assumed. In this manner, non-oxide materials as silicon nitride which have the potential to oxidize, will not be entirely consumed through conversion to the oxide.

In order to generate phase stability using the NASA CET86 program, the composition of constituents in both the gas and solid phases were each normalized to 1. Alkali is varied with respect to the solid ceramic phase. Two arbitrary alkali levels are chosen in this series of calculations. These include an alkali concentration at 0.1 and 1 percent of the total moles of solids considered in each system (Table 3.23). This permits:

- A sufficiently high concentration of volatile alkali for reaction with the ceramic phase as opposed to low alkali concentrations which would remain as volatile complexes over the solid ceramic matrix.
- Retention of a portion of unreacted ceramic matrix material in the thermodynamically projected solution, which simulates the actual process.
- A simulation of the alkali concentrations which the filter materials would experience after long-term exposure at process conditions.

Notably the alkali levels chosen in this series of calculations exceed those concentrations that are expected at process conditions. The

TABLE 3.23

PROJECTED ALKALI EQUILIBRIUM CONCENTRATIONS
RELEASED AT THE KRW GASIFIER⁽¹²⁾

Coal	Coal Feed Rate, lb/hr	Temp., °C	Press., atm	Effluent Gas Flow Rate, lb/hr	NaCl(g), lb/hr (Mole/hr)	KCl(g), lb/hr (Mole/hr)	Comment
Upper Freeport	981	1008	18.8	6622.3	0.0371 (0.287)	0.0244 (0.148)	NFR*
Western Kentucky	1145	978	18.7	5267.3	0.0949 (0.736)	0.0621 (0.373)	FR
Brook- ville	1385	950	18.7	6033.9	0.0024 (0.018)	0.0015 (0.009)	FR
North Dakota Lignite	2358	805	18.7	6252.1	0.0087 (0.067)	0.0055 (0.033)	FR
Upper Freeport	981	1008	18.8	7223.5	0.0404 (0.313)	0.0266 (0.162)	FR
Average:					(0.284)	(0.146)	

*NFR: No Fines Recycle; FR: Fines Recycle.

Mullite Filter = 9.16kg.

21.5 moles mullite:0.28 moles/hr NaCl = 100:1.

concentration of alkali released into the effluent stream varies as a function of:

- Coal feed composition and feed rate.
- Process conditions (i.e., air- or oxygen-blown gasification or combustion).
- Process operating temperature and pressure.

Alternately, the alkali effluent concentration which reaches the cross-flow filter can vary with the

- Inclusion of sulfur removal systems with sorbents (i.e., limestone or dolomite) which also contain and release alkali at process conditions.

Similarly, the concentration of alkali that reaches the filter may be significantly different from the concentration which is directly released at the gasifier or combustor outlet. This may be the result of condensation of the initially released alkali as:

- Aerosol fines or droplets.
- Aerosol fines or droplets which deposit along cooler component metal surfaces.
- Surface coatings along entrained fines.
- Phases which are formed through reaction with bulk gas constituents (i.e., sulfur).

Further reaction between the alkali and fines could also occur prior to contact with the ceramic filter matrix. The extent to which this reaction may occur is considered to be limited due to the relatively short residence time between the gasifier or combustor outlet and the ceramic filter, and the reaction kinetics which drives gas phase alkali into the aluminosilicate structure. Similarly, if char or ash fines are

collected along the filter surface and/or adhere to phases within the filter pores, and are not removed during pulse jet cleaning, then the potential exists for reaction of the fines with alkali after long-term, high temperature filter operation.

The thermodynamically projected alkali concentrations (Appendix A) released at the gasifier or combustor outlet assume that equilibrium has been achieved. These levels, however, should be viewed as maximum release concentrations since the calculations do not incorporate the potential for reduction based on:

- Possible collapse of the coal structure through particle agglomeration or glass phase formation which traps alkali within the resulting char or ash.
- Variation in the feed material alkali concentrations.
- Possible inhomogeneity throughout the process system which does not permit complete mixing or reaction of all gas and solid phase constituents.

Tables 3.24 through 3.25 illustrate the phases that are projected to occur at process conditions for cross-flow filters containing alumina, mullite, cordierite, or silicon nitride. These materials are chosen as representative of the principal constituent phases in the cross-flow filters. Since deposition and/or reaction of alkali with the ceramic matrix may occur locally, the data generated in Tables 3.24 through 3.29 serve as a guide for identifying whether the filters are inert to chemical reactions with alkali, sulfur, and/or the process gases at specific process operating temperatures and pressures. The fact that alkali may be driven into the ceramic matrix does not imply immediate ceramic material degradation. Critical issues which need to be addressed include:

- Identification of the rate and extent of reaction of alkali with the various ceramic constituent phases.

- Identification of the influence of alkali reaction with possible change in the ceramic material's properties.

The following Sections discuss the thermodynamic equilibrium projections for each of the ceramic cross-flow filter material phases in the fixed-bed, fluid-bed, and entrained-bed gasification, direct coal fired turbine, and pressurized fluidized-bed combustion systems.

Alumina (Al_2O_3)

Alpha-alumina is projected to result at equilibrium when alumina is reacted with nitrogen at temperatures and pressures identified for the fixed-bed, fluid-bed, and entrained-bed gasification, direct coal fired turbine, and pressurized fluidized-bed combustion processes (Table 3.24).

The stability of the α -alumina phase is projected to be maintained during exposure to process gases in the absence of sulfur (i.e., H_2S under gasification and SO_2 under combustion) and alkali (i.e., NaCl).

Process gases which contain sodium in the absence of sulfur are projected to lead to the:

- Condensation of solid NaCl in the low temperature fixed-bed and fluid-bed gasification effluent streams.
- Formation of solid $\beta\text{-NaAlO}_2$ in the higher temperature entrained-bed gasification, direct coal fired turbine, and pressurized fluidized-bed combustion effluent streams. This reaction, as well as deposition of liquid sodium chloride results as the process sodium concentration increases.

TABLE 3.24

THERMAL STABILITY OF CERAMIC CROSS-FLOW
MATERIALS IN NITROGEN
AT FILTER OPERATING CONDITIONS

Process	:Fixed-Bed	:Fluid-Bed	:Entrained-Bed	: Direct Coal:	Pressurized
	: <----- Gasification ----->			: Fired	: Fluidized
	:	:	:	: Turbines	: Bed
	:	:	:	:	: Combustion
Temp., °C	: 590	: 700	: 870	: 980	: 870
Press.,	:	:	:	:	:
atm	: 20	: 20	: 30	: 12	: 10
Alumina	:Al ₂ O ₃ (a)	:Al ₂ O ₃ (a)	: Al ₂ O ₃ (a)	: Al ₂ O ₃ (a)	: Al ₂ O ₃ (a)
Mullite	:Al ₆ Si ₂ O ₁₃	:Al ₆ Si ₂ O ₁₃	: Al ₆ Si ₂ O ₁₃	: Al ₆ Si ₂ O ₁₃	: Al ₆ Si ₂ O ₁₃
Cordierite:	Al ₂ SiO ₅	: Al ₂ SiO ₅	: Al ₂ SiO ₅	: Al ₆ Si ₂ O ₁₃	: Al ₂ SiO ₅
	:MgSiO ₃ (cl)	:MgSiO ₃ (re)	: MgSiO ₃ (re)	: MgSiO ₃ (re)	: MgSiO ₃ (re)
	:SiO ₂ (hqz)	: SiO ₂ (hqz)	: SiO ₂ (hcr)	: SiO ₂ (hcr)	: SiO ₂ (hcr)
Silicon	: Si ₃ N ₄ (a)	: Si ₃ N ₄ (a)	: Si ₃ N ₄ (a)	: Si ₃ N ₄ (a)	: Si ₃ N ₄ (a)
Nitride	:	:	:	:	:

Alumina: Al₂O₃Mullite: 3Al₂O₃•2SiO₂Cordierite: 2MgO•2Al₂O₃•5SiO₂Silicon Nitride: Si₃N₄.

TABLE 3.25

STABILITY OF CERAMIC CROSS-FLOW FILTER
MATERIALS IN PROCESS GASES AT
OPERATING CONDITIONS

Process	:Fixed-Bed	:Fluid-Bed	:Entrained-Bed:	Direct Coal:	Pressurized
	: <----- Gasification ----->			: Fired	: Fluidized
	:	:	:	: Turbines	: Bed
	:	:	:	:	: Combustion
Temp., °C	: 590	: 700	: 870	: 980	: 870
Press.,	:	:	:	:	:
atm	: 20	: 20	: 30	: 12	: 10
Gas	: 0.34 N ₂	: 0.1 N ₂	: 0.81 N ₂	: 15.16 O ₂	: 3.45 O ₂
Composition	: 1.48 CO ₂	: 12.25 CO ₂	: 7.95 CO ₂	: 70.62 N ₂	: 75.25 N ₂
(wt%)	: 22.70 H ₂ O	: 17.47 H ₂ O	: 25.00 H ₂ O	: 7.57 CO ₂	: 13.63 CO ₂
	: 44.45 CO	: 37.00 CO	: 38.84 CO	: 6.63 H ₂ O	: 7.33 H ₂ O
	: 23.29 H ₂	: 27.97 H ₂	: 26.38 H ₂	: 0.02 SO ₂	: 0.34 SO ₂
	: 5.94 CH ₄	: 4.31 CH ₄	: 0.10 CH ₄	:	:
	: 1.06 H ₂ S	: 0.90 H ₂ S	: 0.92 H ₂ S	:	:
Alumina	: Al ₂ O ₃ (a)	: Al ₂ O ₃ (a)	: Al ₂ O ₃ (a)	: Al ₂ O ₃ (a)	: Al ₂ O ₃ (a)
Mullite	: Al ₆ Si ₂ O ₁₃	: Al ₆ Si ₂ O ₁₃	: Al ₆ Si ₂ O ₁₃	: Al ₆ Si ₂ O ₁₃	: Al ₆ Si ₂ O ₁₃
Cordierite:	Al ₂ SiO ₅	: Al ₂ SiO ₅	: Al ₂ SiO ₅	: Al ₆ Si ₂ O ₁₃	: Al ₂ SiO ₅
	:MgSiO ₃ (cl)	:MgSiO ₃ (re)	: MgSiO ₃ (re)	: MgSiO ₃ (re)	: MgSiO ₃ (re)
	:SiO ₂ (hqz)	:SiO ₂ (hqz)	: SiO ₂ (hcr)	: SiO ₂ (hcr)	: SiO ₂ (hcr)
Silicon	:Si ₃ N ₄ (a)	:Si ₃ N ₄ (a)	: Si ₃ N ₄ (a)	: Si ₃ N ₄ (a)	: Si ₃ N ₄ (a)
Nitride	:SiO ₂ (hqz)	:SiO ₂ (hqz)	: SiO ₂ (hcr)	: SiO ₂ (hcr)	: SiO ₂ (hcr)
	:	:	:	: C(gr)	: C(gr)

TABLE 3.26

PROJECTED CONDENSED PHASES RESULTING FROM THE REACTION
OF ALUMINA WITH SODIUM AND SULFUR
AT FILTER PROCESS CONDITIONS*

Process	: Fixed-Bed	: Fluid-Bed	: Entrained-Bed	: Direct Coal	: Pressurized
	: <----- Gasification ----->			: Fired	: Fluidized
	:	:	:	: Turbines	: Bed
	:	:	:	:	: Combustion
Temp., °C	: 590	: 700	: 870	: 980	: 870
Press.,	:	:	:	:	:
atm	: 20	: 20	: 30	: 12	: 10
Moles/Phase**	:	:	:	:	:
0.999Al ₂ O ₃	: Al ₂ O ₃ (a)	: Al ₂ O ₃ (a)	: Al ₂ O ₃ (a)	: Al ₂ O ₃ (a)	: Al ₂ O ₃ (a)
0.001NaCl	: NaCl	: NaCl	: NaAlO ₂ (β)	: NaAlO ₂ (β)	: NaAlO ₂ (β)
--- S***	:	:	:	:	:
0.990Al ₂ O ₃	: Al ₂ O ₃ (a)	: Al ₂ O ₃ (a)	: Al ₂ O ₃ (a)	: Al ₂ O ₃ (a)	: Al ₂ O ₃ (a)
0.010NaCl	: NaCl	: NaCl	: NaAlO ₂ (β)	: NaAlO ₂ (β)	: NaAlO ₂ (β)
--- S	:	:	: NaCl(l)	: NaCl(l)	: NaCl(l)
0.999Al ₂ O ₃	: Al ₂ O ₃ (a)	: Al ₂ O ₃ (a)	: Al ₂ O ₃ (a)	: Al ₂ O ₃ (a)	: Al ₂ O ₃ (a)
0.001NaCl	: NaCl	: NaCl	: NaAlO ₂ (β)	: Na ₂ SO ₄ (l)	: Na ₂ SO ₄
0.002S	:	:	:	:	:
0.990Al ₂ O ₃	: Al ₂ O ₃ (a)	: Al ₂ O ₃ (a)	: Al ₂ O ₃ (a)	: Al ₂ O ₃ (a)	: Al ₂ O ₃ (a)
0.010NaCl	: NaCl	: NaCl	: NaAlO ₂ (β)	: Na ₂ SO ₄ (l)	: Na ₂ SO ₄
0.002S	:	:	: NaCl(l)	:	:

* Solid or liquid phases are projected with mole fractions of greater than 0.5×10^{-8} .

- ** Moles/Phase:
- Combined moles of ceramic matrix and alkali (NaCl) are set equal to 1.
 - Gas phase sulfur is maintained at a constant concentration for all process conditions. Total moles of gas phase constituents are set equal to 1.
 - Ratio of moles of gas phase to moles of solids is set equal to 2.

*** S: H₂S for Fixed-Bed, Fluid-Bed, and Entrained-Bed Gasification.
SO₂ for Direct Coal Fired Turbines and Pressurized Fluidized Bed Combustion.

TABLE 3.27

PROJECTED CONDENSED PHASES RESULTING FROM THE REACTION
OF MULLITE WITH SODIUM AND SULFUR
AT FILTER PROCESS CONDITIONS

Process	: Fixed-Bed : : <----- Gasification -----> :	: Fluid-Bed : : : :	: Entrained-Bed : : : :	: Direct Coal : : Fired : : Turbines :	: Pressurized : : Fluidized : : Bed : : Combustion :
Temp., °C :	590	: 700	: 870	: 980	: 870 :
Press., :		:	:	:	:
atm :	20	: 20	: 30	: 12	: 10 :
Moles/Phase	:	:	:	:	:
0.999Mull*	: Al ₂ O ₃ (a)	: Al ₂ O ₃ (a)	: Al ₂ O ₃ (a)	: Al ₂ O ₃ (a)	: Al ₂ O ₃ (a) :
0.001NaCl	: Al ₆ Si ₂ O ₁₃	: Al ₆ Si ₂ O ₁₃	: Al ₆ Si ₂ O ₁₃	: Al ₆ Si ₂ O ₁₃	: Al ₆ Si ₂ O ₁₃ :
--- S**	: ***	: ***	: ***	: (b)	: (b) :
0.990Mull	: Al ₂ O ₃ (a)	: Al ₂ O ₃ (a)	: Al ₂ O ₃ (a)	: Al ₂ O ₃ (a)	: Al ₂ O ₃ (a) :
0.010NaCl	: Al ₆ Si ₂ O ₁₃	: Al ₆ Si ₂ O ₁₃	: Al ₆ Si ₂ O ₁₃	: Al ₆ Si ₂ O ₁₃	: Al ₆ Si ₂ O ₁₃ :
--- S	: (a)	: (b)	: (b)	: (b)	: (b) :
0.999Mull	: Al ₂ O ₃ (a)	: Al ₂ O ₃ (a)	: Al ₂ O ₃ (a)	: Al ₆ Si ₂ O ₁₃	: Al ₆ Si ₂ O ₁₃ :
0.001NaCl	: Al ₆ Si ₂ O ₁₃	: Al ₆ Si ₂ O ₁₃	: Al ₆ Si ₂ O ₁₃	: Na ₂ SO ₄ (l)	: Na ₂ SO ₄ :
0.002S	: ***	: ***	: ***	:	:
0.990Mull	: Al ₂ O ₃ (a)	: Al ₂ O ₃ (a)	: Al ₂ O ₃ (a)	: Al ₆ Si ₂ O ₁₃	: Al ₆ Si ₂ O ₁₃ :
0.010NaCl	: Al ₆ Si ₂ O ₁₃	: Al ₆ Si ₂ O ₁₃	: Al ₆ Si ₂ O ₁₃	: Na ₂ SO ₄ (l)	: Na ₂ SO ₄ :
0.002S	: (a)	: (b)	: (b)	:	:

* Mull: Mullite (Al₆Si₂O₁₃).

** S: H₂S for Fixed-Bed, Fluid-Bed, and Entrained-Bed Gasification.
SO₂ for Direct Coal Fired Turbines and Pressurized Fluidized Bed
Combustion.

*** Projected alkali aluminosilicate phases are below mole fractions of
0.5 x 10⁻⁵.

(a) Na₂Al₂Si₆O₁₆(1).

(b) Na₂Al₂Si₆O₁₆(2).

TABLE 3.28

PROJECTED CONDENSED PHASES RESULTING FROM THE REACTION
OF CORDIERITE WITH SODIUM AND SULFUR
AT FILTER PROCESS CONDITIONS

Process	Fixed-Bed : <----- :	Fluid-Bed Gasification :	Entrained-Bed -----> :	Direct Coal Fired Turbines :	Pressurized Fluidized Bed Combustion :
Temp., °C	590	700	870	980	870
Press., atm	20	20	30	12	10
Moles/Phase	:	:	:	:	:
0.999Cord*	Al_2SiO_5	Al_2SiO_5	Al_2SiO_5	$\text{Al}_6\text{Si}_2\text{O}_{13}$	Al_2SiO_5
0.001NaCl	$\text{MgSiO}_3(\text{cl})$	$\text{MgSiO}_3(\text{re})$	$\text{MgSiO}_3(\text{re})$	$\text{MgSiO}_3(\text{re})$	$\text{MgSiO}_3(\text{re})$
--- S**	$\text{SiO}_2(\text{hqz})$	$\text{SiO}_2(\text{hqz})$	$\text{SiO}_2(\text{hcr})$	$\text{SiO}_2(\text{hcr})$	$\text{SiO}_2(\text{hcr})$
	:	:	:	(b)	(b)
0.990Cord	Al_2SiO_5	Al_2SiO_5	Al_2SiO_5	$\text{Al}_6\text{Si}_2\text{O}_{13}$	Al_2SiO_5
0.010NaCl	$\text{MgSiO}_3(\text{cl})$	$\text{MgSiO}_3(\text{re})$	$\text{MgSiO}_3(\text{re})$	$\text{MgSiO}_3(\text{re})$	$\text{MgSiO}_3(\text{re})$
--- S	$\text{SiO}_2(\text{hqz})$	$\text{SiO}_2(\text{hqz})$	$\text{SiO}_2(\text{hcr})$	$\text{SiO}_2(\text{hcr})$	$\text{SiO}_2(\text{hcr})$
	(a)	(b)	(b)	(b)	(b)
0.999Cord	Al_2SiO_5	Al_2SiO_5	Al_2SiO_5	$\text{Al}_6\text{Si}_2\text{O}_{13}$	Al_2SiO_5
0.001NaCl	$\text{MgSiO}_3(\text{cl})$	$\text{MgSiO}_3(\text{re})$	$\text{MgSiO}_3(\text{re})$	$\text{MgSiO}_3(\text{re})$	$\text{MgSiO}_3(\text{re})$
0.002S	$\text{SiO}_2(\text{hqz})$	$\text{SiO}_2(\text{hqz})$	$\text{SiO}_2(\text{hcr})$	$\text{SiO}_2(\text{hcr})$	$\text{SiO}_2(\text{hcr})$
	:	:	:	(b)	(b)
0.990Cord	Al_2SiO_5	Al_2SiO_5	Al_2SiO_5	$\text{Al}_6\text{Si}_2\text{O}_{13}$	Al_2SiO_5
0.010NaCl	$\text{MgSiO}_3(\text{cl})$	$\text{MgSiO}_3(\text{re})$	$\text{MgSiO}_3(\text{re})$	$\text{MgSiO}_3(\text{re})$	$\text{MgSiO}_3(\text{re})$
0.002S	$\text{SiO}_2(\text{hqz})$	$\text{SiO}_2(\text{hqz})$	$\text{SiO}_2(\text{hcr})$	$\text{SiO}_2(\text{hcr})$	$\text{SiO}_2(\text{hcr})$
	(a)	(b)	(b)	(b)	(b)

* Cord: Cordierite.

** S: H_2S for Fixed-Bed, Fluid-Bed, and Entrained-Bed Gasification.
 SO_2 for Direct Coal Fired Turbines and Pressurized Fluidized Bed Combustion.

(a) $\text{Na}_2\text{Al}_2\text{Si}_6\text{O}_{16}(1)$.

(b) $\text{Na}_2\text{Al}_2\text{Si}_6\text{O}_{16}(2)$.

TABLE 3.29

PROJECTED CONDENSED PHASES RESULTING FROM THE REACTION
OF SILICON NITRIDE WITH SODIUM AND SULFUR
AT FILTER PROCESS CONDITIONS

Process	:Fixed-Bed : <----- Gasification -----> :	:Fluid-Bed : :	:Entrained-Bed : :	: Direct Coal : Fired : Turbines	: Pressurized : Fluidized : Bed : Combustion
Temp., °C	: 590	: 700	: 870	: 980	: 870
Press.,	:	:	:	:	:
atm	: 20	: 20	: 30	: 12	: 10
Moles/Phase	:	:	:	:	:
0.999SN*	:Si ₃ N ₄ (a)	:Si ₃ N ₄ (a)	: SiO ₂ (hcr)	: Si ₃ N ₄ (a)	: Si ₃ N ₄ (a)
0.001NaCl	:SiO ₂ (hqz)	:SiO ₂ (hqz)	: (a)	: SiO ₂ (hcr)	: SiO ₂ (hcr)
--- S**	:NaCl	:NaCl	:	: C(gr)	: C(gr)
	:	:	:	:	: NaCl(l)
0.990SN	:Si ₃ N ₄ (a)	:Si ₃ N ₄ (a)	: SiO ₂ (hcr)	: Si ₃ N ₄ (a)	: Si ₃ N ₄ (a)
0.010NaCl	:SiO ₂ (hqz)	:SiO ₂ (hqz)	: (a)	: SiO ₂ (hcr)	: SiO ₂ (hcr)
--- S	:NaCl	:NaCl	:	: NaCl(l)	: NaCl(l)
	:	:	:	: C(gr)	: C(gr)
0.999SN	:Si ₃ N ₄ (a)	:Si ₃ N ₄ (a)	: SiO ₂ (hcr)	: Si ₃ N ₄ (a)	: Si ₃ N ₄ (a)
0.001NaCl	:SiO ₂ (hqz)	:SiO ₂ (hqz)	: (a)	: SiO ₂ (hcr)	: SiO ₂ (hcr)
0.002S	:NaCl	:NaCl	:	: C(gr)	: C(gr)
	:	:	:	:	: NaCl(l)
0.990SN	:Si ₃ N ₄ (a)	:Si ₃ N ₄ (a)	: SiO ₂ (hcr)	: Si ₃ N ₄ (a)	: Si ₃ N ₄ (a)
0.010NaCl	:SiO ₂ (hqz)	:SiO ₂ (hqz)	: (a)	: SiO ₂ (hcr)	: SiO ₂ (hcr)
0.002S	:NaCl	:NaCl	:	: NaCl(l)	: NaCl(l)
	:	:	:	: C(gr)	: C(gr)

* SN: Silicon Nitride.

** S: H₂S for Fixed-Bed, Fluid-Bed, and Entrained-Bed Gasification.
SO₂ for Direct Coal Fired Turbines and Pressurized Fluidized Bed Combustion.

(a) Na₂Si₂O₅(3).

With sulfur present in the effluent gases, sodium is project to:

- Condense as solid NaCl in the low temperature fixed-bed and fluid-bed gasification system.
- Be driven initially into the alumina lattice forming solid β -NaAlO₂ in the higher temperature entrained-bed gasification process. This reaction, as well as deposition of liquid sodium chloride results as the process sodium concentrations are increased.
- Condense as liquid Na₂SO₄ in the direct coal fired turbine system, and as solid Na₂SO₄ in the pressurized fluidized-bed combustion system.

The relatively high sodium concentrations used in these calculations represent long-term exposure of an alumina filter to process gases. The thermodynamic equilibrium calculations indicate that under fixed-bed gasification conditions, sodium is retained within the sodium chloride phase to temperatures between 1000 and 1100K (1340 and 1520°F) prior to being partitioned into the liquid NaCl phase and the solid β -NaAlO₂ phase. Liquid NaCl is retained within the fixed-bed gasification system to temperatures between 1200 and 1300K (1700 and 1880°F), while β -NaAlO₂ is retained within the system to temperatures between 1300 and 1400K (1880 and 2080°F).

In equilibrium with these solid phases, NaCl is projected as the principal gas phase species, with minor contributions of dimeric sodium chloride (Na₂Cl₂), NaOH, and Na at elevated operating temperatures. Chloride is partitioned between the condensed and gas phase alkali chlorides and HCl. Similarly, in the fixed-bed gasification process, sulfur is partitioned between H₂S and COS.

Similar phases are projected to result in the fluid-bed and entrained-bed gasification systems.

In the direct coal fired turbine system, sodium reacts with sulfur to form solid sodium sulfate up to temperatures between 1100 and 1200K (1520 and 1700°F). At higher process temperatures, liquid sodium sulfate is projected as a stable phase. Sodium in the direct coal fired turbine system is not driven into the alumina structure. Alternately at temperatures below 900K (1160°F), solid aluminum sulfate $[Al_2(SO_4)_3]$ may be formed.

In equilibrium with the direct coal fired turbine condensed phases, sodium exists as principally gaseous NaCl at elevated temperature [$>1200K$ (1700°F)] with minor contributions of NaOH, Na_2Cl_2 , and Na_2SO_4 . Sulfur is partitioned between the condensed sodium sulfate complexes and the volatile SO_2 , SO_3 , and H_2SO_4 species. Chloride is partitioned between volatile HCl, NaCl, Cl_2 , and Cl.

Similar phases and transitions are projected for the reaction of alumina with sodium and sulfur in the pressurized fluidized-bed combustion system.

Mullite ($3Al_2O_3 \cdot 2SiO_2$)

Mullite is projected to be thermally stable when exposed to nitrogen at cross-flow filter temperatures and pressures in the fixed-bed, fluid-bed, and entrained-bed gasification, direct coal fired turbine, and pressurized fluidized-bed combustion systems.

In the absence of sulfur or sodium, the stability of mullite is projected to be maintained during exposure to process gases at filter operating temperatures and pressures.

Without sulfur in the various process gases, sodium is projected to:

- Be driven into the mullite lattice, forming solid sodium aluminosilicate ($Na_2Al_2Si_2O_{10}$) in all process systems as shown in the following reaction:

A phase transition in the solid sodium aluminosilicate structure is projected between 900 and 1000K (1160 and 1340°F). Unlike alumina, the silica structure in mullite actively reacts with sodium.

With sulfur present in the process gases, sodium is projected to:

- Be driven into the solid sodium aluminosilicate phase of the mullite structure in the fixed-bed, fluid-bed, and entrained-bed gasification systems.
- React with sulfur, forming liquid sodium sulfate in the direct coal fired turbine system, and solid sodium sulfate in the pressurized fluidized-bed combustion system. Sodium is not driven into the mullite structure in either of these systems.

At temperatures between 700 and 800K (800 and 980°F) in the fixed-bed gasification system, sodium is driven into the aluminosilicate lattice, forming solid sodium aluminosilicate ($\text{Na}_2\text{Al}_2\text{Si}_8\text{O}_{18}$). A phase transition in the sodium aluminosilicate structure occurs between 900 and 1000K (1160 and 1340°F). A further transition is projected to occur between 1300 and 1400K (1880 and 2060°F) in which sodium is transformed into a liquid sodium silicate phase ($\text{Na}_2\text{Si}_2\text{O}_5$).

In the direct coal fired turbine, sodium initially forms solid sodium sulfate. At process temperatures of 1200K (1700°F), liquid sodium sulfate forms. The potential exists for conversion of sodium sulfate into the sodium aluminosilicate complex between 1200 and 1300K (1700 and 1880°F). At higher temperatures [1300-1400K (1880-1127°F)], the predominant sodium complex is again the liquid sulfate structure.

Cordierite ($\text{Mg}_2\text{Al}_4\text{Si}_5\text{O}_{18}$)

In nitrogen, the equilibrium phases which are projected to result for cordierite at fixed-bed, fluid-bed, and entrained-bed gasification, and pressurized fluidized-bed combustion process temperatures and pressures include $\text{Al}_2\text{Si}_2\text{O}_5$, MgSiO_3 , and SiO_2 . Under direct coal fired turbine conditions, $\text{Al}_6\text{Si}_2\text{O}_{13}$, MgSiO_3 , and SiO_2 are projected to result as stable solids. Using the NASA CET86 thermodynamic data base, cordierite is not identified at equilibrium as the stable solid phase.

Assuming that the mixed oxide solution (Al_2SiO_5 , MgSiO_3 , and SiO_2 as projected by the NASA CET86 code) represents cordierite, multiple phase transitions are shown to occur within the magnesium silicate and silicon dioxide structures as a function of process temperature. These transitions include:

An additional phase transition is considered to occur between 1143 and 1253K (1598 and 1796°F) which produces mullite ($\text{Al}_6\text{Si}_2\text{O}_{13}$) from the aluminosilicate (Al_2SiO_5) lattice. Since cordierite is fabricated at temperatures which exceed cross-flow filter process temperatures, the phase transitions which were just described are assumed to have occurred during fabrication. Calculations at 1673-1873K (2552-2912°F) were not performed to verify the actual formation of the cordierite structure. Assuming that the phases generated under the nitrogen environment are representative of cordierite, any further change (i.e., reactions or phase transitions) which is projected to result could occur due to the

*cl = clinoenstatite; re = rhombic enstatite; pr = protoenstatite;
lqz = low quartz; hqz = high quartz; hcr = cristobalite.

interaction of the solid phases with either the bulk gases or the inclusion of sodium and/or sulfur species.

In the absence of sulfur in the process gases, sodium is projected to:

- Be driven into a solid sodium aluminosilicate structure for all process systems. The affinity to drive sodium into the lattice is greater under direct coal fired turbine and pressurized fluidized-bed combustion conditions in comparison to the reactions which are projected to result under the gasification environments. The sodium aluminosilicate phase coexists with Al_2SiO_5 in the pressurized fluidized-bed combustion system, or with the mullite structure which forms in the direct coal fired turbine system.
- Undergo a phase transition in the solid sodium aluminosilicate lattice between temperatures of 863 and 973K (1094 and 1292°F), similar to the phase transitions explored for mullite.

Similar phases and reactions are projected when sulfur is present in the process gases.

Silicon Nitride (Si_3N_4)

In a nitrogen environment, silicon nitride is projected to be thermally stable for all cross-flow filter operating temperatures and pressures. For a system in which the gas to silicon nitride mole ratio is set equal to 2, silicon nitride is projected to be partially converted into an oxide in the fixed-bed, fluid-bed, and entrained-bed gasification system. A transition from the quartz to cristobalite structure is expected as shown in the following reaction:

In the direct coal fired turbine and pressurized fluidized-bed combustion system for a gas to silicon nitride mole ratio of 2, both the silicon nitride and oxide are projected to coexist with carbon deposits. This is considered to reflect reactions at the gas/ceramic interface which form a locally reducing environment within the immediate vicinity of the ceramic filter surface.

In the absence of process gas sulfur, sodium is projected to:

- Form solid NaCl over the $\text{Si}_3\text{N}_4/\text{SiO}_2$ substrate in the fixed-bed and fluid-bed gasification systems.
- Form sodium silicate (Na_2SiO_3) over SiO_2 in the entrained-bed gasification system. Complete conversion of silicon nitride to the oxide structure is principally the result of the higher operating temperatures.
- Form liquid NaCl and carbon deposits over $\text{Si}_3\text{N}_4/\text{SiO}_2$ in the direct coal fired turbine and pressurized fluidized-bed combustion systems.

Similar reactions are projected to result when sulfur is present in the process gases. In these calculations the gas to silicon nitride mole ratio was set equal to 2. Due to the locally reducing environment formed at the silicon nitride surface during oxidation, sodium is not converted into condensed sulfate complexes.

In the fixed-bed and fluid-bed gasification systems, silicon nitride is present as a stable solid phase in equilibrium with quartz to temperatures of 1000-1100K (1340-1520°F). Conversion of quartz to the cristobalite phase at temperatures >1100K (1520°F) reduces the stability of the silicon nitride filter matrix. These reactions are also projected for the entrained-bed gasification system, however, the extent of conversion to the oxide phase is greater than in the fixed-bed or fluid-bed gasification systems due principally to the higher filter operating temperature in the entrained-bed gasification system. If the fixed-bed, fluid-bed, or

entrained-bed gasification systems were operated to temperatures $>1100\text{K}$ ($>1520^\circ\text{F}$), sodium is expected to be driven into a solid sodium silicate ($\text{Na}_2\text{Si}_2\text{O}_5$) phase. At temperatures between 1100 and 1200K (1520 and 1700°F), the solid $\text{Na}_2\text{Si}_2\text{O}_5$ phase melts forming a liquid. Due to the locally reducing environment generated by carbon deposition in the direct coal fired turbine and pressurized fluidized-bed combustion systems, sodium is not driven into the silicate lattice.

An additional series of calculation was performed using SOLGASMIX to demonstrate whether SiO_2 , if formed along the pores or surfaces of the silicon nitride grains, would remain as a stable phase at filter process conditions, or whether it would undergo volatilization. Two subsequent series of calculations were performed to similarly demonstrate the stability of Si_2ON_2 and Si_3N_4 in the process gas environments.

In the initial series of calculations, Si_2ON_2 and Si_3N_4 were not permitted to exist as possible equilibrium phases. Given this constraint, SOLGASMIX projected the formation and stability of the solid SiO_2 phase in equilibrium with very low partial pressures of gaseous SiO , SiH_4 , and SiS for all process systems considered.

In the second series of calculations, both SiO_2 and Si_2ON_2 were permitted to form in the equilibrium solution. Similar to the initial series of calculations, if Si_2ON_2 were to form in the various gasification and combustion environments, it would remain as a stable phase. The partial pressures of the volatile silicon compounds over the oxynitride phase were, however, projected to be higher ($<10^{-10}$ atm) than the partial pressures projected over SiO_2 .

In the third series of calculations, SiO_2 , Si_2ON_2 , and Si_3N_4 were permitted to form in the equilibrium solution. In this system both Si_2ON_2 and Si_3N_4 were projected to coexist as stable solid phases in the gasification and combustion environments. With the exception of gaseous SiS , very low partial pressures of gaseous silicon phases were projected to

be in equilibrium with the $\text{Si}_2\text{ON}_2/\text{Si}_3\text{N}_4$ solids. The partial pressure of SiS in the fluid-bed gasifier was projected at 10^{-8} atm; in the entrained-bed gasifier at 10^{-5} atm; in the direct coal fired turbine at 10^{-3} atm; and in the pressurized fluidized-bed combustion system at 10^{-3} atm. The formation of gaseous SiS, in the absence of volatile chlorides (i.e., HCl) and alkali (i.e., NaCl and KCl), could potentially pose stability problems for the Si_3N_4 filter material during process operations.

A final series of calculations was performed using the NASA CET86 program to demonstrate the stability of Si_3N_4 in pressurized fluidized-bed combustion gases which not only contained chloride, but also 20 ppb gas phase alkali. The following volatile silicon-containing species were included in this set of calculations:

Si, SiC, SiC_2 , $\text{SiC}_4\text{H}_{12}$, SiCl, SiCl_2 , SiCl_3 , SiCl_4 ,
 SiH, SiH_4 , SiHCl_3 , SiH_2Cl , SiH_2Cl_2 , SiN, Si_2 , Si_3 ,
 SiO, SiS, Si_2C , Si_2N .

The calculations were designed to simulate reactions at the Si_3N_4 /gas phase interface, using a gas-to-solid phase mole ratio of 1. Under these conditions, complete oxidation of Si_3N_4 filter material is not projected to occur. At 870°C (1600°F), the principal volatile species formed over the $\text{SiO}_2/\text{Si}_3\text{N}_4$ matrix at systems pressures between 1 and 20 atm include:

SiS, SiO, SiH_2Cl_2 , SiHCl_3 , and SiCl_2 .

Although the equilibrium calculations project oxidation and volatilization of the Si_3N_4 surface, data reported in the literature indicate that the kinetics for the oxidation reactions is limited at systems temperatures below 1000°C (1830°F). Experimental verification will be needed to demonstrate whether the presence of chlorides in the process gas environment promotes oxidation and/or volatilization of the Si_3N_4 filter matrix at the relatively low filter operating temperatures.

3.1.3.3 Projected Char and Ash Fines Reactions with Ceramic Cross-Flow Filter Material Phases

The atomic absorption analysis of the New York University pressurized fluidized-bed combustor ash (Section 3.1.2.2) was used in the thermodynamic equilibrium calculations in an attempt to identify possible interactions of the elemental constituents present in the ash fines with the various phases present in the cross-flow filter materials. A 10:1 weight ratio of ceramic [i.e., alumina (Al_2O_3), mullite ($\text{Al}_6\text{Si}_2\text{O}_{13}$), cordierite ($\text{Mg}_2\text{Al}_4\text{Si}_5\text{O}_{18}$), silicon nitride (Si_3N_4)] to ash fines was considered in this set of calculations. Table 3.30 summarizes the projected ash/ceramic interactions in a pressurized fluidized-bed combustion system operating at 870°C (1600°F) and 10 atm.

The reaction of alumina (Al_2O_3) in the cross-flow filters with the SiO_2 or MgO present in the pressurized fluidized-bed combustor ash fines is projected to lead to the formation of $\text{Al}_6\text{Si}_2\text{O}_{13}$ and MgAl_2O_4 . In these calculations, alkali which is present in the ash fines is not projected to be driven into the aluminosilicate phase. Once deposited along the ceramic filter surface and equilibrium has been achieved, sodium and potassium present in the ash fines have the potential to be converted into a corresponding solid sulfate. Similarly, alumina, calcium sulfate, and iron oxide are not projected to react with the cross-flow filter alumina phase.

When the pressurized fluidized bed combustion ash contacts cross-flow filters made of mullite ($\text{Al}_6\text{Si}_2\text{O}_{13}$), magnesium and sodium within the ash fines have the potential to react with the filter matrix and form MgAl_2O_4 , MgSiO_3 , and $\text{Na}_2\text{Al}_2\text{Si}_5\text{O}_{18}$. If equilibrium is achieved, a portion of the sodium and potassium present in the ash fines is projected to be converted into solid sulfates. Ash phase alumina, calcium sulfate, and iron oxide are not projected to react with the mullite phase of the cross-flow filter element.

TABLE 3.30

THERMODYNAMICALLY PROJECTED STABLE SOLID PHASES
RESULTING FROM THE REACTION OF ASH FINES WITH
CERAMIC CROSS-FLOW FILTER MATERIAL PHASES

Ash: Fines Generated at the New York
University Pressurized Fluidized
Bed Combustor
Temperature: 870°C (1600°F)
Pressure: 10 atm

Filter Material Phase	Alumina Al_2O_3	Mullite $\text{Al}_6\text{Si}_2\text{O}_{13}$	Cordierite $\text{Mg}_2\text{Al}_4\text{Si}_5\text{O}_{18}$	Silicon Nitride Si_3N_4
NYU Ash Constituent:				
Al_2O_3	Al_2O_3	$\text{Al}_6\text{Si}_2\text{O}_{13}$	Al_2SiO_5 MgSiO_3 SiO_2	Si_3N_4 SiO_2 Al_2SiO_5 C
SiO_2	Al_2O_3 $\text{Al}_6\text{Si}_2\text{O}_{13}$	$\text{Al}_6\text{Si}_2\text{O}_{13}$ SiO_2	Al_2SiO_5 MgSiO_3 SiO_2	Si_3N_4 SiO_2 C
Fe_2O_3	Al_2O_3 Fe_2O_3	$\text{Al}_6\text{Si}_2\text{O}_{13}$ Fe_2O_3 SiO_2	Al_2SiO_5 MgSiO_3 SiO_2 Fe_2O_3	Si_3N_4 SiO_2 FeS Fe C
CaSO_4	Al_2O_3 CaSO_4	$\text{Al}_6\text{Si}_2\text{O}_{13}$ CaSO_4 SiO_2	Al_2SiO_5 MgSiO_3 SiO_2 CaSO_4	Si_3N_4 SiO_2 CaS C
MgO	Al_2O_3 MgAl_2O_4	$\text{Al}_6\text{Si}_2\text{O}_{13}$ MgAl_2O_4 MgSiO_3	Al_2SiO_5 MgSiO_3 SiO_2	Si_3N_4 SiO_2 MgSiO_3 MgS C
Na_2O	Al_2O_3 Na_2SO_4	$\text{Al}_6\text{Si}_2\text{O}_{13}$ $\text{Na}_2\text{Al}_2\text{Si}_2\text{O}_{10}$ Na_2SO_4	Al_2SiO_5 MgSiO_3 SiO_2 $\text{Na}_2\text{Al}_2\text{Si}_2\text{O}_{10}$	Si_3N_4 SiO_2 $\text{Na}_2\text{Si}_2\text{O}_5$ $\text{NaCl}(1)$ C
K_2O	Al_2O_3 K_2SO_4	$\text{Al}_6\text{Si}_2\text{O}_{13}$ K_2SO_4 SiO_2	Al_2SiO_5 MgSiO_3 SiO_2 K_2SO_4	Si_3N_4 SiO_2 $\text{K}_2\text{Si}_2\text{O}_5(1)$ C

When the NASA CET86 thermodynamic database is used, cordierite ($\text{Mg}_2\text{Al}_4\text{Si}_5\text{O}_{18}$) is projected to exist as Al_2SiO_5 , MgSiO_3 , and SiO_2 . Alumina in the ash fines is projected to react with the cordierite matrix and form Al_2SiO_5 ; magnesium (MgO) is projected to react and form MgSiO_3 , while calcium sulfate and iron oxide are projected to remain inert. Potassium (K_2O) in the fines is projected to be converted into a solid sulfate phase at equilibrium, while sodium is projected to be driven into the ceramic matrix, forming $\text{Na}_2\text{Al}_2\text{Si}_2\text{O}_{10}$.

In the 870°C (1600°F), 10 atm pressurized fluidized-bed combustion environment, silicon nitride (Si_3N_4) has the affinity to be partially converted into SiO_2 . Alumina from the ash fines appears to have the potential to "dissolve" into the SiO_2 layer and form Al_2SiO_5 . Free SiO_2 in the ash has the potential to increase the SiO_2 concentration at the ash/ceramic interface. Magnesium (MgO) present in the ash is projected to form both MgSiO_3 and MgS , while calcium sulfate at the ash/ceramic interface is projected to be converted into calcium sulfide. Sodium within the ash fines is projected to be partitioned between reactions which drive sodium into the SiO_2 layer, forming $\text{Na}_2\text{Si}_2\text{O}_6$, and reactions with gas phase chloride which lead to the formation of liquid NaCl . Potassium is similarly projected to be driven into the SiO_2 layer, forming liquid $\text{K}_2\text{Si}_4\text{O}_9$. Iron oxide is projected to be reduced to FeS and elemental iron at the $\text{SiO}_2/\text{Si}_3\text{N}_4$ interface. At equilibrium carbon is projected to form at the $\text{Si}_3\text{N}_4/\text{ash}$ interface.

In summary, the data presented in Table 3.30 indicate that:

- In contrast with alumina, mullite, and cordierite, multiple reactions of the elemental constituents present in the ash fines are expected to occur within the SiO_2 layer of the Si_3N_4 matrix, not only forming complex silicates, but also liquid phases (i.e., NaCl and $\text{K}_2\text{Si}_4\text{O}_9$).

- If magnesium were present as MgO in the ash fines, reactions leading to the formation of $MgSiO_3$ are projected to occur with each filter matrix.
- In the presence of gas phase sulfur (SO_2) and chloride (HCl), and a high Al/Si mole ratio (i.e., alumina) in the oxide ceramic filter material phase, sodium is projected to be retained with the ash, and be converted into solid Na_2SO_4 .
- In the presence of gas phase sulfur (SO_2) and chloride (HCl), and a low Al/Si mole ratio (i.e., cordierite) in the oxide ceramic filter material phases, sodium is projected to be driven into the filter matrix forming a complex aluminosilicate ($Na_2Al_2Si_6O_{18}$).
- Alkali which is present in ash fines and which contacts the non-oxide ceramic surface (i.e., reaction bonded silicon nitride) has the potential to form a silicate phase. At pressurized fluidized-bed combustion temperatures, potassium silicate is projected as a liquid phase, while sodium silicate is projected as a solid phase. Sodium which is present in the ash fines is also expected to react with gas phase chloride and form liquid $NaCl$.

Tables 3.31 through 3.40 illustrate the potential reaction products that are projected to form at equilibrium as a result of the interaction of the various constituents in the char or ash fines with the various phases present in the ceramic materials. Based on these calculations which utilize the NASA CET86 thermodynamic data, subtle differences in the fines/ceramic reaction products are projected to exist. They are as follows:

TABLE 3.31

**THERMODYNAMICALLY PROJECTED STABLE SOLID PHASES
RESULTING FROM THE REACTION OF CHAR FINES WITH
CERAMIC CROSS-FLOW FILTER MATERIAL PHASES IN
FIXED-BED GASIFICATION SYSTEMS**

Ash: Fines Generated at the KRW Fluid
Bed Gasifier

Temperature: 590°C (1094°F)

Pressure: 1, 5, 10, 15, 20 atm

Filter Material Phase	Al_2O_3	$Al_6Si_2O_{13}$	$Mg_2Al_4Si_5O_{18}$	Si_3N_4
KRW Char Constituent:				
C	Al_2O_3	Al_2SiO_5 Al_2O_3	Al_2SiO_5 $MgSiO_3$ SiO_2 $Mg_2Al_4Si_5O_{18}$ (b)	Si_3N_4 SiO_2
Al_2O_3	Al_2O_3	Al_2SiO_5 Al_2O_3	Al_2SiO_5 $MgSiO_3$ SiO_2 $Mg_2Al_4Si_5O_{18}$ (b)	Si_3N_4 SiO_2 Al_2SiO_5
SiO_2	Al_2O_3 Al_2SiO_5	Al_2SiO_5 Al_2O_3	Al_2SiO_5 $MgSiO_3$ SiO_2 $Mg_2Al_4Si_5O_{18}$ (b)	Si_3N_4 SiO_2
Fe_2O_3	Al_2O_3 $FeAl_2O_4$	Al_2SiO_5 Al_2O_3 $FeAl_2O_4$	Al_2SiO_5 $MgSiO_3$ SiO_2 $Mg_2Al_4Si_5O_{18}$ (b) $FeAl_2O_4$	Si_3N_4 SiO_2 Fe_2O_3
CaO	Al_2O_3 $CaAl_2O_4$	Al_2SiO_5 Al_2O_3 $CaAl_2O_4$	Al_2SiO_5 $MgSiO_3$ SiO_2 $Mg_2Al_4Si_5O_{18}$ (b) $CaMgSi_2O_8$	Si_3N_4 SiO_2 CaS
MgO	Al_2O_3 $MgAl_2O_4$	Al_2SiO_5 Al_2O_3 $MgAl_2O_4$	Al_2SiO_5 $MgSiO_3$ SiO_2 $Mg_2Al_4Si_5O_{18}$ (b)	Si_3N_4 SiO_2 $MgS(d)$ $MgSiO_3(d)$
Na_2O (Gas Phase Chloride)	Al_2O_3 $NaCl$	Al_2SiO_5 Al_2O_3 $Mg_2Al_4Si_5O_{18}$	Al_2SiO_5 $MgSiO_3$ SiO_2 $Mg_2Al_4Si_5O_{18}$	Si_3N_4 SiO_2 $NaCl$
Na_2O (No Gas Phase Chloride)	Al_2O_3 $NaAlO_2$	Al_2SiO_5 Al_2O_3 $Mg_2Al_4Si_5O_{18}$	Al_2SiO_5 $MgSiO_3$ SiO_2 $Mg_2Al_4Si_5O_{18}$	Si_3N_4 SiO_2 $Na_2SiO_3(e)$ $Na_2S(f)$
K_2O (Gas Phase Chloride)	Al_2O_3 KCl	Al_2SiO_5 Al_2O_3 $KCl(a)$ $K_2Al_2Si_2O_8$	Al_2SiO_5 $MgSiO_3$ SiO_2 $KCl(c)$ $K_2Al_2Si_2O_8$ $Mg_2Al_4Si_5O_{18}$ (b)	Si_3N_4 SiO_2 KCl
K_2O (No Gas Phase Chloride)	Al_2O_3 K_2CO_3 $KAlO_2$	Al_2SiO_5 Al_2O_3 $K_2Al_2Si_2O_8$ $Mg_2Al_4Si_5O_{18}$	Al_2SiO_5 $MgSiO_3$ SiO_2 KCl $K_2Al_2Si_2O_8$ $Mg_2Al_4Si_5O_{18}$ (b)	Si_3N_4 SiO_2 $Na_2SiO_3(f)$ $Na_2S(g)$ $K_2Si_2O_7$

(a) KCl (a): Present at 10, 15, 20 atm.

(b) $Mg_2Al_4Si_5O_{18}$ (b): Present at 5, 10, 15, 20 atm.

(c) KCl (c): Present at 20 atm.

(d) MgS (d): Present at 1 atm; $MgSiO_3$ (d): Present at 5, 10, 15, 20 atm.

(e) Na_2S (e): Present at 1, 5 atm; $Na_2Si_2O_5$ (e): Present at 10, 15, 20 atm.

(f) Na_2S (f): Present at 5 atm; $Na_2Si_2O_5$ (f): Present at 10, 15, 20 atm.

TABLE 3.32

**THERMODYNAMICALLY PROJECTED STABLE SOLID PHASES
RESULTING FROM THE REACTION OF CHAR FINES WITH
CERAMIC CROSS-FLOW FILTER MATERIAL PHASES IN
FLUID-BED GASIFICATION SYSTEMS**

Ash: Fines Generated at the KRW Fluid
Bed Gasifier
Temperature: 700°C (1292°F)
Pressure: 1, 5, 10, 15, 20 atm

Filter Material Phase	Al_2O_3	$\text{Al}_6\text{Si}_2\text{O}_{13}$	$\text{Mg}_2\text{Al}_4\text{Si}_5\text{O}_{18}$	Si_3N_4
KRW Char Constituent:				
C	Al_2O_3	Al_2SiO_5 Al_2O_3	Al_2SiO_5 MgSiO_3 SiO_2	Si_3N_4 SiO_2 C(c)
Al_2O_3	Al_2O_3	Al_2SiO_5 Al_2O_3	Al_2SiO_5 MgSiO_3 SiO_2	Si_3N_4 SiO_2 Al_2SiO_5 C(c)
SiO_2	Al_2O_3 Al_2SiO_5	Al_2SiO_5 Al_2O_3	Al_2SiO_5 MgSiO_3 SiO_2	Si_3N_4 SiO_2 C(c)
Fe_2O_3	Al_2O_3 FeAl_2O_4	Al_2SiO_5 Al_2O_3 FeAl_2O_4	Al_2SiO_5 FeAl_2O_4 MgSiO_3 SiO_2	Si_3N_4 SiO_2 FeSiO_2 C(c)
CaSO_4	Al_2O_3 CaAl_2O_7	Al_2SiO_5 Al_2O_3 $\text{CaAl}_2\text{Si}_2\text{O}_8$	Al_2SiO_5 MgSiO_3 SiO_2 $\text{CaAl}_2\text{Si}_2\text{O}_8$	Si_3N_4 SiO_2 CaS C(c)
MgO	Al_2O_3 MgAl_2O_4	Al_2SiO_5 Al_2O_3 MgAl_2O_4	Al_2SiO_5 MgSiO_3 SiO_2	Si_3N_4 SiO_2 MgSiO_3 C(c)
Na_2O (Gas Phase Chloride)	Al_2O_3 NaCl(a)	Al_2SiO_5 Al_2O_3 $\text{Na}_2\text{Al}_2\text{Si}_6\text{O}_{18}$	Al_2SiO_5 MgSiO_3 SiO_2 $\text{Na}_2\text{Al}_2\text{Si}_6\text{O}_{18}$	Si_3N_4 SiO_2 C(c) NaCl(a)
Na_2O (No Gas Phase Chloride)	Al_2O_3 NaAlO ₂	Al_2SiO_5 Al_2O_3 $\text{Na}_2\text{Al}_2\text{Si}_6\text{O}_{18}$	Al_2SiO_5 MgSiO_3 SiO_2 $\text{Na}_2\text{Al}_2\text{Si}_6\text{O}_{18}$	Si_3N_4 SiO_2 C(c) $\text{Na}_2\text{Si}_2\text{O}_5$
K_2O (Gas Phase Chloride)	Al_2O_3 KCl(b)	Al_2SiO_5 Al_2O_3 $\text{K}_2\text{Al}_2\text{Si}_2\text{O}_8$	Al_2SiO_5 MgSiO_3 SiO_2 $\text{K}_2\text{Al}_2\text{Si}_2\text{O}_8$	Si_3N_4 SiO_2 C(c) KCl(b)
K_2O (No Gas Phase Chloride)	Al_2O_3 K_2CO_3	Al_2SiO_5 Al_2O_3 $\text{K}_2\text{Al}_2\text{Si}_2\text{O}_8$	Al_2SiO_5 MgSiO_3 SiO_2 $\text{K}_2\text{Al}_2\text{Si}_2\text{O}_8$	Si_3N_4 SiO_2 C(c) $\text{K}_2\text{Si}_4\text{O}_9$

(a) NaCl (s): Present at 10, 15, 20 atm.

(b) KCl (s): Present at 5, 10, 15, 20 atm.

(c) C (s): Present at 1 atm.

TABLE 3.33

THERMODYNAMICALLY PROJECTED STABLE SOLID PHASES
 RESULTING FROM THE REACTION OF CHAR FINES WITH
 CERAMIC CROSS-FLOW FILTER MATERIAL PHASES IN
 ENTRAINMENT-BED GASIFICATION SYSTEMS

Ash: Fines Generated at the KRW Fluid
 Bed Gasifier

Temperature: 870°C (1600°F)

Pressure: 1, 5, 10, 15, 20, 30 atm

Filter Material Phase	Al_2O_3	$\text{Al}_6\text{Si}_2\text{O}_{13}$	$\text{Mg}_2\text{Al}_4\text{Si}_5\text{O}_{18}$	Si_3N_4
KRW Char Constituent:				
C	Al_2O_3	$\text{Al}_6\text{Si}_2\text{O}_{13}$	Al_2SiO_5 MgSiO_3 SiO_2	Si_3N_4 SiO_2 C(a)
Al_2O_3	Al_2O_3	$\text{Al}_6\text{Si}_2\text{O}_{13}$ Al_2O_3	Al_2SiO_5 MgSiO_3 SiO_2	Si_3N_4 SiO_2 Al_2SiO_5 C(a)
SiO_2	Al_2O_3 $\text{Al}_6\text{Si}_2\text{O}_{13}$	$\text{Al}_6\text{Si}_2\text{O}_{13}$ Al_2SiO_5	Al_2SiO_5 MgSiO_3 SiO_2	Si_3N_4 SiO_2 C(a)
Fe_2O_3	Al_2O_3 FeAl_2O_4	$\text{Al}_6\text{Si}_2\text{O}_{13}$ Al_2SiO_5 FeAl_2O_4	Al_2SiO_5 MgSiO_3 SiO_2 FeAl_2O_4	Si_3N_4 SiO_2 Fe_2O_3 C(a)
CaSO_4	Al_2O_3 CaAl_2O_7	$\text{Al}_6\text{Si}_2\text{O}_{13}$ Al_2O_3 $\text{CaAl}_2\text{Si}_2\text{O}_8$	Al_2SiO_5 MgSiO_3 SiO_2 $\text{CaAl}_2\text{Si}_2\text{O}_8$	Si_3N_4 SiO_2 CaS C(a)
MgO	Al_2O_3 MgAl_2O_4	$\text{Al}_6\text{Si}_2\text{O}_{13}$ Al_2SiO_5 MgAl_2O_4	Al_2SiO_5 MgSiO_3 SiO_2	Si_3N_4 SiO_2 MgSiO_3 C(a)
Na_2O	Al_2O_3	$\text{Al}_6\text{Si}_2\text{O}_{13}$ Al_2O_3 $\text{Na}_2\text{Al}_2\text{Si}_6\text{O}_{18}$	Al_2SiO_5 MgSiO_3 SiO_2 $\text{Na}_2\text{Al}_2\text{Si}_6\text{O}_{18}$	Si_3N_4 SiO_2 C(a)
K_2O	Al_2O_3	$\text{Al}_6\text{Si}_2\text{O}_{13}$ Al_2O_3 $\text{K}_2\text{Al}_2\text{Si}_2\text{O}_8$	Al_2SiO_5 MgSiO_3 SiO_2 $\text{K}_2\text{Al}_2\text{Si}_2\text{O}_8$	Si_3N_4 SiO_2 C(a)

(a) C (s): Present at 1 and 5 atm.

TABLE 3.34

THERMODYNAMICALLY PROJECTED STABLE SOLID PHASES
 RESULTING FROM THE REACTION OF CHAR FINES WITH
 CERAMIC CROSS-FLOW FILTER MATERIAL PHASES IN
 DIRECT COAL FIRED TURBINE SYSTEMS

Ash: Fines Generated at the KRW Fluid
 Bed Gasifier
 Temperature: 980°C (1800°F)
 Pressure: 1, 5, 10, 12, 15, 20 atm

Filter Material Phase	Al_2O_3	$\text{Al}_6\text{Si}_2\text{O}_{13}$	$\text{Mg}_2\text{Al}_4\text{Si}_5\text{O}_{18}$	Si_3N_4
KRW Char Constituent:				
Al_2O_3	Al_2O_3	$\text{Al}_6\text{Si}_2\text{O}_{13}$	$\text{Al}_6\text{Si}_2\text{O}_{13}$ MgSiO_3 SiO_2	Si_3N_4 SiO_2 C $\text{Al}_6\text{Si}_2\text{O}_{13}$
SiO_2	Al_2O_3 $\text{Al}_6\text{Si}_2\text{O}_{13}$	$\text{Al}_6\text{Si}_2\text{O}_{13}$ SiO_2	$\text{Al}_6\text{Si}_2\text{O}_{13}$ MgSiO_3 SiO_2	Si_3N_4 SiO_2 C
Fe_2O_3	Al_2O_3 Fe_2O_3	$\text{Al}_6\text{Si}_2\text{O}_{13}$ Fe_2O_3 SiO_2	$\text{Al}_6\text{Si}_2\text{O}_{13}$ MgSiO_3 SiO_2 Fe_2O_3	Si_3N_4 SiO_2 FeS_2 Fe C
CaSO_4	Al_2O_3 CaSO_4	$\text{Al}_6\text{Si}_2\text{O}_{13}$ Al_2O_3 $\text{CaAl}_2\text{Si}_2\text{O}_8$ CaSO_4 (b)	$\text{Al}_6\text{Si}_2\text{O}_{13}$ $\text{CaAl}_2\text{Si}_2\text{O}_8$ CaSO_4 MgSiO_3 SiO_2 (d)	Si_3N_4 SiO_2 CaS_2 C
MgO	Al_2O_3 MgAl_2O_4	$\text{Al}_6\text{Si}_2\text{O}_{13}$ MgAl_2O_4 MgSiO_3	$\text{Al}_6\text{Si}_2\text{O}_{13}$ MgSiO_3 SiO_2	Si_3N_4 SiO_2 MgSiO_3 MgS C (e)
Na_2O	Al_2O_3 Na_2SO_4 (l) (a)	$\text{Al}_6\text{Si}_2\text{O}_{13}$ Al_2O_3 $\text{NaAl}_2\text{Si}_2\text{O}_8$ NaSO_4 (l) (c)	$\text{Al}_6\text{Si}_2\text{O}_{13}$ MgSiO_3 $\text{NaAl}_2\text{Si}_2\text{O}_8$ SiO_2	Si_3N_4 SiO_2 C
K_2O	Al_2O_3 K_2SO_4	$\text{Al}_6\text{Si}_2\text{O}_{13}$ K_2SO_4 SiO_2	$\text{Al}_6\text{Si}_2\text{O}_{13}$ K_2SO_4 MgSiO_3 SiO_2	Si_3N_4 SiO_2 C

(a) Na_2SO_4 (liquid): Present at 5, 10, 12, 15 atm.

(b) CaSO_4 (s): Present at 5, 10, 12, 15 atm;

$\text{CaAl}_2\text{Si}_2\text{O}_8$ (s): Present at 1 atm.

(c) Al_2O_3 (s): Present at 1, 5 atm;

Na_2SO_4 (liquid): Present at 10, 12, 15 atm.

(d) CaSO_4 (s): Present at 5, 10, 12, 15 atm;

$\text{CaAl}_2\text{Si}_2\text{O}_8$ (s): Present at 1, 5 atm.

(e) MgS (s): Present at 1, 5, 10, 12 atm;

MgSiO_3 (s): Present at 5, 10, 12, 15 atm.

TABLE 3.35

THERMODYNAMICALLY PROJECTED STABLE SOLID PHASES
 RESULTING FROM THE REACTION OF CHAR FINES WITH
 CERAMIC CROSS-FLOW FILTER MATERIAL PHASES IN
 PRESSURIZED FLUIDIZED-BED COMBUSTION SYSTEMS

Ash: Fines Generated at the KRW Fluid
 Bed Gasifier

Temperature: 870°C (1600°F)

Pressure: 1, 5, 10, 15, 20 atm

Filter Material Phase	Al_2O_3	$\text{Al}_6\text{Si}_2\text{O}_{13}$	$\text{Mg}_2\text{Al}_4\text{Si}_5\text{O}_{18}$	Si_3N_4
KRW Char Constituent:				
Al_2O_3	Al_2O_3	$\text{Al}_6\text{Si}_2\text{O}_{13}$ Al_2O_3	Al_2SiO_5 MgSiO_3 SiO_2	Si_3N_4 SiO_2 C^2 Al_2SiO_5
SiO_2	Al_2O_3 $\text{Al}_6\text{Si}_2\text{O}_{13}$	$\text{Al}_6\text{Si}_2\text{O}_{13}$ Al_2SiO_5	Al_2SiO_5 MgSiO_3 SiO_2	Si_3N_4 SiO_2 C^2
Fe_2O_3	Al_2O_3 Fe_2O_3	$\text{Al}_6\text{Si}_2\text{O}_{13}$ Fe_2O_3 SiO_2	Al_2SiO_5 Fe_2O_3 MgSiO_3 SiO_2	Si_3N_4 SiO_2 FeS^2 Fe C
CaSO_4	Al_2O_3 CaSO_4	$\text{Al}_6\text{Si}_2\text{O}_{13}$ CaSO_4 SiO_2 (a)	Al_2SiO_5 CaSO_4 MgSiO_3 SiO_2	Si_3N_4 SiO_2 CaS^2 C
MgO	Al_2O_3 MgAl_2O_4	$\text{Al}_6\text{Si}_2\text{O}_{13}$ MgAl_2O_4 MgSiO_3	Al_2SiO_5 MgSiO_3 SiO_2	Si_3N_4 SiO_2 MgSiO_3 MgS C (c)
Na_2O	Al_2O_3 Na_2SO_4	$\text{Al}_6\text{Si}_2\text{O}_{13}$ $\text{Na}_2\text{Al}_2\text{Si}_8\text{O}_{16}$ Al_2O_3 Na_2SO_4 (b)	Al_2SiO_5 MgSiO_3 $\text{Na}_2\text{Al}_2\text{Si}_8\text{O}_{16}$ SiO_2	Si_3N_4 SiO_2 C^2
K_2O	Al_2O_3 K_2SO_4	$\text{Al}_6\text{Si}_2\text{O}_{13}$ K_2SO_4 SiO_2	Al_2SiO_5 K_2SO_4 MgSiO_3 SiO_2	Si_3N_4 SiO_2 C^2

(a) SiO_2 (s): Present at 5, 10, 15, 20 atm.

(b) Al_2O_3 (s): Present at 1 atm;

Na_2SO_4 (s): Present at 5, 10, 15, 20 atm.

(c) MgS (s): Present at 1, 5, 10 atm;

MgSiO_3 (s): Present at 5, 10, 15, 20 atm.

TABLE 3.36

THERMODYNAMICALLY PROJECTED STABLE SOLID PHASES
RESULTING FROM THE REACTION OF ASH FINES WITH
CERAMIC CROSS-FLOW FILTER MATERIAL PHASES IN
FIXED-BED GASIFICATION SYSTEMS

Ash: Fines Generated at the NYU
Pressurized Fluidized Bed Combustor
Temperature: 590°C (1094°F)
Pressure: 1, 5, 10, 15, 20 atm

Filter Material Phase	Al_2O_3	$\text{Al}_6\text{Si}_2\text{O}_{13}$	$\text{Mg}_2\text{Al}_4\text{Si}_5\text{O}_{18}$	Si_3N_4
NYU Ash Constituent:				
Al_2O_3	Al_2O_3	Al_2SiO_5 Al_2O_3	Al_2SiO_5 MgSiO_3 SiO_2 $\text{Na}_2\text{Al}_2\text{Si}_6\text{O}_{18}$ (s)	Si_3N_4 SiO_2 Al_2SiO_5
SiO_2	Al_2O_3 Al_2SiO_5	Al_2SiO_5 Al_2O_3	Al_2SiO_5 MgSiO_3 SiO_2 $\text{Na}_2\text{Al}_2\text{Si}_6\text{O}_{18}$ (s)	Si_3N_4 SiO_2
Fe_2O_3	Al_2O_3 FeAl_2O_4	Al_2SiO_5 Al_2O_3 FeAl_2O_4	Al_2SiO_5 MgSiO_3 SiO_2 $\text{Na}_2\text{Al}_2\text{Si}_6\text{O}_{18}$ (s) FeAl_2O_4	Si_3N_4 SiO_2 FeS^2
CaSO_4	Al_2O_3 CaAl_2O_7	Al_2SiO_5 Al_2O_3 $\text{CaAl}_2\text{Si}_2\text{O}_8$	Al_2SiO_5 MgSiO_3 SiO_2 $\text{Na}_2\text{Al}_2\text{Si}_6\text{O}_{18}$ (s) $\text{CaMgSi}_2\text{O}_6$	Si_3N_4 SiO_2 CaS^2
MgO	Al_2O_3 MgAl_2O_4	Al_2SiO_5 Al_2O_3 MgAl_2O_4	Al_2SiO_5 MgSiO_3 SiO_2 $\text{Na}_2\text{Al}_2\text{Si}_6\text{O}_{18}$ (s)	Si_3N_4 SiO_2 MgS^2 MgSiO_3
Na_2O	Al_2O_3 NaAlO_2 NaCl	Al_2SiO_5 Al_2O_3 $\text{Na}_2\text{Al}_2\text{Si}_6\text{O}_{18}$	Al_2SiO_5 MgSiO_3 SiO_2 $\text{Na}_2\text{Al}_2\text{Si}_6\text{O}_{18}$	Si_3N_4 SiO_2 Na_2SiO_5 (c) Na_2S^2 (s) NaCl
K_2O	Al_2O_3 KCl K_2CO_3 NaAlO_2 (d)	Al_2SiO_5 Al_2O_3 KCl (e) $\text{K}_2\text{Al}_2\text{Si}_2\text{O}_8$	Al_2SiO_5 MgSiO_3 SiO_2 KCl (f) $\text{K}_2\text{Al}_2\text{Si}_2\text{O}_8$ $\text{Na}_2\text{Al}_2\text{Si}_6\text{O}_{18}$ (s)	Si_3N_4 SiO_2 KCl^2 $\text{K}_2\text{Si}_4\text{O}_9$

- (a) $\text{Na}_2\text{Al}_2\text{Si}_6\text{O}_{18}$ (s): Present at 5, 10, 15, 20 atm.
 (b) MgS (s): Present at 1 atm.
 (c) Na_2S (s): Present at 1, 5 atm; $\text{Na}_2\text{Si}_2\text{O}_5$ (s): Present at 10, 15, 20 atm.
 (d) NaAlO_2 (s): Present at 15, 20 atm.
 (e) KCl (s): Present at 10, 15, 20 atm.
 (f) KCl (s): Present at 20 atm.

TABLE 3.37

THERMODYNAMICALLY PROJECTED STABLE SOLID PHASES
RESULTING FROM THE REACTION OF ASH FINES WITH
CERAMIC CROSS-FLOW FILTER MATERIAL PHASES IN
FLUID-BED GASIFICATION SYSTEMS

Ash: Fines Generated at the NYU
Pressurized Fluidized Bed Combustor
Temperature: 700°C (1292°F)
Pressure: 1, 5, 10, 15, 20 atm

Filter Material Phase	Al_2O_3	$\text{Al}_6\text{Si}_2\text{O}_{13}$	$\text{Mg}_2\text{Al}_4\text{Si}_5\text{O}_{18}$	Si_3N_4
NYU Ash Constituent:				
Al_2O_3	Al_2O_3	Al_2SiO_5 Al_2O_3	Al_2SiO_5 MgSiO_3 SiO_2	Si_3N_4 SiO_2 Al_2SiO_5 C(c)
SiO_2	Al_2O_3 Al_2SiO_5	Al_2SiO_5 Al_2O_3	Al_2SiO_5 MgSiO_3 SiO_2	Si_3N_4 SiO_2 C(z)
Fe_2O_3	Al_2O_3 FeAl_2O_4	Al_2SiO_5 Al_2O_3 FeAl_2O_4	Al_2SiO_5 FeAl_2O_4 MgSiO_3 SiO_2	Si_3N_4 SiO_2 FeS_2 C(c)
CaSO_4	Al_2O_3 CaAl_2O_7	Al_2SiO_5 Al_2O_3 $\text{CaAl}_2\text{Si}_2\text{O}_8$	Al_2SiO_5 MgSiO_3 SiO_2 $\text{CaAl}_2\text{Si}_2\text{O}_8$	Si_3N_4 SiO_2 CaS C(c)
MgO	Al_2O_3 MgAl_2O_4	Al_2SiO_5 Al_2O_3 MgAl_2O_4	Al_2SiO_5 MgSiO_3 SiO_2	Si_3N_4 SiO_2 MgSiO_3 C(c)
Na_2O (Gas Phase Chloride)	Al_2O_3 NaAlO_2 NaCl(z)	Al_2SiO_5 Al_2O_3 $\text{Na}_2\text{Al}_2\text{Si}_6\text{O}_{18}$	Al_2SiO_5 MgSiO_3 SiO_2 $\text{Na}_2\text{Al}_2\text{Si}_6\text{O}_{18}$	Si_3N_4 SiO_2 C(c) $\text{Na}_2\text{Si}_2\text{O}_5$ NaCl
K_2O (Gas Phase Chloride)	Al_2O_3 K_2CO_3 KCl(b)	Al_2SiO_5 Al_2O_3 $\text{K}_2\text{Al}_2\text{Si}_2\text{O}_8$	Al_2SiO_5 MgSiO_3 SiO_2 $\text{K}_2\text{Al}_2\text{Si}_2\text{O}_8$	Si_3N_4 SiO_2 C(c) $\text{K}_2\text{Si}_4\text{O}_9$ KCl(c)

(a) NaCl (s): Present at 5, 10, 15, 20 atm.

(b) KCl (s): Present at 5, 10, 15, 20 atm.

(c) C (s): Present at 1 atm.

TABLE 3.38

THERMODYNAMICALLY PROJECTED STABLE SOLID PHASES
RESULTING FROM THE REACTION OF ASH FINES WITH
CERAMIC CROSS-FLOW FILTER MATERIAL PHASES IN
ENTRAINED-BED GASIFICATION SYSTEMS

Ash: Fines Generated at the NYU
Pressurized Fluidized Bed Combustor
Temperature: 870°C (1600°F)
Pressure: 1, 5, 10, 15, 20, 30 atm

Filter Material Phase	Al_2O_3	$\text{Al}_6\text{Si}_2\text{O}_{13}$	$\text{Mg}_2\text{Al}_4\text{Si}_5\text{O}_{18}$	Si_3N_4
NYU Char Constituent:				
Al_2O_3	Al_2O_3	$\text{Al}_6\text{Si}_2\text{O}_{13}$	Al_2SiO_5 MgSiO_3 SiO_2	Si_3N_4 SiO_2 Al_2SiO_5 C(a)
SiO_2	Al_2O_3 $\text{Al}_6\text{Si}_2\text{O}_{13}$	$\text{Al}_6\text{Si}_2\text{O}_{13}$ Al_2SiO_5	Al_2SiO_5 MgSiO_3 SiO_2	Si_3N_4 SiO_2 C(a)
Fe_2O_3	Al_2O_3 FeAl_2O_4	$\text{Al}_6\text{Si}_2\text{O}_{13}$ Al_2SiO_5 FeAl_2O_4	Al_2SiO_5 MgSiO_3 SiO_2 FeAl_2O_4	Si_3N_4 SiO_2 Fe_2 C(a)
CaSO_4	Al_2O_3 CaAl_2O_7	$\text{Al}_6\text{Si}_2\text{O}_{13}$ Al_2O_3 $\text{CaAl}_2\text{Si}_2\text{O}_8$	Al_2SiO_5 MgSiO_3 SiO_2 $\text{CaAl}_2\text{Si}_2\text{O}_8$	Si_3N_4 SiO_2 CaS C(a)
MgO	Al_2O_3 MgAl_2O_4	$\text{Al}_6\text{Si}_2\text{O}_{13}$ Al_2SiO_5 MgAl_2O_4	Al_2SiO_5 MgSiO_3 SiO_2	Si_3N_4 SiO_2 MgSiO_3 C(a)
Na_2O	Al_2O_3 NaAlO_2	$\text{Al}_6\text{Si}_2\text{O}_{13}$ Al_2O_3 $\text{Na}_2\text{Al}_2\text{Si}_6\text{O}_{16}$	Al_2SiO_5 MgSiO_3 SiO_2 $\text{Na}_2\text{Al}_2\text{Si}_6\text{O}_{16}$	Si_3N_4 SiO_2 C(a) Na_2SiO_5
K_2O	Al_2O_3 $\text{K}_2\text{CO}_3\text{(b)}$	$\text{Al}_6\text{Si}_2\text{O}_{13}$ Al_2O_3 $\text{K}_2\text{Al}_2\text{Si}_2\text{O}_8$	Al_2SiO_5 MgSiO_3 SiO_2 $\text{K}_2\text{Al}_2\text{Si}_2\text{O}_8$	Si_3N_4 SiO_2 C(a) $\text{K}_2\text{Si}_4\text{O}_9\text{(l)}$

(a) C (s): Present at 1 and 5 atm.

(b) K_2CO_3 (s): Present at 20 and 30 atm.

TABLE 3.39

THERMODYNAMICALLY PROJECTED STABLE SOLID PHASES
RESULTING FROM THE REACTION OF ASH FINES WITH
CERAMIC CROSS-FLOW FILTER MATERIAL PHASES IN
DIRECT COAL FIRED TURBINE SYSTEMS

Ash: Fines Generated at the NYU
Pressurized Fluidized Bed Combustor
Temperature: 980°C (1800°F)
Pressure: 1, 5, 10, 12, 15, 20 atm

Filter Material Phase	Al_2O_3	$Al_6Si_2O_{13}$	$Mg_2Al_4Si_5O_{18}$	Si_3N_4
NYU Ash Constituent:				
Al_2O_3	Al_2O_3	$Al_6Si_2O_{13}$	$Al_6Si_2O_{13}$ $MgSiO_3$ SiO_2	Si_3N_4 SiO_2 C $Al_6Si_2O_{13}$
SiO_2	Al_2O_3 $Al_6Si_2O_{13}$	$Al_6Si_2O_{13}$ SiO_2	$Al_6Si_2O_{13}$ $MgSiO_3$ SiO_2	Si_3N_4 SiO_2 C
Fe_2O_3	Al_2O_3 Fe_2O_3	$Al_6Si_2O_{13}$ Fe_2O_3	$Al_6Si_2O_{13}$ $MgSiO_3$ SiO_2 Fe_2O_3	Si_3N_4 SiO_2 FeS_2 Fe C
$CaSO_4$	Al_2O_3 $CaSO_4$	$Al_6Si_2O_{13}$ Al_2O_3 $CaAl_2Si_2O_8$ $CaSO_4$ (a)	$Al_6Si_2O_{13}$ $CaAl_2Si_2O_8$ $CaSO_4$ $MgSiO_3$ SiO_2 (b)	Si_3N_4 SiO_2 CaS C
MgO	Al_2O_3 $MgAl_2O_4$	$Al_6Si_2O_{13}$ $MgAl_2O_4$ $MgSiO_3$	$Al_6Si_2O_{13}$ $MgSiO_3$ SiO_2	Si_3N_4 SiO_2 $MgSiO_3$ MgS C (c)
Na_2O	Al_2O_3 $Na_2SO_4(1)$	$Al_6Si_2O_{13}$ Al_2O_3 $Na_2Al_2Si_2O_8$ $Na_2SO_4(1)$ (d)	$Al_6Si_2O_{13}$ $MgSiO_3$ $Na_2Al_2Si_2O_8$ SiO_2	Si_3N_4 SiO_2 C $Na_2Si_2O_5(1)$
K_2O	Al_2O_3 K_2SO_4	$Al_6Si_2O_{13}$ K_2SO_4 SiO_2	$Al_6Si_2O_{13}$ K_2SO_4 $MgSiO_3$ SiO_2	Si_3N_4 SiO_2 C $K_2Si_4O_9(1)$

- (a) $CaSO_4$ (s): Present at 5, 10, 12, 15, 20 atm;
 $CaAl_2Si_2O_8$ (s): Present at 1 atm.
 (b) $CaSO_4$ (s): Present at 5, 10, 12, 15, 20 atm;
 $CaAl_2Si_2O_8$ (s): Present at 1, 5 atm.
 (c) MgS (s): Present at 1, 5, 10, 12 atm;
 (d) Al_2O_3 (s): Present at 1, 5, 10 atm;
 Na_2SO_4 (liquid): Present at 10, 12, 15, 20 atm.

TABLE 3.40

THERMODYNAMICALLY PROJECTED STABLE SOLID PHASES
RESULTING FROM THE REACTION OF ASH FINES WITH
CERAMIC CROSS-FLOW FILTER MATERIAL PHASES IN
PRESSURIZED FLUIDIZED-BED COMBUSTION SYSTEMS

Ash: Fines Generated at the New York
University Pressurized Fluidized
Bed Combustor

Temperature: 870°C (1600°F)

Pressure: 1, 5, 10, 15, 20 atm

Filter Material Phase	Al_2O_3	$\text{Al}_6\text{Si}_2\text{O}_{13}$	$\text{Mg}_2\text{Al}_4\text{Si}_5\text{O}_{18}$	Si_3N_4
NYU Ash Constituent:				
Al_2O_3	Al_2O_3	$\text{Al}_6\text{Si}_2\text{O}_{13}$	Al_2SiO_5 MgSiO_3 SiO_2	Si_3N_4 SiO_2 Al_2SiO_5 C
SiO_2	Al_2O_3 $\text{Al}_6\text{Si}_2\text{O}_{13}$	$\text{Al}_6\text{Si}_2\text{O}_{13}$ SiO_2	Al_2SiO_5 MgSiO_3 SiO_2	Si_3N_4 SiO_2 C
Fe_2O_3	Al_2O_3 Fe_2O_3	$\text{Al}_6\text{Si}_2\text{O}_{13}$ Fe_2O_3 SiO_2	Al_2SiO_5 MgSiO_3 SiO_2 Fe_2O_3	Si_3N_4 SiO_2 FeS Fe C
CaSO_4	Al_2O_3 CaSO_4	$\text{Al}_6\text{Si}_2\text{O}_{13}$ CaSO_4 SiO_2 (a)	Al_2SiO_5 MgSiO_3 SiO_2 CaSO_4	Si_3N_4 SiO_2 CaS C
MgO	Al_2O_3 MgAl_2O_4	$\text{Al}_6\text{Si}_2\text{O}_{13}$ MgAl_2O_4 MgSiO_3	Al_2SiO_5 MgSiO_3 SiO_2	Si_3N_4 SiO_2 MgSiO_3 MgS C (c)
Na_2O	Al_2O_3 Na_2SO_4	$\text{Al}_6\text{Si}_2\text{O}_{13}$ $\text{Na}_2\text{Al}_2\text{Si}_6\text{O}_{18}$ Na_2SO_4 Al_2O_3 (b)	Al_2SiO_5 MgSiO_3 SiO_2 $\text{Na}_2\text{Al}_2\text{Si}_6\text{O}_{18}$	Si_3N_4 SiO_2 $\text{Na}_2\text{Si}_2\text{O}_5$ NaCl(l) Na_2S C (d)
K_2O	Al_2O_3 K_2SO_4	$\text{Al}_6\text{Si}_2\text{O}_{13}$ K_2SO_4 SiO_2	Al_2SiO_5 MgSiO_3 SiO_2 K_2SO_4	Si_3N_4 SiO_2 $\text{K}_2\text{Si}_2\text{O}_5$ C (e)

- (a) SiO_2 (s): Present at 5, 10, 15 and 20 atm.
 (b) Al_2O_3 (s): Present at 1 atm;
 Na_2SO_4 (s): Present at 5, 10, 15 and 20 atm.
 (c) MgS (s): Present at 1, 5 and 10 atm.
 (d) NaCl(l) : Present at 10, 15 and 20 atm;
 Na_2S (s): Present at 1 atm;
 $\text{Na}_2\text{Si}_2\text{O}_5$ (s): Present at 5, 10, 15 and 20 atm.

- Carbon is not projected to form over silicon nitride in the low temperature fixed-bed gasification environment. Conversely, as temperature is increased in the fluid- and entrained-bed gasifier, and in the direct coal fired turbine and pressurized fluidized-bed combustion systems, carbon is projected to deposit at the $\text{SiO}_2/\text{Si}_3\text{N}_4$ interface.
- In the reducing fixed-bed gasification environment, the low level of alkali in the acidic ($\text{Fe}_2\text{O}_3 > \text{CaO} + \text{MgO}$) gasifier char effectively reacts with gas phase chloride, forming solid sodium or potassium chloride over the alumina or silicon nitride ceramic surface. Conversely, in the presence of chloride, alkali in the acidic char ash has the potential to react with the aluminosilicate structure of the mullite or cordierite matrix. In the presence of chloride, the higher alkali content in the basic ($\text{Fe}_2\text{O}_3 < \text{CaO} + \text{MgO}$) combustor ash is projected to react with all ceramic matrices, forming either alkali aluminates, aluminosilicates, or silicates. Potassium carbonate is also projected to form as a stable solid over the alumina matrix when chloride is present in the fixed-bed gasifier effluent stream.
- In the fluid-bed gasification system, the presence of the higher alkali content in the basic ash promotes formation of sodium aluminates, aluminosilicates, and silicates over all of the ceramic materials. Under these conditions potassium exists as a carbonate or chloride over the alumina matrix, while it is driven into an aluminosilicate phase in mullite and cordierite, and into a silicate at the $\text{Si}_3\text{N}_4/\text{SiO}_2$ interface.

- Similar to the fixed- and fluid-bed gasification environment, the concentration related differences in the alkali content of the ash fines is projected for the fines/ceramic interaction in the entrained-bed gasification environment. Due to the projected higher filter operating temperature in the entrained-bed gasification system, potassium silicate is projected to result as a liquid at the $\text{Si}_3\text{N}_4/\text{SiO}_2$ interface.
- In the oxidizing direct coal fired turbine environment, alkali in either the acidic or basic ashes is projected to be converted into sulfate phases. Over alumina, sodium sulfate is projected to exist as a liquid, while potassium sulfate will form as a solid. Over mullite, sodium from the fines will be partitioned into a liquid sulfate phase, as well as an aluminosilicate phase. Over cordierite, only solid sulfates of potassium will be formed, while sodium is projected to be driven into the aluminosilicate lattice. Due to the low concentration of alkali in the acidic char/ash, alkali is projected to volatilize, if equilibrium conditions are achieved at the $\text{Si}_3\text{N}_4/\text{SiO}_2$ interface. In the higher alkali containing basic ash, both sodium and potassium are projected to react with the Si_3N_4 matrix, forming liquid silicates.
- For either the acidic or basic ashes in the pressurized fluidized bed combustion system, sodium and potassium form solid sulfates over the alumina matrix; mixtures of solid sodium and potassium sulfate, and sodium aluminosilicate over the mullite matrix; solid sodium aluminosilicate and potassium sulfate over the cordierite matrix. Differences exist between the acidic and basic ashes when the fines are equilibrated at the Si_3N_4 surface in the pressurized fluidized-bed combustion gas environment. In this system,

as in the direct coal fired turbine system, the low alkali content of the acidic char/ash volatilizes and does not lead to the formation of the stable solid or liquid alkali phases. For the higher alkali containing basic ash, sodium is partitioned between a solid silicate and sulfide, and a liquid chloride, while potassium is driven entirely into a liquid silicate phase.

- In the reducing fixed- and fluid-bed gasification environment, iron is driven into an aluminate phase over alumina, mullite, and cordierite, and is converted into a sulfide at the $\text{Si}_3\text{N}_4/\text{SiO}_2$ interface. The iron aluminate formation is retained at the higher operating temperatures of the entrained-bed gasification environment over alumina, mullite, and cordierite. Iron is, however, projected to be reduced to its elemental state at the $\text{Si}_3\text{N}_4/\text{SiO}_2$ interface.
- In the oxidizing environment of the direct coal fired turbine and pressurized fluidized-bed combustion systems, iron remains as a stable oxide over alumina, mullite, and cordierite, but is partially reduced to elemental iron and converted to a sulfide at the $\text{Si}_3\text{N}_4/\text{SiO}_2$ interface.
- In the fixed-bed gasification environment, calcium which is present in the fines is projected to react with alumina to form a calcium aluminate; to react with mullite and form a calcium aluminosilicate; to react with cordierite and form a calcium magnesium silicate; and to be converted into a sulfide at the $\text{Si}_3\text{N}_4/\text{SiO}_2$ interface. Similar reactions are projected for calcium in the fluid- and entrained-bed gasification environment, with the exception that calcium is expected to exist as calcium aluminosilicate over cordierite.

- In the higher temperature, oxidizing environment of the direct coal fired turbine system, calcium is projected to form a solid sulfate over alumina; to be partitioned into a solid sulfate and into the aluminosilicate lattice of mullite and cordierite; and to form sulfides at the $\text{Si}_3\text{N}_4/\text{SiO}_2$ interface. In the pressurized fluidized-bed combustion system, calcium which is present in the fines is projected to form only the solid sulfate over the alumina, mullite, and cordierite matrix, and the sulfide at the $\text{Si}_3\text{N}_4/\text{SiO}_2$ interface.
- Magnesium which is present in the fines is projected to react with alumina and mullite in the ceramic matrix, forming magnesium aluminates; to react with cordierite, forming magnesium silicates; and to form sulfides and silicates at the $\text{Si}_3\text{N}_4/\text{SiO}_2$ interface in the fixed-bed gasification environment. Similar reactions are projected in the fluid- and entrained-bed gasification environment, with the exception that only the magnesium silicate phase and not the sulfide is projected at the $\text{Si}_3\text{N}_4/\text{SiO}_2$ interface.
- In the oxidizing pressurized fluidized-bed combustion gas environment, magnesium forms an aluminate over alumina; an aluminate and silicate over cordierite; and a silicate and sulfide at the $\text{Si}_3\text{N}_4/\text{SiO}_2$ interface.

Tables 3.41 and 3.42 provide a summary of the projected thermodynamic equilibrium fines/ceramic phase interactions.

TABLE 3.41

SUMMARY OF THE THERMODYNAMIC PROJECTIONS ILLUSTRATING
CERAMIC CROSS-FLOW FILTER MATERIAL STABILITY WITH
ACIDIC CHAR/ASH

Acidic Char/Ash: $[\text{Fe}_2\text{O}_3 > (\text{CaO} + \text{MgO})]$
Pressures: 1-30 atm

Phase/ Process	Alumina	Aluminosilicate	Cordierite	Silicon Nitride
Fixed-Bed Gasification Temp: 590°C	FeAl_2O_4 CaAl_2O_7 MgAl_2O_4 NaAlO_2 $\text{NaCl}, ^2\text{KCl}$ K_2CO_3	FeAl_2O_4 $\text{CaAl}_2\text{Si}_2\text{O}_8$ MgAl_2O_4 $\text{Na}_2\text{Al}_2\text{Si}_2\text{O}_8$ $\text{K}_2\text{Al}_2\text{Si}_2\text{O}_8$ KCl	FeAl_2O_4 $\text{CaMgSi}_2\text{O}_8$ MgSiO_3 $\text{Na}_2\text{Al}_2\text{Si}_2\text{O}_8$ $\text{K}_2\text{Al}_2\text{Si}_2\text{O}_8$ KCl	Al_2SiO_5 FeS, CaS MgSiO_3 Na_2SiO_5 $\text{Na}_2\text{S}, \text{KCl}$
Fluid-Bed Gasification Temp: 700°C	FeAl_2O_4 CaAl_2O_7 MgAl_2O_4 NaAlO_2 $\text{NaCl}, ^2\text{KCl}$ K_2CO_3	FeAl_2O_4 $\text{CaAl}_2\text{Si}_2\text{O}_8$ MgAl_2O_4 $\text{Na}_2\text{Al}_2\text{Si}_2\text{O}_8$ $\text{K}_2\text{Al}_2\text{Si}_2\text{O}_8$	FeAl_2O_4 $\text{CaMgSi}_2\text{O}_8$ MgSiO_3 $\text{Na}_2\text{Al}_2\text{Si}_2\text{O}_8$ $\text{K}_2\text{Al}_2\text{Si}_2\text{O}_8$	FeS CaS MgSiO_3 Na_2SiO_5 K_2SiO_5 $\text{NaCl}, ^4\text{KCl}$ C
Entrained-Bed Gasification Temp: 870°C	FeAl_2O_4 CaAl_2O_7 MgAl_2O_4	FeAl_2O_4 $\text{CaAl}_2\text{Si}_2\text{O}_8$ MgAl_2O_4 $\text{Na}_2\text{Al}_2\text{Si}_2\text{O}_8$ $\text{K}_2\text{Al}_2\text{Si}_2\text{O}_8$	FeAl_2O_4 $\text{CaMgSi}_2\text{O}_8$ MgSiO_3 $\text{Na}_2\text{Al}_2\text{Si}_2\text{O}_8$ $\text{K}_2\text{Al}_2\text{Si}_2\text{O}_8$	FeS CaS MgSiO_3 C
Direct Coal Fired Turbine Temp: 980°C	Fe_2O_3 CaSO_4 MgAl_2O_4 $\text{Na}_2\text{SO}_4 (1)$	Fe_2O_3 $\text{CaAl}_2\text{Si}_2\text{O}_8$ CaSO_4 MgAl_2O_4 MgSiO_3 $\text{Na}_2\text{SO}_4 (1)$ $\text{Na}_2\text{Al}_2\text{Si}_2\text{O}_8$	Fe_2O_3 $\text{CaAl}_2\text{Si}_2\text{O}_8$ CaSO_4 MgSiO_3 $\text{Na}_2\text{Al}_2\text{Si}_2\text{O}_8$ K_2SO_4	FeS, Fe CaS MgSiO_3 MgS C
Pressurised Fluidised-Bed Combustion Temp: 870°C	Fe_2O_3 CaSO_4 MgAl_2O_4 Na_2SO_4 K_2SO_4	Fe_2O_3 CaSO_4 MgAl_2O_4 MgSiO_3 $\text{Na}_2\text{Al}_2\text{Si}_2\text{O}_8$ Na_2SO_4 K_2SO_4	Fe_2O_3 CaSO_4 MgSiO_3 $\text{Na}_2\text{Al}_2\text{Si}_2\text{O}_8$ K_2SO_4	FeS, Fe CaS MgSiO_3 MgS C

TABLE 3.42

**SUMMARY OF THE THERMODYNAMIC PROJECTIONS ILLUSTRATING
CERAMIC CROSS-FLOW FILTER MATERIAL STABILITY WITH
BASIC CHAR/ASH**

Basic Ash: $[\text{Fe}_2\text{O}_3 < (\text{CaO} + \text{MgO})]$
Pressures: 1-30 atm

Phase/ Process	Alumina	Aluminosilicate	Cordierite	Silicon Nitride
Fixed-Bed Gasification Temp: 590°C	FeAl_2O_4 CaAl_2O_7 MgAl_2O_4 NaAlO_2 KCl K_2CO_3	FeAl_2O_4 $\text{CaAl}_2\text{Si}_2\text{O}_8$ MgAl_2O_4 $\text{Na}_2\text{Al}_2\text{Si}_2\text{O}_8$ $\text{K}_2\text{Al}_2\text{Si}_2\text{O}_8$ KCl	FeAl_2O_4 $\text{CaMgSi}_2\text{O}_8$ MgSiO_3 $\text{Na}_2\text{Al}_2\text{Si}_2\text{O}_8$ $\text{K}_2\text{Al}_2\text{Si}_2\text{O}_8$ KCl	FeS CaS, MgS MgSiO_3 Na_2SiO_5 $\text{Na}_2\text{S, NaCl}$ K_2SiO_9 KCl
Fluid-Bed Gasification Temp: 700°C	FeAl_2O_4 CaAl_2O_7 MgAl_2O_4 NaAlO_2 NaCl, KCl K_2CO_3	FeAl_2O_4 $\text{CaAl}_2\text{Si}_2\text{O}_8$ MgAl_2O_4 $\text{Na}_2\text{Al}_2\text{Si}_2\text{O}_8$ $\text{K}_2\text{Al}_2\text{Si}_2\text{O}_8$	FeAl_2O_4 $\text{CaAl}_2\text{Si}_2\text{O}_8$ MgSiO_3 $\text{Na}_2\text{Al}_2\text{Si}_2\text{O}_8$ $\text{K}_2\text{Al}_2\text{Si}_2\text{O}_8$	FeS CaS MgSiO_3 Na_2SiO_5 NaCl, KCl K_2SiO_9 $\text{K}_2\text{C}_4\text{O}_9$
Entrained-Bed Gasification Temp: 870°C	FeAl_2O_4 CaAl_2O_7 MgAl_2O_4 NaAlO_2 K_2CO_3	FeAl_2O_4 $\text{CaAl}_2\text{Si}_2\text{O}_8$ MgAl_2O_4 $\text{Na}_2\text{Al}_2\text{Si}_2\text{O}_8$ $\text{K}_2\text{Al}_2\text{Si}_2\text{O}_8$	FeAl_2O_4 $\text{CaAl}_2\text{Si}_2\text{O}_8$ MgSiO_3 $\text{Na}_2\text{Al}_2\text{Si}_2\text{O}_8$ $\text{K}_2\text{Al}_2\text{Si}_2\text{O}_8$	Fe CaS MgSiO_3 Na_2SiO_5 $\text{K}_2\text{SiO}_9(1)$
Direct Coal Fired Turbine Temp: 980°C	Fe_2O_3 CaSO_4 MgAl_2O_4 $\text{Na}_2\text{SO}_4(1)$ K_2SO_4	Fe_2O_3 CaSO_4 $\text{CaAl}_2\text{Si}_2\text{O}_8$ MgAl_2O_4 MgSiO_3 $\text{Na}_2\text{SO}_4(1)$ $\text{Na}_2\text{Al}_2\text{Si}_2\text{O}_8$ K_2SO_4	Fe_2O_3 CaSO_4 $\text{CaAl}_2\text{Si}_2\text{O}_8$ MgSiO_3 $\text{Na}_2\text{Al}_2\text{Si}_2\text{O}_8$ K_2SO_4	FeS, Fe CaS, MgS MgSiO_3 $\text{Na}_2\text{SiO}_5(1)$ $\text{K}_2\text{SiO}_9(1)$
Pressurised Fluidised-Bed Combustion Temp: 870°C	Fe_2O_3 CaSO_4 MgAl_2O_4 Na_2SO_4 K_2SO_4	Fe_2O_3 CaSO_4 MgAl_2O_4 MgSiO_3 Na_2SO_4 $\text{Na}_2\text{Al}_2\text{Si}_2\text{O}_8$ K_2SO_4	Fe_2O_3 CaSO_4 MgSiO_3 $\text{Na}_2\text{Al}_2\text{Si}_2\text{O}_8$ K_2SO_4	FeS, Fe CaS, MgS MgSiO_3 $\text{NaCl}(1)$ Na_2S Na_2SiO_5 $\text{K}_2\text{SiO}_9(1)$

3.1.4 Ceramic Cross-Flow Filter Test Experience

A preliminary evaluation of cross-flow filter materials used in conjunction with contiguous Westinghouse/DOE programs⁽¹³¹⁻¹³⁴⁾ is described in this Section. Data are presented which:

- Demonstrate the affinity of the alumina/mullite filter material for reaction with gas phase sodium chloride.
- Review the chemical and physical properties of two alumina/mullite filter materials that have been exposed at the subpilot-scale fluid-bed gasifier at METC in 1985.
- Compare the chemical and physical properties of an unused alumina/mullite substrate with similar material that had been fabricated into a filter element and exposed in the subpilot-scale pressurized fluidized-bed combustor at New York University.
- Identify the chemical and physical properties of the alumina/mullite filter material that was fabricated for use at the Texaco gasifier.
- Provide a comparison between the properties of the various alumina/mullite filter fabrication lots.

3.1.4.1 Chemical Affinity of Alumina/Mullite for Sodium

Ceramic cross-flow filter materials used in the early 1980 configurations consisted of alumina/mullite. Typically the filter bodies were fabricated from flat plates with ribs that were stacked together and fired to form 6x6x2 inch units. Plates were bonded at the rib tip of one plate to the flat surface of adjacent plates. Rib height

dimensions that were initially selected were 0.15 inches, with a rib spacing of 0.60 inches. Pore size ranged from a nominal 10 to 144 μm for these materials.

Previous efforts conducted at Westinghouse⁽¹³⁵⁾ regarding the chemical characterization of the original alumina/mullite filter materials (Nos. 427 and 485) using scanning electron microscopy (SEM) and energy dispersive x-ray analysis (EDAX) indicate that the alumina/mullite matrices contain not only aluminum, but also silicon as the predominant phase (Figures 3.31 and 3.32). Traces of calcium, titanium, iron, and magnesium were also identified within the alumina/mullite matrix. The silicon rich phase appears as the predominant phase along the surface of the material.

Qualitative determination of the trace element concentration contained within the alumina/mullite matrix was performed by emission spectroscopy techniques. These data are presented in Table 3.43. The emission spectroscopy data also illustrate that aluminum and silicon are present as major constituents. Similarly, quantitative atomic absorption analysis was performed on the No. 427 and 485 materials in order to identify not only the total concentration of alkali contained within the original matrix material, but also the distribution of alkali within various phases (Table 3.44). Soluble alkali are considered to consist of water soluble chlorides (NaCl , Na_2Cl_2 , KCl , and K_2Cl_2), hydroxides (NaOH and KOH), sulfates (Na_2SO_4 and K_2SO_4), and water glass phases (feldspars and nephelines). Insoluble alkali are considered to be contained within the aluminosilicate lattice or "glassy" amorphous phases. The atomic absorption data presented in Table 3.44 indicate that sodium exists predominantly within the acid insoluble lattice of the No. 427 alumina matrix, but within the acid soluble phase of the No. 485 alumina matrix. Potassium exists predominantly within the acid insoluble fraction of both materials.

Figure 3.31 - Scanning Electron Micrographs and Energy Dispersive X-Ray Analysis of the Alumina/Mullite Filter No. 427 Surface

Figure 3.32 - Scanning Electron Micrographs and Energy Dispersive X-Ray Analysis of the Alumina/Mullite Filter No. 485 Surface

TABLE 3.43

EMISSION SPECTROSCOPY ANALYSIS OF
ALUMINA/MULLITE FILTER MATERIALS, Wt%

Element	Filter No. 427	Filter No. 485
Al	<10	<10
Ag	<0.001	<0.001
B	0.01	0.005
Ba	0.02	0.02
Be	<0.0005	<0.0005
Bi	<0.003	<0.003
Ca	>1	>>1
Cd	<0.01	<0.01
Co	<0.002	<0.002
Cr	0.003	0.003
Cu	0.005	0.003
Fe	0.3	0.3
Ga	0.005	0.005
Ge	<0.01	<0.01
K	0.5	0.5
Li	0.007	0.006
Mg	>1	>>1
Mn	0.003	0.002
Mo	<0.001	<0.001
Na	0.2	0.2
Nb	<0.005	<0.005
Ni	0.003	0.003
Pb	<0.003	<0.003
Sb	<0.02	<0.02
Si	>>1	>>1
Sn	<0.003	<0.003
Sr	0.006	0.006
Ti	0.5	0.5
V	0.004	0.004
W	<0.01	<0.01
Zn	<0.003	<0.003
Zr	0.007	0.004

TABLE 3.44

ATOMIC ABSORPTION ANALYSIS OF
ALUMINA/MULLITE FILTER MATERIALS, Wt%

Alumina/Mullite Filter	Soluble*		Insoluble		Total	
	Na	K	Na	K	Na	K
No. 427	<0.11	<0.06	0.10	0.12	<0.21	<0.18
	<0.11	<0.06	0.12	0.13	<0.23	<0.19
	<0.09	<0.07	0.14	0.14	<0.23	<0.21
No. 485	0.15	0.08	0.05	0.19	0.20	0.27
	0.15	0.08	0.05	0.15	0.20	0.23
	0.15	0.08	0.05	0.18	0.20	0.26

*Water and acid soluble phases.

Bench-scale tests were performed where approximately 0.125 inch diameter cakes of Exxon 3rd stage cyclone catch PFBC ash were supported on similar size discs of the alumina/mullite filter material, and exposed to 815 and 925°C (1500 and 1700°F) and 138 psig in an argon gas environment laden with 80 ppm NaCl. Analyses of the PFBC ash cake exposed to temperatures of 815°C (1500°F) indicate that the water soluble phase forms as the major gettered phase in the PFBC ash, with the formation of the secondary acid soluble phase, and minor formation of the acid insoluble complex (Table 3.45). When the Exxon 3rd stage cyclone catch PFBC ash is exposed to gaseous NaCl at temperatures of 925°C (1700°F) for one hour, a 2.5-fold sodium increase over background results. A 4.4-fold sodium increase results after one hour of exposure to 80 ppm NaCl at temperatures of 815°C (1500°F). Analyses indicate that sodium is driven into the insoluble fraction of the material, with limited reaction of the alkali within either the water or acid soluble complexes at the higher reaction temperature.

The alumina/mullite filter materials used to support the Exxon 3rd stage cyclone catch PFBC ash cake were also shown to react with alkali (Table 3.46). Analyses of the alumina/mullite filter material after exposure to the argon gas environment containing 80 ppm NaCl at 150 psig total pressure for one and four hours at temperatures of 815°C (1500°F) indicate that alkali is primarily driven into the condensed water soluble phase (i.e., chlorides, hydroxides, and sulfates). Only a slight increase in the sodium acid soluble phase is detected after four hours of exposure, while a ten- to sixteen-fold increase in the amorphous, acid insoluble, sodium content is detected over background.

Under similar test conditions the total gettering capacity of the alumina/mullite filter material decreases as the reaction temperature is increased to 925°C (1700°F). Although at higher temperatures, NaCl is expected to remain in the gas phase, minimizing the concentration of condensed sodium in the water soluble fraction of the alumina/mullite filter material, reaction of the alkali with the

TABLE 3.45

ATOMIC ABSORPTION ANALYSIS OF
EXXON 3rd STAGE CYCLONE CATCH PFBC ASH, Wt%

Ash Cake Thickness: 1/8 inch
Gauge Pressure: 10 atm
Gas Velocity: 30 cm/min
Alkali Concentration: 80 ppm NaCl/Ar

Material	Exposure Time, hrs	Exposure Temp., °C (°F)	Water Soluble		Acid Soluble		Acid Insoluble		Total	
			Na	K	Na	K	Na	K	Na	K
PFBC Ash	-	-	<0.02	0.017	0.29	0.52	0.39	1.23	<0.70	1.77
PFBC Ash	1	815(1500)	1.81	0.08	0.88	0.05	0.48	0.06	3.17	0.19
			0.64	0.01	0.91	0.03	0.52	0.03	2.07	0.07
			2.99	0.16	0.65	0.08	0.39	0.1	4.03	0.34
PFBC Ash	4	815(1500)	8.52	0.31	0.50	0.02	0.26	0.02	7.28	0.35
			5.11	0.28	0.57	0.01	0.11	0.02	5.79	0.31
			3.58	0.42	0.71	0.01	0.39	0.02	4.68	0.45
PFBC Ash	1	925(1700)	0.19	0.01	0.58	0.01	0.95	0.01	1.72	0.03

TABLE 3.46

ATOMIC ABSORPTION ANALYSIS OF THE
ALUMINA/MULLITE FILTER MATERIALS AFTER EXPOSURE TO
ALKALI AND PFBC ASH, Wt%

Gauge Pressure: 10 atm

Gas Velocity: 30 cm/min

Alkali Concentration: 80 ppm NaCl/Ar

Material	Exposure Time, hrs	Exposure Temp., °C (°F)	Water Soluble		Acid Soluble		Acid Insoluble		Total	
			Na	K	Na	K	Na	K	Na	K
Alumina	-	-	<0.01	<0.01	0.09	<0.02	<0.01	0.17	<0.11	<0.20
			<0.01	<0.01	0.10	0.02	<0.01	0.16	<0.12	0.19
			<0.01	<0.01	0.09	0.02	<0.01	0.18	<0.11	<0.21
Alumina	1	815(1500)	8.09	0.03	0.15	0.01	0.13	0.04	8.37	0.08
			7.50	0.05	0.13	0.02	0.09	0.05	7.72	0.12
			7.43	0.06	0.14	0.02	0.09	0.05	7.66	0.13
Alumina	4	815(1500)	2.98	0.01	0.17	0.02	0.14	0.04	3.29	0.07
			3.00	0.01	0.14	0.01	0.20	0.05	3.34	0.07
			3.09	0.05	0.13	0.02	0.13	0.08	3.35	0.15
Alumina	1	925(1700)	0.35	<0.01	0.23	0.02	0.22	0.02	0.80	<0.05
			0.19	<0.01	0.24	0.02	0.18	0.02	0.61	<0.05
			0.32	<0.01	0.25	0.01	0.22	0.02	0.79	<0.04
Alumina	4	925(1700)	0.02	<0.01	0.22	<0.01	0.99	<0.01	1.23	<0.03
			0.02	<0.01	0.24	<0.01	0.80	<0.01	1.06	<0.03
			0.02	<0.01	0.28	<0.01	0.94	<0.01	1.24	<0.03

insoluble alumina/mullite lattice increases (20-fold increase after one hour; 100-fold increase after four hours over background). From these data it appears that the migration of sodium from the water soluble phase into the acid soluble phase, and finally into the acid insoluble phase depends on both exposure time and temperature.

As sodium is removed from the gas stream by the alumina/mullite filter material, potassium which is originally present in the filter matrix is simultaneously released. At 815°C (1500°F), approximately one-third of the background insoluble potassium remains within the acid insoluble phase after sodium gettering, while one-third repartitions into the water soluble phase, and the remainder is released into the gas stream.

Exposure of the alumina/mullite matrix to 925°C (1700°F) further depletes the insoluble potassium concentration relative to the background content. Recapture of the released insoluble potassium into either the water soluble or the acid soluble phase does not occur at 925°C (1700°F). The release of background potassium coupled with sodium gettering generally increases as a function of both exposure time and temperature.

The preliminary experiments which were performed at Westinghouse in 1981 were intended to simulate the interaction of loosely attached ash along the alumina/mullite filter surface. In summary, data which were generated in this study demonstrated:

- The potential for the capture of sodium by PFBC ash, as well as the alumina/mullite filter material at temperatures of 815°C (1500°F) and 925°C (1700°F).
- That as gas phase sodium is captured by either the PFBC ash or the alumina/mullite filter material, potassium, which is originally present, is released.

- That due to the relatively low concentrations of alkali in the original PFBC ash and alumina/mullite matrix in comparison to the reacted concentrations, capture of alkali is considered to have occurred from reaction of the materials with the gas phase alkali, with limited or negligible transfer of alkali from the ash to/from the alumina/mullite support material.

Unfortunately during conduct of this work, the original and the alkali-exposed alumina/mullite materials were not subjected to strength analysis (i.e., 4-point bend testing).

3.1.4.2 METC Fluid-Bed Gasifier Alumina/Mullite Filter Tests

Ceramic Filter Fabrication and Process Exposure Conditions

The initial ceramic filters were fabricated into 6x6x2 inch cross-flow bodies with flanges. A photo of the section which was removed from a filter (WCXF2) which had been exposed for 50 hours in the bench-scale fluid-bed gasifier at METC in August 1985 is shown in Figure 3.33. Test conditions that this filter experienced are shown in Table 3.47. During the first 40 hours of operation, the filter efficiency was identified at 99.9 percent.⁽¹³⁶⁾ In subsequent hours of testing the filter efficiency dropped to 98.4-99.4 percent. Visual inspection of the filter after removal from the system indicated that the element had broken along one side of the thin mounting flange. This break was considered to have occurred during initial installation, and finally to have separated after many cycles of jet pulse cleaning.

Improvements were made to the initial filter design which included a much thicker and more rugged flange, and a dip coating of ceramic bonding material applied to the back of the new filter element which was where prior delaminations had been considered to originate.

Figure 3.33 - Section Removed from the WCF2
 Alumina/Mullite Filter after Exposure
 to the METC Fluid-Bed Gasifier Process
 Gas (8/16/85)

TABLE 3.47

CROSS-FLOW FILTER TEST CONDITIONS AT THE METC FLUID-BED GASIFIER⁽¹³⁶⁾

Element	Operating Conditions			Time Hrs	Collection Efficiency %	Comment
	Temperature °C(°F)	Pressure psig	Face Velocity ft/min			
WCXF2 (8/16/85)	271 (520)	150	3.6	8	99.2	(a)
	640(1000)	150	3.6	16	99.95	
	760(1400)	150	5.0	17	99.98	
	760(1400)	150	5.0	8	98.4-99.4	
WCXF4 (11/5/85)	650(1200)	150	2.6-3.7	48	99.5	(b)
	815(1500)	150	5.5	50	98.7	(c)
	760(1400)	93	11.6	8	97-88	(d)

(a) Performance excellent; high efficiency; low filter pressure drop; cleaned effectively. Crack in the thin flange resulted in lowered performance.

(b) Small delaminations at front face. Crack was repaired and element reused.

(c) Test proceeded with stable performance.

(d) Significant delamination of filter element. Very low inlet dust loading. Steam line failure resulted in a wet dust cake.

After dip coating, the element was subsequently high fired. Notably the slip coating had not penetrated the filter to a significant extent. During the first 50 hours of testing this unit (WCXF4) in the METC gasifier, filter efficiencies of 99.5 percent were attained. Inspection of the filter after 50 hours of operation indicated that a minor delamination had occurred, and that a small leak at the sealing face had resulted. The leak was patched, and the filter was reinstalled for continued testing until a filtering efficiency of 96 percent resulted. Upon removal and inspection, several delaminations had occurred, as well as a break directly across one of the filter faces. A section which was removed from the WCXF4 filter after exposure in the METC gasifier is shown in Figure 3.34.

Physical Morphology of Filters Exposed to the METC Bench-Scale Gasifier Process Gases

Chemical characterization of sections removed from both the WCXF2 (8-16-85) and WCXF4 (11-5-85) filters was conducted using scanning electron microscopy (SEM), energy dispersive x-ray analysis (EDAX), atomic absorption, emission spectroscopy, and x-ray diffraction (XRD) techniques. Similarly, physical characterization of samples from each filter material included 4-point bend strength and porosity determination. Notably, the external surface of the WCXF2 filter appeared grey or black, while the external surface of the WCXF4 filter had a tan or orangish appearance. Each of the four-point bend strength test fracture surfaces were visually scanned to identify any obvious defects which may indicate a possible cause for failure at the fracture site. Typically the fractured surface consists of an area that is lighter in appearance all along the sample's edge, with a somewhat darker internal appearance. In one sample of the WCXF2 material, a relatively large pore (0.5-0.6 mm) was evident along the fracture, and when viewed under low magnification, the pore appeared to contain a greyish, discontinuous, "sparkling" area. Further SEM/EDAX and

Figure 3.34 - Section Removed from the WCXF4 Alumina/
Mullite Filter after Exposure to the
METC Fluid-Bed Gasifier Process Gas
(11/5/85)

microprobe analyses were performed on the WCXF2 fracture surface containing the large pore, as well as its mirror fracture surface. The following sections describe the results of these analyses.

Morphology and Surface Analysis of the WCXF2 and WCXF4 Filter Materials

Figure 3.33 illustrates a section of the WCXF2 (8-16-85) filter after exposure in the METC gasifier. The flat and rib surfaces of the filter are darkened with retained fines which are seen to penetrate into the interior of both the clean and dirty side ribs, as well as along the filter plates. The corners formed by the rib-to-plate intersection often contain heavier deposits of the fines, and when viewed along the cross-section, the fines appear to be carried through the inner substrate. The "salt and pepper" appearance of the fines trapped within the filter is more evident in Figure 3.35.

Process data for the WCXF2 test indicates that the filter had experienced approximately 41 hours of the process gas at temperatures of 540-760°C (1000-1400°F), and pressures of 150 psig. At these conditions, porosity in the ceramic filter matrix appears to have been retained; the bond formed at the rib tip to flat plate has remained intact; and the filter catch fine particles appear to have been retained within pores and on the filter matrix surface. It is not possible to determine whether the filtered fines are "fused" or "reacted" with the filter matrix, or held to the surface as a result of the particle morphology which traps or lodges the particles in pores and crevices.

SEM/EDAX characterization was performed on both the surface of a clean gas channel, as well as on a dirty gas channel, and on a cross-section of a fractured rib surface. The morphology of the clean gas channel shown in Figure 3.36 is seen to contain many large pores, and an EDAX area scan characterizes this region to be predominantly aluminum, with secondary contributions of silicon, and minor concentrations of calcium, and traces of iron. At higher magnification the surface

Figure 3.35 - Cross-Section of the Ribbed Surface of the WCXF2
Alumina/Mullite Filter Exposed in the METC Gasifier
(8/16/85)

Figure 3.36 - Scanning Electron Micrographs and Energy Dispersive X-Ray
Analysis of a Clean Gas Channel Surface in the WCXP2
Alumina/Mullite Filter Exposed at METC

appears to contain spherical, agglomerated or flocculated particle formations ($<1\text{ }\mu\text{m}$) which are also predominantly aluminum, with secondary silicon, minor calcium, and trace iron contributions. A relatively smooth, perhaps molten appearance of the surface is evident with mullite rods embedded within this phase. Large particles which may have been part of the filter fines catch are also evident.

SEM/EDAX data for the WCXF2 dirty gas channel are presented in Figure 3.37. Similar to the clean channel, the dirty gas flow channel has a rather mottled surface appearance containing large pores. Area scans indicate that the composition consists of aluminum, silicon, calcium, and iron. High magnification of the surface indicates the presence of a higher concentration of mullite rods in comparison to the clean channel surface. Mullite appears to be embedded in a molten phase. A somewhat more dense concentration of the filter fines catch seems to have resulted on this surface. Once again, the spherical $<1\text{ }\mu\text{m}$ particles are observed along the smooth filter matrix phase. The spherical particles are seen to agglomerate into larger particle formations, and appear to fuse with each other.

SEM/EDAX of the WCXF2 rib cross-section is shown in Figure 3.38. Large pores are evident, as well as mullite rods within the internal pore cavity. Again mullite rods appear to be embedded in a smooth, perhaps molten phase. Fines appear to be randomly retained along the cross-sectioned surface. At high magnification, the spherical agglomerated or flocculated particle formations, as well as what may have been the filter catch fines are seen to be positioned along the smooth filter matrix phase. Significant compositional changes are not evident for the various formations (i.e., substrate, spherical particles, filter fines, etc.).

Although further data and analysis are required, it appears that the smooth filter matrix phase may be the preferred site for capture and retention of the filter fines catch, and the formation of the spherical, agglomerated particles.

Figure 3.34 illustrates a section of the WCXF4 (11-5-85) filter after exposure in the METC gasifier. The flat ribbed surfaces are discolored as a result of retained fines. The dirty gas channels appear to be tan, while the clean gas channels are somewhat more orangish in appearance. The fines collected along the filter gas channel surfaces, as well as within the rib or plate areas are granular in appearance, and at higher magnification are shown to contain dark black particles. In several location underlying the fines there seems to be a region of the filter matrix which has become discolored. Perhaps leaching of the iron has occurred from the fines, and has reacted with the aluminosilicate filter material. The orangish discoloration does not appear to be the result of finely entrapped particles.

The cross-sectioned area shown in Figure 3.34 has substantial porosity, and shows limited bonding along the rib tip to flat plate seam. Fines are seen to accumulate in the tip-to-plate corners, and appear to be carried into the interior of the filter matrix. Several large internal pores are shown to accumulate fines (Figure 3.39).

SEM/EDAX characterization was performed on the WCXF4 clean gas channel, on the dirty gas channel, and along the cross-sectioned surface of the rib. Figure 3.40 indicates that the clean gas channel retains many large pores. High magnification reveals that the mottled surface contains mullite rods embedded in a melt-like phase, with adherent fines. Due to the presence of fines, the EDAX area scan identifies magnesium, potassium, titanium, and iron with aluminum, silicon, and calcium. The captured filter fines (Figure 3.40, Photo 3, Spot 1) contain sulfur. The particles in this region are not trapped within a pore, but are "attached" to a smooth phase of the filter matrix. In several areas shown in Photo 3 of Figure 3.40, $<2\text{ }\mu\text{m}$ size holes are evident which may have resulted from outgassing of subsurface volatile phases.

Figure 3.37 - Scanning Electron Micrographs and Energy Dispersive X-Ray Analysis of a Dirty Gas Channel Surface in the WCXP2 Alumina/Mullite Filter Exposed at METC

Figure 3.38 - Scanning Electron Micrographs and Energy Dispersive X-Ray Analysis of a Cross-Sectioned Rib Surface in the WCF2 Alumina/Mullite Filter Exposed at METC

Figure 3.39 - Cross-Section of the Ribbed Surface of the WCXF4
Alumina/Mullite Filter Exposed in the METC Gasifier
(11/5/85)

Figure 3.41 illustrates the morphology of the filter surface along the dirty gas channel. A significantly denser covering of fines is evident in comparison with the clean gas channel. Along an area of this surface which has a somewhat less dense covering, the EDAX area scan identifies the presence of predominantly silicon rich, major aluminum and calcium phases, with minor or trace concentrations of iron, magnesium, potassium, and titanium. In the heavier deposit areas, the EDAX area scan identifies the presence of silicon and calcium rich phase(s), with magnesium, iron, titanium, and potassium present as minor constituents. Aluminum in this area is substantially reduced, indicating a lower contribution from the filter matrix. The fines appear as discrete particles, as well as clusters of particles.

Figure 3.42 illustrates the morphology of the cross-sectioned rib. Large pores are evident. Once again the mullite rods are embedded in a "melt-like" phase. In Photo 3 of Figure 3.42, a crack through the "melt-like" phase is very apparent. Captured fines are observed along the "melt-like" phase, and in the pore cavities. Sulfur is present in the captured fines. Particle formations that are $<1\text{ }\mu\text{m}$ are evident in Photo 4 of Figure 3.42. These are perhaps similar to the spherical formations which were described along the WCXF2 filter.

Although further data and analysis are required, the preliminary data seem to indicate that the "melt-like" phase as opposed to the mullite rods is the site for retention of fines. Whether these fines are fused or reacted with the filter substrate remains to be determined.

Microprobe analysis for sulfur and iron was performed along the edge of the cross-sectioned rib of the WCXF4 filter (Figure 3.43). Sulfur and iron were selected since these elements were considered to represent the composition of fines that would be distinctly different from that of the filter matrix. Sulfur is shown to penetrate beneath the surface of the filter matrix, and to be localized along the pore

Figure 3.40 - Scanning Electron Micrographs and Energy Dispersive X-Ray Analysis of a Clean Gas Channel Surface in the WJXP4 Alumina/Mullite Filter Exposed at MBTC

Figure 3.41 - Scanning Electron Micrographs and Energy Dispersive X-Ray Analysis of a Dirty Gas Channel Surface in the WCKP4 Alumina/Mullite Filter Exposed at METC

Figure 3.42 - Scanning Electron Micrographs and Energy Dispersive X-Ray Analysis of a Cross-Sectioned Rib Surface in the WOXF4 Alumina/Mullite Filter Exposed at METC

Figure 3.43 - Microprobe Analysis of the Cross-Sectioned Rib Surface
in the WCXF4 Alumina/Mullite Filter Exposed at METC

cavity. Although the SEM in Figure 3.43 does not distinctly show the location of the captured fines, the sulfur-laden pore cavity may have been an area where fines collected.

Alternately, iron is present along the WCXF4 filter surface and extends approximately 10 μm into the interior of the rib cross-section. This may correspond to the "bleeding" or discoloration along the edge that was previously described. Within the cross-section, localized higher intensity areas of iron are evident, but do not correspond with the sulfur locations. Iron may result from fines carried into the substrate, while sulfur may have resulted from gas phase sulfur reacting with the substrate, or from complexes within fines that are captured by the substrate. Further investigation is required to fully understand this effect.

Samples from both WCXF2 and WCXF4 were removed for 4-point bend strength testing (See discussion in Section 3.1.4.5). Each fractured surface was visually screened to identify whether any obvious differences could be discerned. Figure 3.44 and 3.45 are examples of the cross-sectioned fracture surface for both filter materials. Typically the fractured surfaces consist of an area that is lighter in appearance all along the sample's edge, with a somewhat darker internal appearance. In the WCXF2 material (Figure 3.44), a relatively large pore is evident along the fracture, and when viewed under low magnification, the pore appeared to contain a greyish, discontinuous, "sparkling" area. Further SEM/EDAX and microprobe analyses were performed on the WCXF2 fracture surface containing the large pore, as well as on its mirror fracture surface. In the WCXF4 material (Figure 3.45), a relatively large void is evident at the cross-section's edge, in addition to a large pore which is almost directly across from the large surface void. A substantial amount of information regarding the flaw formation mechanism cannot be generated through general screening observations of the cross-section fracture surface. Both WCXF2 and WCXF4 samples appear to have failed in areas which contain isolated, enlarged pores.

Figure 3.44 - WCXF2 Four-Point Bend Fracture Surface

Figure 3.45 - WCXF4 Four-Point Bend Fracture Surface

From the phase contrast shown in the back-scattering electron micrographs (BSE) for the WCXF2 filter in Figure 3.46, the fractured surface appears to contain several phases. Notably, along the edges of the cross-sectioned surface is a dense, lighter phase. Voids or pores are evident in the blackened areas. In the interior of the ceramic matrix, however, are large "greyish" regions, in particular, around the relatively large pore. Photo 3 in Figure 3.46b illustrates the pore cavity, while the mirrored surface in Photo 4, illustrates the section of material removed from the pore during fracture. Higher magnification SEM and BSE micrographs shown in Figure 3.47 illustrate the synergism between the discrete phases. Notice the tiny holes burnt into the grey areas as a result of the SEM/BSE characterization. Generally, this type of burning is indicative of a carbon-like phase.

Spherical particle formations appear as "knob-like globules" in the grey FSE regions (Figure 3.48). Microprobe analysis identifies the lighter areas of the BSE micrographs as either silicon-, aluminum-, calcium-rich, pure aluminum-rich, or aluminum-silicon-rich complexes. Oxygen is generally present in these areas. The grey region is, however, identified to contain higher concentrations of carbon. Although the sample had been carbon coated in order to minimize charging during SEM analysis, the deposited carbon layer is considered to be relatively thin in comparison to the concentration detected in the grey areas. The concentration of the thin film is observed along the aluminum-silicon-rich areas. From discussions with the filter supplier, the presence of the large carbon-rich areas is considered to have resulted from carbonaceous material which had been used for pore formation in the original fabrication process, and which had not been fully burnt out during the high temperature firing cycles.

Chemical and Physical Properties Characterization of Filters Exposed to METC Process Gases

Chemical characterization of the WCXF2 and WCXF4 filter samples was performed using atomic absorption, emission spectroscopy, and x-ray diffraction (XRD) analysis techniques. An attempt was made to remove a

Removed Material

Pore

Figure 3.46a - Scanning and Back-Scattering Electron Micrographs of the WCX2 Four-Point Bend Fracture Surface

Figure 3.46b - Higher Magnification Scanning and Back-Scattering Electron Micrographs of the WCXF2 Four-Point Bend Fracture Surface

Figure 3.47a - High Magnification Scanning and Back-Scattering Electron Micrographs of the WCXF2 Four-Point Bend Fracture Surface Showing the Synergism Between Phases

"clean" interior section from each of these materials for analysis, in addition to analyzing material along the exterior of the filter ribs or plates that had been discolored from process fines. Table 3.48 illustrates the atomic absorption and emission spectroscopy results for these analyses. With the exception of iron, no discernable differences are apparent between the interior versus exterior of the filter matrices. For both WCXF2 and WCXF4, the concentration of iron is 0.06 weight percent greater in the filter material which contains the collected filter fines.

Table 3.48 also presents the atomic absorption results from an unused alumina/mullite filter which had been fabricated in 1988. The concentration of the major elements are seen to vary somewhat between samples. This variation is considered to result perhaps from either the starting materials or from the formulation and fabrication procedures, as opposed to contributions from the collected filter fines. The quantity of fines remaining along each filter prior to analysis is substantially reduced due to physical cleaning of each filter after removal from the gasifier, in comparison to the quantity of fines actually collected along the filter during processing.

Review of the emission spectroscopy data presented in Table 3.49 illustrates that the trace and minor elements do not substantially vary between

- The 1985 WCXF2 and WCXF4 filters and the unused 1988 filter.
- The 1985 WCXF2 filter and the 1985 WCXF4 filter
- The interior and exterior portion of the WCXF2 or WCXF4 material.

Only chromium, titanium, strontium, and copper are identified at higher concentrations in the external material from WCXF4, while copper has a somewhat higher concentration in the internal WCXF2 and WCXF4 matrices.

ELEMENT & LINE	WEIGHT PERCENT	ATOMIC PERCENT	PRECISION 2 SIGMA	K-RATIO	ITER
AL KA	45.10	48.79	0.63	0.3424	
SI KA	38.66	40.18	0.85	0.1293	
K KA	1.88	1.40	0.22	0.0122	
CA KA	8.96	6.53	0.32	0.0649	
TI KA	3.17	1.93	0.25	0.0231	
FE KA	2.23	1.17	0.25	0.0192	9
TOTAL	100.00				

Figure 3.47b - Energy Dispersive X-Ray Analysis of the Light Phase(s)
Along the WCXF2 Four-Point Bend Fractured Surface

Figure 3.48 Microprobe Analysis of the WCXF2 Four Point Bend Fractured Surface

TABLE 3.48

PRINCIPAL PHASE CHARACTERIZATION OF
THE ALUMINA/MULLITE FILTERS EXPOSED TO THE
METC FLUID-BED GASIFIER PROCESS GASES

	WCXF2 Exterior 1985	WCXF2 Interior 1985	WCXF4 Exterior 1985	WCXF4 Interior 1985	Alumina (Unused) 1988
<hr/>					
Atomic Absorption Analysis, Wt%					
Al ₂ O ₃	55.81	56.28	56.42	54.09	52.29
SiO ₂	36.83	36.66	36.11	35.33	39.64
Fe ₂ O ₃	0.56	0.50	0.58	0.52	0.46
CaO	5.35	5.42	5.41	5.29	4.79
MgO	2.57	2.58	2.61	2.57	2.60
K ₂ O	0.28	0.25	0.31	0.32	0.31
Na ₂ O	0.19	0.19	0.20	01.9	0.18
<hr/>					
X-Ray Diffraction Analysis,					
Major Phase:	:<-----Mullite----->:<-----Mullite----->:				Mullite
Minor Phase:	:<-----Corundum----->:<-----Corundum----->:				Corundum

TABLE 3.49

**EMISSION SPECTROSCOPY CHARACTERIZATION OF
THE ALUMINA/MULLITE FILTERS EXPOSED TO THE
METC FLUID-BED GASIFIER PROCESS GASES**

	WCXF2 Exterior 1985	WCXF2 Interior 1985	WCXF4 Exterior 1985	WCXF4 Interior 1985	Alumina (Unused) 1988
Emission Spectroscopy, Wt%					
Al	>10	>10	>10	>10	>10
Ag	<0.001	<0.001	<0.001	<0.001	<0.001
B	0.02	0.02	0.02	0.02	0.02
Ba	0.03	0.03	0.03	0.03	0.03
Be	<0.001	<0.001	<0.001	<0.001	<0.001
Bi	<0.003	<0.003	<0.003	<0.003	<0.003
Ca	3	3	3	3	3
Cd	<0.03	<0.03	<0.03	<0.03	<0.03
Co	<0.003	<0.003	<0.003	<0.003	<0.003
Cr	0.01	0.01	0.02	0.01	0.01
Cu	0.003	0.01	0.01	0.02	0.003
Fe	0.3	0.3	0.3	0.3	0.3
Ga	<0.03	<0.03	<0.03	<0.03	<0.03
Ge	<0.02	<0.03	<0.03	<0.03	<0.03
K	0.2	0.2	0.2	0.2	0.2
Li	0.005	0.008	0.006	0.006	0.006
Mg	1	1	1	1	1
Mn	0.01	0.01	0.01	0.01	<0.01
Mo	<0.01	<0.01	<0.01	<0.01	<0.01
Na	0.1	0.1	0.1	0.1	0.1
Nb	<0.03	<0.03	<0.03	<0.03	<0.03
Ni	<0.01	<0.01	<0.01	<0.01	<0.01
Pb	<0.02	<0.02	<0.02	<0.02	<0.02
Sb	<0.03	<0.03	<0.03	<0.03	<0.03
Si	>10	>10	>10	>10	>10
Sn	<0.01	<0.01	<0.01	<0.01	<0.01
Sr	0.01	0.01	0.02	0.01	0.01
Ti	0.03	0.03	0.04	0.03	0.03
V	0.01	0.01	0.01	0.01	0.01
Zn	0.02	0.02	0.02	0.02	<0.02
Zr	0.02	0.02	0.02	0.02	0.02

Figures 3.49 and 3.50 present the results from x-ray characterization of the 1985 WCXF2 and 1988 alumina filter materials. The principal phase in each of these materials is mullite, with secondary contributions of corundum. A somewhat higher concentration of corundum is identified in the WCXF2 processed material. Further verification is required to define this variation as a result of material formulation/fabrication or possible phase change that may have resulted during exposure to the METC process gases. In both XRD patterns, the presence of a glass phase is considered to be virtually nonexistent due to the shallow slope between the two theta angles of 10 and 24.

Physical properties characterization of the WCXF2 and WCXF4 materials were conducted to determine material's strength (4-point bend strength test), density, and porosity (See discussion in Section 3.1.4.5 of this Section). Unfortunately, a sample of the unused 1985 filter material was not available to perform similar analyses, and therefore comparison of the data generated with reference or background materials cannot be made. Similarly, possible trends illustrating loss of material strength or variation in porosity as a result of exposure to the METC process gases cannot be identified. These data do, however, indicate that material strength, density, and porosity vary somewhat with location within the filter material (i.e., material parallel or perpendicular to the dirty gas channel).

3.1.4.3 Alumina/Mullite Cross-Flow Filter Materials Fabricated for Use at the Subpilot-Scale Pressurised Fluidised-Bed Combustor at New York University (7/1988)

The mid-ribbed design of the alumina/mullite filters fabricated in July 1988 for use at the New York University combustor consisted of a 12x12x4 inch filter element, with a filter wall thickness of 0.10 inch, rib height of 0.25 inch, and rib thickness of 0.125 inch, with two ribs

Figure 3.49 - X-Ray Diffraction Analysis of the WCXF2
Alumina/Mullite Filter Material after
Exposure at METC

Figure 3.50 - X-Ray Diffraction Analysis of an Alumina/Mullite Filter
Fabricated for Use at the New York University Combustor

per inch. Analysis of the material prior to exposure at the New York combustor consisted of determining the elemental composition based on atomic absorption and emission spectroscopy analysis, phase characterization using x-ray diffraction (XRD), scanning electron microscopy/energy dispersive x-ray analysis (SEM/EDAX), 4-point bend testing, porosity, and density determination.

Post-test analysis of a section removed from a filter that had been exposed to the New York process gases after 52 hours at temperatures of 800 to 815°C (1470 to 1500°F), and 30 hours at temperatures of 705°C (1300°F) included SEM/EDAX and XRD characterization. The filter which had been selected for this exercise was labeled M2M (Module 2, Middle). The filter had delaminated during testing, and a small section had been removed from the base of the element near the flange. Analyses of this section are presented in the following discussion.

Analysis of the combustion gas produced during combustion of an eastern bituminous Kittanning coal with Ohio lime injection at 925°C (1700°F) and pressures of 100 psig was performed. The gas phase which contacted the filter was identified to contain 8% O₂, 13% CO₂, approximately 7% H₂O, 3 ppm SO₂, and 350 ppm NO.

Figure 3.51 illustrates the morphology of the alumina material in a filter which had been fabricated in July 1988. Figure 3.52 illustrates the morphology of an alumina/mullite filter from the same fabrication lot after exposure at the New York University combustor. The rod-like mullite phase is evident within the "melt-like" phase of the alumina/mullite matrix prior to combustion gas exposure (Figure 3.51).

SEM analysis of the section of material removed from the M2M filter shows a difference in morphology along the surface which was fractured during testing, in comparison to the surface of the original

Figure 3.51a - Scanning Electron Micrographs of a Cross-Sectioned Area from a Rib in an Alumina/Mullite Filter Fabricated for Use at the New York Combustor

Figure 3.51b - Higher Magnification Scanning Electron Micrographs of a Cross-Sectioned Area from a Rib in an Alumina/Mullite Filter Fabricated for Use at the New York Combustor

Figure 3.52a - Scanning Electron Micrographs of a Fracture Surface
in an Alumina/Mullite Filter Exposed in the New York
University Combustor

Figure 3.52b - Higher Magnification Scanning Electron Micrographs of a Fracture Surface in an Alumina/Mullite Filter Exposed in the New York University Combustor

Figure 3.52c - Scanning Electron Micrographs Showing the Crystal Formations and Ash Deposits Along the Alumina/Mullite Fracture Surface from a Filter Exposed in the New York University Combustor

Figure 3.52d - Scanning Electron Micrographs Showing the Crystal Formations and Ash Deposits Along the Alumina/Mullite Fracture Surface and Within Pores of a Filter That Was Exposed to the New York University Combustor Process Gases

Element	Weight Percent
Al	40.08
Si	42.48
S	4.07
K	0.87
Ca	9.81
Ti	0.83
Fe	2.07

Figure 3.52e - Energy Dispersive X-Ray Analysis Area Scan of the Alumina/Mullite Fracture Surface

material which had been manually fractured. Pores are relatively evident, as well as adjacent pore interconnects which lead to channeling in some areas. A molten-like surface surrounds the pore regions, as opposed to the "textured" phase of the original material.

The outer surface of this fracture is pinkish in appearance, indicative of a thin layer of process fines. The EDAX area scan indicates that the surface is rich in aluminum and silicon, and also contains calcium, sulfur, potassium, titanium, and iron. At high magnification of the M2M filter (Figure 3.52b), the rather large pores are seen to contain the mullite rods, however, they do not appear as discrete phases within the internal pore cavity. The rods are typically embedded within a "melt-like" phase. Particulate fines are identified along the fracture surface, as well as within the pore cavity.

A unique feature shown in Figures 3.52c and 3.52d is the formation of "cubic crystals" along the surface of the "melt-like" phase that surrounds the pores. These crystals are identified in Figure 3.53 (Area 2) by EDAX to consist of silicon, aluminum, magnesium, calcium, potassium, titanium, and iron, which is dissimilar from the smooth phase which supports the crystal formation. The smooth substrate surface (Figure 3.53, Area 1) is identified to consist primarily of aluminum, with silicon present, and traces of calcium and sulfur. Filter catch fines are also attached in these areas.

In several areas, "cubic crystals" appear to be positioned along the surface of the filter matrix. Efforts to discern the nature of the bond at the crystal cluster/surface interface could not be achieved at this magnification or sample orientation. At this time, we believe that the crystals are the result of crystallization of anorthite from the filter matrix, as opposed to reaction of the combustion process gas with the alumina/mullite filter matrix, or deposition of process fines.

Figure 3.53a - Scanning Electron Micrographs of the Crystal Formations
Along the Alumina/Mullite Fracture Surface

Figure 3.53b - Energy Dispersive X-Ray Analysis of the Various Phases
Along the Alumina/Mullite Fracture Surface

Figure 3.54a shows the adherence of combustion ash fines along the aluminum substrate at the edge of a pore. The ash agglomerate is seen to contain spherical particles that are less than 4 μm , and are rich in silicon, sulfur, aluminum, calcium, titanium, potassium, and iron. The large particle adjacent to the agglomerate is seen to consist primarily of aluminum and silicon, with sulfur, calcium, potassium, and iron present. An attempt was made to discern the type of bonding or interaction of the combustor fines with the alumina substrate. Although a separation between the ash and filter material is evident, contact and bonding has perhaps occurred directly beneath the ash particle.

Figure 3.55 illustrates an ash formation which extends directly into the alumina substrate pore cavity. Notably, both formations shown in Figures 3.54 and 3.55 are positioned along the smooth substrate phase.

Photo 7 in Figure 3.56 (top) shows the affinity of the New York University combustion fines along the internal surface of the alumina pore cavity, while Photo 8 (Figure 3.56 bottom) illustrates a dense ash deposit along the smooth surface between adjacent pores. One unique feature that is shown in Photo 8 in Figure 3.56 is the separation of a thin layer of what appears to be the matrix surface.

XRD analysis of the M2M material indicates the presence of mullite as the principal phase, with contributions of anorthite and corundum (Figure 3.57). The percentage of these phases in relationship to each other is 74 percent mullite, 18 percent anorthite, and 9 percent corundum. The existence of an amorphous phase is considered to be negligible.

Figure 3.58 illustrates the resulting XRD patterns for samples taken from an unused 1988 filter, and from the M2M filter exposed to the New York University process gases, both of which were produced in the

Figure 3.54a - High Magnification Scanning Electron Micrographs
Illustrating the Ash Deposit-Ceramic Matrix Interface

Figure 3.54b - Energy Dispersive X-Ray Analysis of the Ash Deposit
and Alumina/Mullite Matrix

Figure 3.55 - Scanning Electron Micrograph and Energy Dispersive X-Ray Analysis of an Ash Deposit Extending into a Pore Cavity in an Alumina/Mullite Filter That Had Been Exposed to the New York University Combustor Process Gases

Figure 3.56 - Scanning Electron Micrographs Illustrating Dense Ash Deposit Areas Along the Alumina/Mullite Matrix after Exposure in the New York University Combustor

Figure 3.57 - X-Ray Diffraction Analysis of the Alumina/Mullite Filter Material after Exposure in the New York University Combustor

Figure 3.58 - X-Ray Diffraction Analysis of the Alumina/Mullite Filter Material Before and After Exposure to the New York University Combustor Process Gases

same fabrication lot. Semi-quantitative x-ray composition analysis indicates that the concentration of mullite has decreased (from 94 to 74 percent), corundum has increased (8 to 9 percent), and anorthite is "formed" after exposure to the combustion gas process conditions. Variation in the quantity of the glass phase, if present, is not detected between these two samples.

The XRD phase change described above should be viewed as preliminary data, with further efforts focused on the possibility of a phase changes or transitions. Caution is warranted since there is the possibility that variation in phase composition may exist within any given filter element, and therefore could be a function of the manufacturing formulation/fabrication procedure, as opposed to changes in the substrate as a result of exposure to process conditions.

3.1.4.4 Alumina/Mullite Cross-Flow Filter Materials Fabricated for Use at the Texaco Entrained-Bed Gasifier (2/1989)

The mid-ribbed open channel design of the alumina/mullite filter fabricated in February 1989 for use at Texaco consisted of a 12x12x4 inch element, with a filter wall thickness of 0.10 inch, rib height of 0.375 inch, and rib thickness of 0.25 inch, with one rib per inch. Preliminary characterization of a section removed from the upper third of an element (i.e., nearest to the close filter end) consisted of scanning electron microscopy/energy dispersive x-ray analysis (SEM/EDAX), x-ray diffraction (XRD), four-point bend strength testing, porosity, and density determination.

SEM/EDAX of a fractured surface along a rib of the unused filter element is shown in Figure 3.59. The presence of large pores (100-300 μm) is evident along this surface. Rod-like formations of mullite are evident in the "melt-like" phase. In addition to the high porosity, another major difference in this material, in comparison to the 7/1988 alumina/mullite filters for the NYU combustor tests is the absence of mullite rods lining the internal cavity of the pores.

Figure 3.59 - Scanning Electron Micrographs and Energy Dispersive X-Ray Analysis of a Cross-Section from a Rib in an Alumina/Mullite Filter Fabricated for Use at Texaco

An EDAX area scan indicates the presence of aluminum and silicon, with minor contributions of calcium, and trace phases of magnesium, potassium, titanium, and iron.

XRD characterization of the material indicates the presence of mullite as the principal crystalline phase, with secondary contributions of anorthite and corundum (Figure 3.60). The broadening of the XRD pattern between the 10 and 24 two theta angles is indicative of amorphous phase(s). Since XRD does not identify the composition of the amorphous complexes, only a semi-quantitative estimate of the concentration of the crystalline phases can be made. These analyses indicate that approximately 70 percent mullite, 17 percent anorthite, and 12 percent corundum is present in this material.

Analysis indicates that the 2/1989 alumina material has a bulk density of 2.00 ± 0.02 g/cm³, and an open and closed porosity of 23 ± 2.5 and 11.9 ± 2.3 percent, respectively. Four-point bend strength tests (See discussion in Section 3.1.4.5) indicate that the material has a strength of 2806 ± 242 psi in sections that are parallel to the dirty gas flow channel, while strength within the thick closed end section of the filter element is determined to be 3810 ± 200 psi.

3.1.4.5 Variation in the Physical Properties and Principal Chemical Phases in the Alumina/Mullite Filter Material

With the exception of the small fracture at the flange, the M2M filter element which was exposed in the New York pressurized fluidized-bed combustor tests was virtually intact after exposure, and was not disassembled for further four-point bend strength testing. An alternate filter element (designated M2B) which had delaminated along the dirty gas channel seam during exposure at NYU was selected and sectioned for four-point bend strength testing.

Figure 3.60 - X-Ray Diffraction Analysis of Alumina/Mullite Filter
Material Fabricated for Use at Texaco

Three plate areas were removed from the M2B filter element. Samples were prepared by cutting areas from each plate that were both parallel and perpendicular to the dirty channel length. Table 3.50 presents the 4-point bend strength data from each sample section. The data indicate that the average strength of the alumina/mullite filter element after exposure in the New York University combustor is 5,000 psi. Notably, variation in material strength exists:

- From one plate to another
- Within any given plate.

Four-point bend strength test data were generated for an unexposed 12x12x4" alumina/mullite filter element which had been fabricated in the same lot as the NYU filter elements. These data indicate an initial strength of 8,995 psi. If the assumption is made that strength variation is minimal between filter elements in any given fabrication lot, these data would appear to indicate a 45% reduction in material strength as a result of exposure to the New York University combustion gas environment. To date, this assumption has not been verified, and therefore caution should be exercised when comparing the possible strength reduction data.

In the preparation of the samples, the surfaces are ground smooth prior to 4-point bend strength testing. This procedure removes the surface layer which could potentially contain reaction products or phase changes that result during exposure of the filter element to process conditions. If fractures occur within this layer, the possible flaws may impart a reduction in material strength which would not be accounted for as a result of sample preparation. Similarly, if the reaction products formed during process exposure contain a phase(s) which imparts strength to the material, an increase in strength would not be detected as a result of sample preparation. The strength data which are currently being generated only reflect the physical characteristics of the bulk material.

TABLE 3.50

FOUR-POINT BEND STRENGTH TEST DATA FOR AN
ALUMINA/MULLITE FILTER ELEMENT AFTER EXPOSURE IN THE
NEW YORK UNIVERSITY COMBUSTOR

Filter Element: M2B

Section	Area	MOR, psi
No. 1	Perpendicular to Dirty Channel	3,766
		5,396
		6,691
	Parallel to Dirty Channel	5,578
		3,759
		3,871
No. 2	Perpendicular to Dirty Channel	5,517
		5,886
		5,985
	Parallel to Dirty Channel	3,312
		6,117
		4,516
No. 3	Perpendicular to Dirty Channel	5,688
		4,989
		5,022
	Parallel to Dirty Channel	3,716
		3,323
		3,994
		4,707

Porosity and density measurements were also generated for samples removed from the alumina/mullite filter element that had been exposed to the New York University combustion gas environment. These data, as well as data generated for samples removed from an unexposed filter from the same fabrication lot are presented in Table 3.51. Both materials appear to be comparable in terms of porosity and density. Scanning electron microscopy analysis of the exposed filter indicates that although fines adhere to the "glassy" phase of the filter matrix, significant pore plugging has not occurred during short term testing. In an attempt to identify a mechanism which permits reduction in material strength, while maintaining porosity and density, we are currently proposing that changes may have occurred within the amorphous or "glassy" phase that bonds or interconnects the mullite rods in the alumina/mullite matrix. These changes include:

- Crystallization of the amorphous or "glassy" phase
- Reaction of the amorphous or "glassy" phase with the effluent gas constituents.

Since the 800-900°C (1470-1650°F) filter operating temperature was below the filter fabrication temperature, the independent effect of temperature on filter material is not expected to have reduced material strength. Since the short term (approximately 100 hours), pressurized fluidized-bed combustion gas exposure appears to have caused crystallization or a phase change within the filter material, a synergistic effect is suggested to have occurred between temperature and the effluent gas, and the alumina/mullite filter matrix. Although this short term, synergistic effect appears to have changed the strength characteristics of the alumina/mullite matrix, a definition is needed to identify a minimal acceptable operating material strength prior to catastrophic degradation of the filter element.

TABLE 3.51

POROSITY AND DENSITY DATA FOR AN
ALUMINA/MULLITE FILTER ELEMENT AFTER EXPOSURE IN THE
NEW YORK UNIVERSITY COMBUSTOR

Filter Element: M2B

Perpendicular to Dirty Gas Channel:

Sample No.	Bulk Density	Percent Dense	Percent Open Porosity	Percent Closed Porosity
1	2.26	73.2	15.4	11.7
2	2.30	74.5	15.5	10.3
3	2.17	70.3	27.2	2.5
4	2.11	68.4	25.0	6.5

Parallel to Dirty Gas Channel:

Sample No.	Bulk Density	Percent Dense	Percent Open Porosity	Percent Closed Porosity
1	2.13	69.0	26.6	4.6
2	2.14	69.0	26.6	4.3
3	2.29	74.2	15.7	9.9
4	2.09	67.7	26.4	5.8

Average:

	Bulk Density	Percent Dense	Percent Open Porosity	Percent Closed Porosity
Exposed (M2B)	2.19±0.08	70.8±2.8	22.3±5.6	7.0±3.3
Unexposed	2.26±0.02	73.1±0.5	18.8±1.7	8.1±1.3

Reaction of the amorphous or "glassy" phase in the alumina/mullite matrix with combustion gas phase constituents as alkali, chlorides, or possibly water vapor is also considered to have an effect on the stability and resulting strength of the exposed filter material. The result of these reactions would within time lead to a lower temperature eutectic phase formation, which reduces the viscosity of the interconnecting phase, and which would subsequently reduce material's strength. Exposure of the filter element to only 100 hours in the pressurized fluidized-bed combustion gas environment is not expected to result in an alkali or chloride concentration that could be identified as a crystalline phase by x-ray diffraction (i.e., >5 weight percent). Due to short term exposure, the low concentration of gas phase alkali or chlorides which could possibly "dissolve" within the amorphous or "glassy" phase of the filter matrix, may not be identified using scanning electron microscopy and/or energy dispersive x-ray diffraction (microprobe) mapping techniques.

The physical properties and phase composition of the WCXF2 and WCXF4 alumina/mullite filters that were exposed to the METC gasifier process gas in 1985-1986 were also determined, as well as a filter that had been fabricated for use in the Texaco gasifier (Table 3.52). Variation in the unused Texaco filter element material strength is shown in Table 3.53. The data indicate that the WCXF2, WCXF4, 7/1988 NYU exposed, and 2/1989 Texaco unused filters have a lower modulus of rupture in comparison with the 7/1988 NYU unused filters. Data also indicate that variation in the filter strength is apparent within each material, whether it is in material that is removed parallel or perpendicular to the dirty gas channel, or material that has been sectioned from the thicker, closed end of the filter element.

The physical properties and phase composition of the alumina/mullite filter materials were determined using four-point bend strength tests, porosity and, density determinations, and x-ray diffraction (XRD) techniques. Table 3.52 summarizes these results.

TABLE 3.52

CHEMICAL AND PHYSICAL PROPERTIES CHARACTERIZATION
OF VARIOUS ALUMINA/MULLITE FILTER MATERIALS

	WCXF2 Filters	WCXF4 Filters	NYU Filters		TEXACO Filters
Date Fabricated	1985	1985	<----7/1988---->		2/1989
Status	Exposed to METC Process Gas	Exposed to METC Process Gas	Unused	Exposed	Unused
Geometry, inches	6x6x2	6x6x2	12x12x4	12x12x4	12x12x4
Configuration	:<---Rectangular-->:		:<---Mid-Ribbed-->:		<--Mid-Ribbed-->
<u>Physical Properties</u>					
MOR, psi					
Parallel to Channel	2389+417(4)*	2070+108(3)	8955+738(8)	4715+1402(10)	3810+200(6)
Perpendicular to Channel	2162+234(4)	2874+337(4)	8425+1196(8)	5203+1487(9)	NA
Closed Filter End	NA	NA	NA	NA	2806+242(6)
Density, g/cm ³					
True	3.087 ⁽¹⁾	3.087 ⁽¹⁾	3.087 ⁽¹⁾	3.087 ⁽¹⁾	3.087 ⁽¹⁾
Bulk	1.96+0.03	2.11+0.09 ⁽²⁾ 1.98+0.02 ⁽³⁾	2.26+0.02	2.19+0.10 ⁽²⁾ 2.21+0.09 ⁽³⁾	2.00+0.0
% Dense	63.4+1.0	68.4+2.6 ⁽²⁾ 64.3+1.0 ⁽³⁾	73.1+0.5	71.0+3.2 ⁽²⁾ 71.5+3.0 ⁽³⁾	64.9+0.9
Porosity					
% Open	28.4+4.2	23.3+5.6 ⁽²⁾ 13.4+2.8 ⁽³⁾	18.8+1.7	21.2+5.4 ⁽²⁾ 21.3+5.9 ⁽³⁾	23.2+2.5
% Closed	8.2+3.8	8.3+3.1 ⁽²⁾ 22.3+2.1 ⁽³⁾	8.1+1.3	7.1+2.8 ⁽²⁾ 7.1+4.6 ⁽³⁾	11.9+2.3
<u>XRD Characterization</u>					
Principal Phase	Mullite	Mullite	Mullite	Mullite	Mullite
Secondary/Minor Phase(s)	Corundum	Corundum	Corundum	Corundum Anorthite Amorphous	Corundum Anorthite Amorphous

* Number of Samples Tested

NA: Not Analyzed

(1) Assumed Value

(2) Parallel to Dirty Gas Channel

(3) Perpendicular to Dirty Gas Channel

TABLE 3.53

FOUR-POINT BEND STRENGTH TEST DATA FOR THE
TEXACO ALUMINA/MULLITE FILTERS

Mid-Ribbed Alumina/Mullite	Dimensions, cm			Load, kg	Stress, psi
	Height	Width	Span		
• Parallel to Gas Flow Channel	0.183	0.710	0.635	2.25	2,561
	0.183	0.710	0.635	2.40	2,732
	0.180	0.712	0.635	2.20	2,580
	0.183	0.711	0.635	2.62	2,983
	0.181	0.712	0.635	2.40	2,791
	0.183	0.712	0.635	2.80	3,188
• Closed End Section	0.380	0.623	0.635	12.4	3,733
	0.382	0.625	0.635	13.3	3,960
	0.381	0.625	0.635	12.6	3,764
	0.381	0.623	0.635	13.8	4,136
	0.380	0.623	0.635	12.0	3,613
	0.373	0.624	0.635	11.7	3,652

Filter material density is also observed to vary somewhat with location within the filter elements. Porosity similarly varies with sample location in a given filter, as well as among the various filter lots. Figure 3.61 illustrates the inverse relationship of porosity and strength.

XRD analysis of the various alumina/mullite materials indicates that the 1985 WCXF2 and WCXF4 filters exposed to the METC process gas, and the unused 7/1988 NYU filter all contained mullite as the principal phase, with minor contributions of corundum. The exposed 7/1988 NYU and 2/1989 Texaco filters were identified to contain mullite as the principal phase, as well as minor contributions of corundum and anorthite. Similarly in the exposed NYU and Texaco filters, a broadening of the XRD pattern resulted between the two theta angles of 10 and 24, indicative of an amorphous structure.

From the data presented in Table 3.52 and Figure 3.61, there does not appear to be a relationship between chemical composition (i.e., phase) and material strength. This may indeed result when the concentration of mullite approaches a critical lower concentration. In the four filter materials analysed, however, mullite is generally 75 percent or greater, and the slight variation in the corundum concentration, and the inclusion of anorthite and/or the amorphous phase as minor constituents, does not appear to directly impact material strength. The only conclusion that can be reached at this time is that alumina/mullite materials which contain mullite at concentrations approaching 95 percent, and which have relatively low total porosity, have high material strength. Further effort is required to elucidate the influence of multiple matrix phases on material strength.

BENCH-SCALE AND FIELD TESTING

• Porosity / Strength Relationship

Figure 3.61 - Ceramic Material Porosity to Strength Relationship

3.1.4.6 Conclusions

- The alumina/mullite filter material has the potential to react with gas phase alkali at temperatures of 815°C (1500°F) and 925°C (1700°F).
- Chemical analysis of the alumina/mullite filter material after four hours of exposure to an argon gas environment containing 80 ppm NaCl at temperatures 815°C (1500°F) demonstrates that a 16-fold increase in sodium over background concentrations results in the amorphous, acid insoluble phase(s).
- Chemical analysis of the alumina/mullite filter material after four hours of exposure to an argon gas environment containing 80 ppm NaCl at temperatures 925°C (1700°F) demonstrates that a 100-fold increase in sodium over background concentrations results in the amorphous, acid insoluble phase(s).
- As gas phase sodium is captured by the alumina/mullite filter material, potassium, which is originally present, is released.
- Material flaws that were observed after four-point bend tests of the METC gasifier WCXF2 and WCXF4 filter samples were attributed to the presence of large pores, and to surrounding areas which contained high concentrations of retained pore forming carbon material.
- Agglomerated or flocculated submicron fines result along the smooth phase(s) (i.e., anorthite, amorphous, or corundum) of the alumina/mullite substrate after exposure to the METC fluid-bed gasifier process gas.

- Submicron crystal formations are observed to result along the smooth phase(s) (i.e., anorthite, amorphous, or corundum) of the alumina substrate after exposure to the New York pressurized fluidized-bed combustion gas.
- The smooth phase(s) (i.e., anorthite, amorphous, or corundum) in the alumina/mullite substrate appears to be the preferred site for particulate capture, as opposed to areas which contain mullite.
- Minor variations in the phase composition of the alumina/mullite substrate may occur within a given filter element; between various filter elements in a given fabrication lot; and between fabrication lots.
- A direct relationship is demonstrated between the total porosity of the alumina/mullite matrix and material strength (<10,000 psi). A definitive relationship of material strength and phase or composition cannot be made at this time.
- Preliminary data indicate that the alumina/mullite ceramic filter material may experience a reduction in material strength after exposure to process conditions as at the NYU pressurized fluidized-bed combustor. Extensive analysis is recommended for strength determinations of unused and exposed filter elements generated within a specific fabrication lot, confirming the observed reduction in strength. Identification of an acceptable operating change in filter material's properties is critical to understanding filter performance and life.

3.2 TASK 2: EVALUATION OF POTENTIAL LONG-TERM HIGH TEMPERATURE DEGRADATION MECHANISMS

3.2.1 Thermodynamic Assessment

The stability of the cross-flow filter materials after long-term, high temperature exposure to coal process conditions is expected to depend on the ability of the ceramic material to withstand degradation from:

- Thermal cycling
- Chemical attack from gas phase volatiles released during coal processing
- Reaction with entrained char/ash fines.

Thermodynamic equilibrium projections have demonstrated the stability of alumina/mullite, cordierite, cordierite-silicon nitride, aluminosilicate foam, and reaction bonded silicon nitride at process temperature and pressure, as well as an inertness for reaction with the process bulk gas chemistry. Calculations have been generated (Section 3.1.3) which demonstrate the potential reaction of ceramic materials with alkali, chlorides, and sulfur contaminants. Caution should, however, be exercised in interpreting these results since thermodynamic equilibrium databases do not possess adequate property data (i.e., heat capacity, enthalpy, entropy, etc.) for glass or amorphous complexes that are known to be present in each of these materials.

Similarly, thermodynamic equilibrium calculations have been used to project potential product phases which could result from reaction of char or ash fines with the ceramic matrix. Analytical data presented in Section 3.1.2 have demonstrated the relative high softening temperature for the process fines in comparison to the identified filter operating process temperature. The issue which still remains to be resolved is whether "softened" or molten fines emitted from the gasifier or combustor impact and stick to the filter surface.

Thermodynamic equilibrium calculations have also shown that in direct coal fired turbine and pressurized fluidized-bed combustion systems which release high alkali concentrations (i.e., 20 ppm) into the effluent gas stream, the potential exists for vapor phase condensation of alkali species (i.e., liquid and/or condensed sulfates). Alternately, under gasification, alkali is projected to remain principally as a chloride, with condensation resulting in the formation of solid alkali chlorides or carbonates.

Tables 3.54 through 3.58 assimilate the thermodynamic phase stability projections, summarizing the influence of temperature, gas phase chemistry, and reaction of fines with the various cross-flow filter material phases during exposure in the five coal process systems. As shown for thermally induced phase change, the potential exists for oxidation of non-oxide ceramics (i.e., cordierite-silicon nitride and reaction bonded silicon nitride) at the higher filter operating temperature in the direct coal fired turbine and pressurized fluidized-bed combustion systems. Depending on the actual process conditions (i.e., thermal cycling) transition between the quartz and cristobalite phase could occur, as well as a thermal mismatch between the oxidized surface layer and the underlying matrix material. Small pores within the cordierite-silicon nitride or reaction bonded silicon nitride material could also fill as a result of oxidation.

The filter operating temperatures are not expected to independently promote volatilization or depletion of the ceramic matrix since each filter material has been fired at fabrication temperatures which exceed the currently identified filter operating temperature. The influence of thermal cycling on each ceramic material in each process remains to be determined since temperature and chemical interactions are expected to play a synergistic role on the stability of the filter material phases.

TABLE 3.54

LONG-TERM CERAMIC CROSS-FLOW FILTER DEGRADATION MECHANISMS
- FIXED-BED GASIFICATION -

590°C (1094°F)

	Alumina/ Mullite	Cordierite	Aluminosilicate Foam	Cordierite- Silicon Nitride	Reaction Bonded Silicon Nitride
<u>THERMAL INFLUENCE:</u>					
Phase Change	None	None	None	None	None
Pore Change	None	None	None	None	None
Volatilization of Matrix	None	None	None	None	None
Thermal Cycling	TBD (a)	TBD	TBD	TBD	TBD

<u>CHEMICAL INFLUENCE:</u>				
Process Gas	None	None	None	None (b)
Volatile Alkali Reactions	:<-----Na ₂ Al ₂ Si ₈ O ₁₆ (c)----->:			None
Volatile Sulfur Reactions	None	None	None	None
Volatile Chloride Reactions	None	None	None	None
Moisture/Steam Reactions	TBD	TBD	TBD	TBD

Particulate Reactions (c)	Alumina:	Cordierite:	Mullite:	Cordierite:	Silicon Nitride:
	FeAl ₂ O ₄	FeAl ₂ O ₄	FeAl ₂ O ₄	FeAl ₂ O ₄	Al ₂ SiO ₅
	CaAl ₄ O ₇	CaMgSi ₂ O ₆	CaAl ₂ Si ₂ O ₈	CaMgSi ₂ O ₆	Na ₂ SiO ₅
	MgAl ₂ O ₄	NaAl ₂ Si ₆ O ₁₆	MgAl ₂ O ₄	NaAl ₂ Si ₆ O ₁₆	K ₂ Si ₄ O ₉
	NaAlO ₂	K ₂ Al ₂ Si ₂ O ₈	Na ₂ Al ₂ Si ₆ O ₁₆	K ₂ Al ₂ Si ₂ O ₈	MgSiO ₃
	Al ₂ SiO ₅		K ₂ Al ₂ Si ₂ O ₈	Silicon Nitride:	
	Mullite:			Al ₂ SiO ₅	
	CaAl ₂ Si ₂ O ₈			Na ₂ SiO ₅	
	MgAl ₂ O ₄			K ₂ Si ₄ O ₉	
	Na ₂ Al ₂ Si ₆ O ₁₆			MgSiO ₃	
	FeAl ₂ O ₄				
	K ₂ Al ₂ Si ₂ O ₈				
Pore Change	TBD	TBD	TBD	TBD	TBD
Density Change	TBD	TBD	TBD	TBD	TBD
Volatilisation of Matrix	None	None	None	None	None

Thermal Cycling	TBD	TBD	TBD	TBD	TBD
<u>SYNERGISTIC INFLUENCE:</u>					
Change in Strength	NE ^(f)	NE	NE	NE	NE

(a) TBD: To Be Determined.

(b) Equilibrium Projections Indicate Oxidation of Si_3N_4 ; Reaction Kinetics, However, Limit Extent of Conversion at Temperatures of 590°C.

(c) Comparable Potassium Reactions Projected for Mullite and Cordierite.

(d) Alkali Reaction Projected for Mullite; No Reaction Projected for Alumina.

(e) Projected Phases Illustrate Interaction of Constituents in Char/Ash Fines with Ceramic Phases at Equilibrium. Possible Localized Solid-Solid Reaction Product at Point of Contact.

(f) NE: Not Expected.

TABLE 3.55

LONG-TERM CERAMIC CROSS-FLOW FILTER DEGRADATION MECHANISMS
- FLUID-BED GASIFICATION -

700°C (1292°F)

Alumina/ Mullite	Cordierite	Aluminosilicate Foam	Cordierite- Silicon Nitride	Reaction Bonded Silicon Nitride
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THERMAL INFLUENCE:

Phase Change

None

None

None

None

None

Pore Change

None

None

None

None

None

Volatilization of
Matrix

None

None

None

None

None

Thermal Cycling

TBD (a)

TBD

TBD

TBD

TBD

CHEMICAL INFLUENCE:

Process Gas	None	None	None	None (b)	None (b)
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Volatile Alkali Reactions	:<-----Na ₂ Al ₂ Si ₆ O ₁₆ ----->:	(c)			None
---------------------------	--	-----	--	--	------

Volatile Sulfur Reactions	None	None	None	None	None
---------------------------	------	------	------	------	------

Volatile Chloride Reactions	None	None	None	None	None
-----------------------------	------	------	------	------	------

Moisture/Steam Reactions	TBD	TBD	TBD	TBD	TBD
--------------------------	-----	-----	-----	-----	-----

Particulate Reactions (e)	Alumina:	Cordierite:	Mullite:	Cordierite:	Silicon Nitride:
	FeAl_2O_4	FeAl_2O_4	FeAl_2O_4	FeAl_2O_4	Al_2SiO_5
	CaAl_4O_7	$\text{CaAl}_2\text{Si}_2\text{O}_8$	$\text{CaAl}_2\text{Si}_2\text{O}_8$	$\text{CaAl}_2\text{Si}_2\text{O}_8$	$\text{Na}_2\text{Si}_2\text{O}_5$
	MgAl_2O_4	$\text{NaAl}_2\text{Si}_6\text{O}_{16}$	MgAl_2O_4	$\text{NaAl}_2\text{Si}_6\text{O}_{16}$	$\text{K}_2\text{Si}_4\text{O}_9$
	NaAlO_2	$\text{K}_2\text{Al}_2\text{Si}_2\text{O}_8$	$\text{Na}_2\text{Al}_2\text{Si}_6\text{O}_{16}$	$\text{K}_2\text{Al}_2\text{Si}_2\text{O}_8$	MgSiO_3
	Al_2SiO_5		$\text{K}_2\text{Al}_2\text{Si}_2\text{O}_8$	Silicon Nitride:	
	Mullite:			Al_2SiO_5	
	$\text{CaAl}_2\text{Si}_2\text{O}_8$			$\text{Na}_2\text{Si}_2\text{O}_5$	
	MgAl_2O_4			MgSiO_3	
	$\text{Na}_2\text{Al}_2\text{Si}_2\text{O}_8$			$\text{K}_2\text{Si}_4\text{O}_9$	
	FeAl_2O_4				
	$\text{K}_2\text{Al}_2\text{Si}_2\text{O}_8$				
Pore Change	TBD	TBD	TBD	TBD	TBD
Density Change	TBD	TBD	TBD	TBD	TBD
Volatilization of Matrix	None	None	None	None	None

Thermal Cycling	TBD	TBD	TBD	TBD	TBD

SYNERGISTIC INFLUENCE:

Change in Strength	Possible (f)	Possible (g)	Possible (h)	Possible (i)	None (j)
--------------------	-----------------	-----------------	-----------------	-----------------	-------------

- (a) TBD: To Be Determined.
- (b) Equilibrium Projections Indicate Oxidation of Si_3N_4 ; Reaction Kinetics, However, Limit Extent of Conversion at Temperatures of 700°C .
- (c) Comparable Potassium Reactions Projected for Mullite and Cordierite.
- (d) Alkali Reaction Projected for Mullite; No Reaction is Projected for Alumina.
- (e) Projected Phases Illustrate Interaction of Char/Ash Constituents with Ceramic Phases at Equilibrium. Possible Localized Solid-Solid Reaction Product at Point of Contact.
- (f) Possible Reaction of Alkali with Grain Boundary or Amorphous Phase Which Bonds Mullite Grains; Limited or Negligible Dissolution of Adjacent Grains.
- (g) Possible Reaction of Alkali with Grain Boundary or Amorphous Phase Bonding Cordierite Grains; Limited or Negligible Dissolution of Adjacent Grains.
- (h) Limited Reaction of Alkali with Uncoated Glass Fibers.
- (i) Possible Reaction of Alkali with Grain Boundary or Amorphous Phase Which Bonds Cordierite-Silicon Nitride Grains; MgSiAlON Stabilizes (Retards) Dissolution of Adjacent Grain Boundaries.
- (j) Reaction of Alkali is Limited to Oxidized Pores or Filter Surface; Lack of Grain Boundary Phase Limits Further Reaction of Alkali with Matrix as in Other Materials.

TABLE 3.56

LONG-TERM CERAMIC CROSS-FLOW FILTER DEGRADATION MECHANISMS
- ENTRAINED-BED GASIFICATION -

870°C (1600°F)

	Alumina/ Mullite	Cordierite	Aluminosilicate Foam	Cordierite- Silicon Nitride	Reaction Bonded Silicon Nitride
<u>THERMAL INFLUENCE:</u>					
Phase Change	None	None	None	:Quartz<->Cristobalite: : Transition of : Oxidized Si ₃ N ₄ : (a) :	
Pore Change	None	None	None	None	None
Volatilization of Matrix	None	None	None	None	None
Thermal Cycling	TBD (b)	TBD	TBD	TBD	TBD

CHEMICAL INFLUENCE:

Process Gas	None	None	None	None (c)	None (c)
Volatile Alkali Reactions	: <----- (f) ----- NaAlO_2	----- $\text{Na}_2\text{Al}_2\text{Si}_6\text{O}_{16}$	-----> : $\text{Na}_2\text{Si}_2\text{O}_5$	-----> : $\text{Na}_2\text{Si}_2\text{O}_5$	-----> : $\text{Na}_2\text{Si}_2\text{O}_5$ (e)
Volatile Sulfur Reactions	None	None	None	: Possible Sulfide : Formation $\text{SiO}_2/\text{Si}_3\text{N}_4$: Si_2ON_2	
Volatile Chloride Reactions	None	None	None	: Possible Chloride : Formation $\text{SiO}_2/\text{Si}_3\text{N}_4$	
Moisture/Steam Reactions	TBD	TBD	TBD	TBD	TBD

Particulate Reactions (g)	Alumina:	Cordierite:	Mullite:	Cordierite:	Silicon Nitride:
	FeAl ₂ O ₄	FeAl ₂ O ₄	FeAl ₂ O ₄	FeAl ₂ O ₄	Al ₂ SiO ₅
	CaAl ₄ O ₇	CaAl ₂ Si ₂ O ₈	CaAl ₂ Si ₂ O ₈	CaAl ₂ Si ₂ O ₈	MgSiO ₃
	MgAl ₂ O ₄	NaAl ₂ Si ₆ O ₁₆	MgAl ₂ O ₄	NaAl ₂ Si ₆ O ₁₆	Na ₂ Si ₂ O ₅
	NaAlO ₂	K ₂ Al ₂ Si ₂ O ₈	Na ₂ Al ₂ Si ₆ O ₁₆	K ₂ Al ₂ Si ₂ O ₈	K ₂ Si ₄ O ₉
	Al ₆ Si ₂ O ₁₃		K ₂ Al ₂ Si ₂ O ₈	Silicon Nitride:	
	Mullite:			Al ₂ SiO ₅	
	CaAl ₂ Si ₂ O ₈			Na ₂ Si ₂ O ₅	
	MgAl ₂ O ₄			K ₂ Si ₄ O ₉	
	Na ₂ Al ₂ Si ₆ O ₁₆			MgSiO ₃	
	K ₂ Al ₂ Si ₂ O ₈				
	FeAl ₂ O ₄				
Pore Change	TBD	TBD	TBD	TBD	TBD
Density Change	TBD	TBD	TBD	TBD	TBD
Volatilization of Matrix	None	None	None	: Release of Sulfides/ : : From SiO ₂ /Si ₃ N ₄ : : Si ₂ ON ₂ :	

Thermal Cycling	TBD	TBD	TBD	TBD
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SYNERGISTIC INFLUENCE:

Change in Strength	Probable (h)	Probable (i)	Probable (j)	Probable (k)	Possible (l)
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- (a) Inherent Si_3N_4 Oxidized Layer Along Pore or Filter Surface; Quartz/Cristobalite Transition at 806°C.
- (b) TBD: To Be Determined.
- (c) Equilibrium Projections Indicate Oxidation of Si_3N_4 ; Reaction Kinetics Are Expected to Enhance Conversion at Temperatures of 870°C.
- (d) Comparable Potassium Reactions Projected for Mullite and Cordierite.
- (e) Reaction of Volatile Alkali with Oxidized SiO_2 Pore or Filter Surface.
- (f) NaAlO_2 Projected for Reaction of Alumina with Volatile Alkali; Possible Formation of Liquid NaCl Along Mullite Filter Matrix Phase.
- (g) Projected Phase Illustrates Interaction of Char/Ash Constituents with Ceramic Phase at Equilibrium; Possible Localized Solid-Solid Reaction Products at Point of Contact.
- (h) Reaction of Alkali with Grain Boundary or Amorphous Phase Bonding Mullite Grains; Limited Dissolution of Adjacent Grains.
- (i) Reaction of Alkali with Grain Boundary or Amorphous Phase Bonding Cordierite Grains; Limited Dissolution of Adjacent Grains.
- (j) Reaction of Alkali with Uncoated Glass Fibers.
- (k) Reaction of Alkali with Grain Boundary or Amorphous Phase Bonding Cordierite-Silicon Nitride Grains; MgSiAlON Stabilizes (Retards) Dissolution of Adjacent Grains
- (l) Reaction of Alkali with Oxidized Pore or Filter Surface; Possible Accelerated Oxidation of Pores Causing Small Pores to Fill; Lack of Grain Boundary Phase Limits Further Reaction with Alkali as in Other Materials.

TABLE 3.57
LONG-TERM CERAMIC CROSS-FLOW FILTER DEGRADATION MECHANISMS
- DIRECT COAL FIRED TUBULAR SYSTEMS -

980°C (1800°F)

	Alumina/ Mullite	Cordierite	Aluminosilicate Foam	Cordierite- Silicon Nitride	Reaction Bonded Silicon Nitride
<u>THERMAL INFLUENCE:</u>					
Phase Change	None	None	None		:Quartz to Cristobalite: :Transition of Oxidized: : Si ₃ N ₄ (a) :
Pore Change	None	Pore	None		: Small Pores May Fill : : With SiO ₂ ; : Thermal Mismatch (a) :
Volatilization of Matrix	None	None	None	None	None
Thermal Cycling	TBD (b)	TBD	TBD	TBD	TBD

CHEMICAL INFLUENCE:

Process Gas	None	None	None	None (c)	None (c)
Volatile Alkali Reactions	$: < \text{NaAlO}_2(f) \text{---} \text{Na}_2\text{Al}_2\text{Si}_6\text{O}_{18} \text{---} > :$	$\text{Na}_2\text{SO}_4(f)$	$\text{Na}_2\text{SO}_4(f)$	None (e)	None (e)
Volatile Sulfur Reactions	None	None	None	$: \text{SiO}_2/\text{Si}_3\text{N}_4 \text{ (Si}_2\text{ON}_2) :$	$: \text{SiO}_2/\text{Si}_3\text{N}_4 \text{ (Si}_2\text{ON}_2) :$
Volatile Chloride Reactions	None	None	None	$: \text{SiO}_2/\text{Si}_3\text{N}_4 \text{ (Si}_2\text{ON}_2) :$	$: \text{SiO}_2/\text{Si}_3\text{N}_4 \text{ (Si}_2\text{ON}_2) :$
Moisture/Steam Reactions	TBD	TBD	TBD	TBD	TBD

Particulate Reactions (g)	Alumina:	Cordierite:	Mullite:	Cordierite:	Silicon Nitride:
	MgAl ₂ O ₄	CaAl ₂ Si ₂ O ₈	CaAl ₂ Si ₂ O ₈	CaAl ₂ SiO ₈	Al ₆ Si ₂ O ₁₃
	Na ₂ SO ₄ (1)	Na ₂ Al ₂ Si ₆ O ₁₆	MgAl ₂ O ₄	Na ₂ Al ₂ Si ₆ O ₁₆	MgSiO ₃
	Al ₆ Si ₂ O ₁₃		MgSiO ₃	Silicon Nitride:	Na ₂ Si ₂ O ₅ (1)
	Mullite:		Na ₂ Al ₂ Si ₆ O ₁₆	Al ₆ Si ₂ O ₁₃	K ₂ Si ₄ O ₉ (1)
	MgAl ₂ O ₄		Na ₂ SO ₄ (1)	MgSiO ₃	
	MgSiO ₃			Na ₂ Si ₂ O ₅ (1)	
	Na ₂ Al ₂ Si ₆ O ₁₆			K ₂ Si ₄ O ₉ (1)	
	CaAl ₂ Si ₂ O ₈				
	Na ₂ SO ₄ (1)				
Pore Change	TBD	TBD	TBD	: Small Pores May Fill :	
				: With SiO ₂ :	
				: Thermal Mismatch :	
Density Change	TBD	TBD	TBD	TBD	TBD
Volatilisation of Matrix	None	None	None	: Chlorides and Sulfide:	
				: Release From SiO ₂ :	
				: Si ₃ N ₄ (Si ₂ ON ₂) :	

Thermal Cycling	TBD	TBD	TBD	TBD	TBD
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SYNERGISTIC INFLUENCE:

Change in Strength	More Probable (h)	More Probable (i)	More Probable (j)	Probable (k)	Possible (l)
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- (a) Inherent Si_3N_4 Oxidized Layer Along Pore or Filter Surface.
- (b) Quartz/Cristobalite Transition at 806°C .
- (c) TBD: To Be Determined.
- (d) Equilibrium Projections Indicate Oxidation of Si_3N_4 ; Reaction Kinetics Promote Conversion at Temperatures of 980°C ; Carbon Deposition Projected.
- (e) Comparable Potassium Reactions Projected for Mullite and Cordierite.
- (f) Possible Formation of Liquid NaCl at $\text{SiO}_2/\text{Si}_3\text{N}_4$ Interface.
- (g) NaAlO_2 Projected for Reaction of Alumina with Volatile Alkali; Possible Formation of Liquid NaCl or Na_2SO_4 Along Mullite in Filter Matrix.
- (h) Projected Phase Illustrates Interaction of Char/Ash Constituents with Ceramic Phase at Equilibrium; Possible Localized Solid-Solid Reaction Products at Point of Contact.
- (i) Accelerated Reaction of Alkali with Grain Boundary or Amorphous Phase Bonding Mullite; Eutectic Phase Formation and Subsequent Dissolution of Adjacent Grains; Possible Accelerated Surface Attack from Liquid NaCl or Na_2SO_4 Deposits.
- (j) Accelerated Reaction of Alkali with Grain Boundary or Amorphous Phase Bonding Cordierite Grains; Possible Eutectic Phase Formation and Subsequent Dissolution of Adjacent Grains.
- (k) Accelerated Reaction of Alkali with Uncoated Glass Fibers; Possible Accelerated Surface Attack from Liquid Na_2SO_4 Deposits.

- (k) Accelerated Reaction of Alkali with Grain Boundary or Amorphous Phase Bonding
Cordierite-Silicon Nitride Grains; Possible Eutectic Formation; Subsequent
Dissolution of Adjacent Grains Retarded by MgSiAlON Formation; Possible Accelerated
Surface Attack in the Presence of Liquid NaCl, $\text{Na}_2\text{Si}_2\text{O}_5$ or $\text{K}_2\text{Si}_4\text{O}_9$.
- (1) Accelerated Reaction of Alkali with Oxidized Pores of Filter Surface; Accelerated
Oxidation of Small Pores Causes Small Pores to Fill; Lack of Grain Boundary Phase
Limits Reaction of Alkali with Matrix as in Other Materials; Accelerated Alkali
Attack in the Presence of Liquid NaCl Formed from Vapor Phase Condensation;
Localized Corrosion Resulting from Formation of Liquid Alkali Silicates at Point of
Fines Contact; Enhanced Volatilization of Si_3N_4 Matrix from Reaction of Gas Phase
Sulfur and Chloride Species.

TABLE 3.58

LONG-TERM CERAMIC CROSS-FLOW FILTER DEGRADATION MECHANISMS
- PRESSURIZED FLUIDIZED-BED COMBUSTION -

870°C (1600°F)

Alumina/ Mullite	Cordierite	Aluminosilicate Foam	Cordierite- Silicon Nitride	Reaction Bonded Silicon Nitride
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THERMAL INFLUENCE:

Phase Change	None	None	None	: Quartz <-> Cristobalite : : Transition of Oxidized : : Si ₃ N ₄ (a) :
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Pore Change	None	None	None	: Small Pores May Fill : : With SiO ₂ : : Thermal Mismatch (a) :
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Volatilization of Matrix	None	None	None	None
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Thermal Cycling	TBD (b)	TBD	TBD	TBD
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<u>CHEMICAL INFLUENCE:</u>				
Process Gas	None	None	None (c)	None (c)
Volatile Alkali Reactions	$: < \text{NaAlO}_2 (f) \text{-----} \text{Na}_2\text{Al}_2\text{Si}_8\text{O}_{16} (d) \text{-----} > : (e)$			
Volatile Sulfur Reactions	None	None		Sulfide Formation : : From $\text{SiO}_2/\text{Si}_3\text{N}_4$: : (Si_2ON_2) :
Volatile Chloride Reactions	None	None		Chloride Formation : : From $\text{SiO}_2/\text{Si}_3\text{N}_4$: : (Si_2ON_2) :
Moisture/Steam Reactions	TBD	TBD	TBD	TBD

Particulate Reactions (g)	Alumina:	Cordierite:	Mullite:	Cordierite:	Silicon Nitride:
	$\text{Al}_6\text{Si}_2\text{O}_{13}$	$\text{Na}_2\text{Al}_2\text{Si}_6\text{O}_{16}$	MgSiO_3	$\text{Na}_2\text{Al}_2\text{Si}_6\text{O}_{16}$	Al_2SiO_5
	MgAl_2O_4		MgAl_2O_4	Silicon Nitride:	MgSiO_3
	Mullite:		$\text{Na}_2\text{Al}_2\text{Si}_6\text{O}_{16}$	Al_2SiO_5	$\text{Na}_2\text{Si}_2\text{O}_5$
	$\text{Na}_2\text{Al}_2\text{Si}_6\text{O}_{16}$			MgSiO_3	$\text{K}_2\text{Si}_4\text{O}_9$ (1)
	MgSiO_3			$\text{Na}_2\text{Si}_2\text{O}_5$	NaCl (1)
	MgAl_2O_4			$\text{K}_2\text{Si}_4\text{O}_9$ (1)	
				NaCl (1)	

Pore Change	TBD	TBD	TBD	: Small Pores May Fill: : With SiO_2 ; : Thermal Mismatch :
Density Change	TBD	TBD	TBD	TBD
Volatilization of Matrix	None	None	None	: Release of Sulfides/ : Chlorides From : $\text{SiO}_2/\text{Si}_3\text{N}_4$ (Si_2ON_2) :
Thermal Cycling	TBD	TBD	TBD	TBD

SYNERGISTIC INFLUENCE:

Change in Strength	Probable (h)	Probable (i)	Probable (j)	Probable (k)	Possible (l)
<hr/>					
(a)	Inherent Si_3N_4 Oxidized Layer Along Pores or Filter Surface; Quartz/Cristobalite Transition at 808°C.				
(b)	TBD: To Be Determined.				
(c)	Equilibrium Projections Indicate Oxidation of Si_2N_4 ; Reaction Kinetics Begin to Promote Conversion at Temperatures of 870°C; Carbon Deposition Projected.				
(d)	Comparable Potassium Reactions Projected for Mullite and Cordierite.				
(e)	Possible Formation of Liquid NaCl at $\text{SiO}_2/\text{Si}_3\text{N}_4$ Interface.				
(f)	NaAlO_2 Projected from Reaction of Alumina with Volatile Alkali; Possible Formation of Liquid NaCl or Solid Na_2SO_4 along Mullite Filter Matrix Phase.				
(g)	Projected Phase Illustrated Interaction of Char/Ash Constituents with Ceramic Phase at Equilibrium; Possible Localized Solid-Solid Reaction Products at Point of Contact.				
(h)	Reaction of Alkali with Grain Boundary or Amorphous Phase Bonding Mullite; Limited Dissolution of Adjacent Grains.				
(i)	Reaction of Alkali with Grain Boundary or Amorphous Phase Bonding Cordierite Grains; Limited Dissolution of Adjacent Grains.				
(j)	Reaction of Alkali with Uncoated Glass Fibers.				
(k)	Reaction of Alkali with Grain Boundary or Amorphous Phase Bonding Cordierite- Silicon Nitride Grains; MgSiAlON Stabilizes (Retards) Dissolution of Adjacent Grains; Possible Accelerated Surface Corrosion in the Presence of Liquid NaCl or Localized Liquid $\text{K}_2\text{Si}_4\text{O}_9$ Formations.				
(l)	Reaction of Alkali with Oxidized Pores or Filter Surface; Possible Accelerated Oxidation of Pores Causing Small Pores to Fill; Lack of Grain Boundary Phase Limits Further Reaction of Alkali as in Other Materials; Accelerated Alkali Corrosion of Substrate Surface in the Presence of Liquid NaCl Formed from Vapor Phase Condensation; Localized Corrosion Resulting from Formation of Liquid Alkali Silicates at Point of Fines Contact; Limited Volatilization of Si_3N_4 Matrix from Reaction with Gas Phase Sulfur or Chloride Species.				

The above discussion has considered the influence of temperature solely on ceramic material stability. The obvious question arises as to whether the gas phase environment (i.e., bulk gas, alkali, chlorides, fines, etc.) has any influence on material stability. With regard to bulk gas chemistry, reactions with either the reducing or oxidizing gas constituents (i.e., CO, CO₂, CH₄, H₂, O₂, and N₂) are not thermodynamically projected to alter the stability of the alumina/mullite, cordierite, or aluminosilicate foam materials. In the direct coal fired turbine and pressurized fluidized-bed combustion systems which operate at temperatures that are greater than 900°C (1650°F), oxidation of Si₃N₄ in cordierite-silicon nitride and reaction bonded silicon nitride is expected to be initiated.

As shown in Tables 3.54 through 3.58, alkali is projected to be driven into the alumina, aluminosilicate, or silicate phases in each material, or to deposit as solid chlorides or sulfates which can subsequently dissolve in the oxidized surface layer of the cordierite-silicon nitride or reaction bonded silicon nitride materials. Each of the ceramic filter materials has the affinity to absorb alkali into its matrix. The rate at which alkali is absorbed is expected to increase with temperature. Current thermodynamic equilibrium calculations do not have the capabilities for predicting the affinity for reaction of volatile alkali with the amorphous or "glassy" phases that are present in each of these materials. This phase is expected to have a higher potential for reaction with alkali in comparison to the crystalline ceramic filter material phases (i.e. alumina, mullite, cordierite, or silicon nitride). The rate at which alkali is absorbed is considered to depend on:

- The effluent gas alkali concentration which is related to both process operating parameters and feed material composition

- Filter operating temperature
- "Glassy" or amorphous phase composition, concentration, and distribution with the matrix material.

Currently the mechanism by which alkali is considered to absorb, react, and possibly degrade the ceramic material is within the grain boundary phase(s). Initially alkali is expected to be absorbed in the "glassy" or amorphous grain boundary phase, causing a lower melting temperature eutectic phase to be formed. This results in ultimately lowering the viscosity of the grain boundary phase, perhaps weakening the structure, and causing loss of material strength. Critical issues include identifying:

- The rate of alkali absorption within the various phases
- The relationship between alkali absorption and material's properties (i.e., strength)
- An acceptable change in material's properties prior to loss of material's performance, life, and/or catastrophic degradation.

Sulfur and chloride species which are present in the gasification or combustion process gases are not expected to react with the principal constituents of the alumina/mullite, cordierite, or aluminosilicate foam materials. At the elevated filter operating temperatures in the entrained-bed gasification, direct coal fired turbine, or pressurized fluidized-bed combustion systems, release of volatile silicon sulfides and chlorides could potentially result from the cordierite-silicon nitride or reaction bonded silicon nitride matrix. This interaction could possibly lead to loss or depletion of the material, and subsequently loss of material strength. Again, the kinetics of the sulfide or chloride reaction with cordierite-silicon nitride or reaction bonded silicon nitride remains to be determined.

Silicon carbide has been shown to experience degradation in the presence of steam.^(127, 128) The reaction of steam is considered to principally oxidize the surface layer of the silicon carbide material or free silicon grains, leading to formation of silica, and possibly the release of volatile silicon species. Silicon carbide which has been used in ceramic candle filters is known to also contain a binder phase, which could potentially react with steam.

In the current study, Westinghouse did not perform a parametric series of thermodynamic calculations exploring the possible influence of steam concentrations on material's stability. Perhaps, at the elevated filter operating temperatures (i.e., entrained-bed gasifier, direct coal fired turbine, and pressurized fluidized-bed combustion system), when cordierite-silicon nitride or reaction bonded silicon nitride are used in the filter element design, possible reactions with steam could result along the material's surface or pores, leading to loss of material, as well as strength, as has been demonstrated for the silicon carbide matrix.

Similarly, the influence of steam has not been identified for the "glassy" or amorphous phases. As shown in previous Westinghouse studies,^(4,6) the influence of steam on alkali absorption by the aluminosilicate fullers earth material, emathlite, caused not only a "glassy" layer to be formed on the surface, but also enhanced alkali absorption into the getter sorbent. The influence of steam on material's stability therefore remains to be determined not only with respect to its reaction with the ceramic matrix, but also with respect to its possible interactions with gas phase alkali at either the surface or within the grain boundary phase of the ceramic material.

At equilibrium, iron, calcium, sodium, potassium, or magnesium present in the char or ash fines have the potential to react with the aluminum, aluminosilicate, or silicate structures of the ceramic cross-flow filter materials, forming complex resulting phases. Particularly

deleterious reactions are projected for the direct coal fired turbine and pressurized fluidized-bed combustion systems where liquid NaCl, Na_2SO_4 , $\text{Na}_2\text{Si}_2\text{O}_5$, or $\text{K}_2\text{Si}_4\text{O}_9$ could result. In-field test data have demonstrated the affinity of char or ash fines along the "glassy" or amorphous surface or within the pores of the ceramic material. Analytical data could not be generated which identify the morphology or composition of the phase at the fines/ceramic interface. Perhaps bonding of the fines with the matrix has occurred through the formation of one or more of the thermodynamically projected phases. Further effort is required to demonstrate the affinity of the fines for reaction with the "glassy" or amorphous phases in each material.

As shown in Tables 3.54 through 3.58 the impact of the chemical influence on change in pore size or material density also remains to be determined. At this time, consideration is given to possible pore filling as a result of high temperature oxidation along the cordierite-silicon nitride or reaction bonded silicon nitride matrix. Similarly, volatilization is proposed for these materials as a result of high temperature sulfide or chloride formation. The influence of thermal cycling on material stability after reaction with alkali, chloride, steam, and/or fines also remains to be determined.

Tables 3.54 through 3.58 attempt to identify the synergistic influence of temperature and chemical interactions on the stability of each ceramic material for each of the five process systems. The proposed resulting material degradation mechanisms focus on the thermodynamic projections, as well as consideration of the actual grain boundary characteristics of the various materials. As shown in the synergistic influence section of Tables 3.54 through 3.58, the high operating temperature of the entrained-bed gasifier, the direct coal fired turbine, and the pressurized fluidized-bed combustion systems could promote accelerated degradation. The influence of the oxidizing environment is expected to further enhance degradation in comparison to reactions in the reducing, gasification environment.

3.2.2 Chemical/Mechanical Assessment

In order to assess the principal chemical degradation mechanisms for each material at process conditions, consideration must be given to not only the chemical composition of each material, but also to the nature of the grain boundary phase. The majority of the materials being considered for cross-flow filters have an amorphous grain boundary phase which is compositionally different from the matrix. Hence the stability of the grain boundary phase under process conditions can affect the performance of the filter material.

The alumina/mullite material is formed in the green (unfired) state from alumina, silica, and pore formers, and when fired, generally contains mullite rods surrounded by a grain boundary glassy or amorphous phase. Atomic absorption analysis of the alumina/mullite material indicates the presence of 52.29 wt% Al_2O_3 , 39.64 wt% SiO_2 , 0.46 wt% Fe_2O_3 , 4.79 wt% CaO , 2.60 wt% MgO , 0.31 wt% K_2O , and 0.18 wt% Na_2O . Review of the phase stability diagram in Figure 3.62 illustrates the potential for mullite, corundum, and probably anorthite to be present as phases at equilibrium in the alumina/mullite material. Since mullite and corundum were identified by XRD, it is likely that anorthite could be present as a grain boundary phase. Uncertainty, however, does exist in how impurities (i.e., magnesium) shift the phase stability fields.

Consideration has been given to the preferential absorption of alkali by the glassy grain boundary phase. If alkali absorption occurs, the properties of the glass phase are expected to be altered (i.e., decrease viscosity, increase propensity for crystallization) as a result of the formation of alkaline earth silicates or more complex silicate phases. This is proposed to have been the mechanism by which anorthite crystals formed in the glass phase surrounding the pores in the alumina/mullite filter material after exposure to the NYU pressurized fluidized-bed combustion gases.

E. F. Osborn and Arsal Muan, revised and redrawn "Phase Equilibrium Diagrams of Oxide Systems," Plate 1, published by the American Ceramic Society and the Edward Orton, Jr., Ceramic Foundation, 1960.

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Figure 3.62 - Phase Stability Diagram for CaO-Al₂O₃-SiO₂ Composite System.⁽⁶¹⁾
 Reprinted by Permission of the American Ceramic Society from
Phase Diagrams for Ceramists, Basic Volume, p. 219. M. K. Reser
 (ed.), E. M. Levin, C. R. Robbins, and H. F. McMurdie, Columbus, OH:
 American Ceramic Society, 1964.

The extent of alkali degradation is difficult to predict since neither the composition of the glassy phase is precisely known, nor are the thermodynamic data available for glass solution impurities. Qualitative projections, however, can be made using the phase stability diagram presented in Figure 3.63. When alkali is added to $\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{SiO}_2$, low melting temperature eutectics are expected to form. Grains that are adjacent to the alkali-rich glassy grain boundary phase are expected to dissolve. When this occurs, the alumina/mullite material is expected to experience a loss of strength. The rate of degradation can only be determined experimentally.

The cordierite material is formed in the green state from talc (hydrated magnesium silicates), alumina, and ball clay (impure hydrated aluminosilicates containing alkali, TiO_2 , etc.). During firing cordierite forms mullite, spinels, and corundum along with glass (Figure 3.64). When alkali contacts the cordierite glass phase, alkali is expected to dissolve in the glass phase, forming low melting temperature eutectics [i.e., 1050°C (1900°F)] (Figure 3.65). The presence of other impurities which are generally present in cordierite, are also expected to further depress the equilibrium glass formation temperature. As in the alumina/mullite material, grains that are adjacent to the alkali-rich glassy grain boundary phase are expected to dissolve. When this occurs, the cordierite material is expected to experience a loss of strength.

Cordierite-silicon nitride (CSN) is initially formed from a mixture of cordierite and silicon nitride. Although the XRD data presented in Section 3.1.2 indicate the presence of $\beta\text{-Si}_3\text{N}_4$, Si_2ON_2 , and α -cordierite in the CSN material after firing, Mg-SiAlON and a glass phase are also considered to result. As previously discussed, the reaction of alkali with the CSN grain boundary glass is expected to occur when the CSN material is exposed to gasification or combustion environments. Although the glass phase has the potential to dissolve

Figure 3.63 - Phase Stability Diagram for Na₂O·Al₂O₃·2SiO₂-CaO·Al₂O₃·2SiO₂-SiO₂ Composite System. (61) Reprinted by Permission of the American Ceramic Society from Phase Diagrams for Ceramists; 1969 Supplement, p. 173. M. K. Reser (ed.), E. M. Levin, C. R. Robbins, and H. F. McMurdie, Columbus, OH: American Ceramic Society, 1969.

R. F. Osborn and Arnold Muan, revised and redrawn, "Phase Equilibrium Diagrams of Oxide Systems," Plate 2, published by the American Ceramic Society and the Edward Orton, Jr., Ceramic Foundation, 1960.

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Figure 3.64 - Phase Stability Diagram for $\text{MgO}-\text{Al}_2\text{O}_3-\text{SiO}_2$ Composite System.⁽⁶¹⁾
Reprinted by Permission of the American Ceramic Society from
Phase Diagram for Ceramists, Basic Volume, p. 246. M. K. Reser
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Figure 3.65 - Phase Stability Diagram for $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ - $\text{MgO} \cdot \text{Al}_2\text{O}_3$ - SiO_2 .⁽⁶¹⁾
Reprinted by Permission of the American Ceramic Society from
Phase Diagrams for Ceramists, 1989 Supplement, p. 175.
M. K. Reser (ed.), E. M. Levin, C. R. Robbins, and
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alkali and degrade, the presence of MgO , Al_2O_3 , and SiO_2 which if incorporated into a Mg-SiAlON crystalline structure, reduces the extent of dissolution of adjacent grains. Therefore precipitous degradation which is expected for the cordierite material after long-term exposure to alkali containing gasification or combustion gas, is not expected to occur in the CSN material. In addition, the CSN material has a lower thermal coefficient of expansion, and higher strength at all temperatures, making it a better thermostructural material than cordierite.

Atomic absorption analysis of the aluminosilicate foam indicates the presence of 54.18 wt% Al_2O_3 , 48.86 wt% SiO_2 , 0.04 wt% Fe_2O_3 , 0.03 wt% CaO , 0.02 wt% MgO , 0.02 wt% K_2O , and 0.16 wt% Na_2O . The foam consists principally of glass fibers that are coated and held together by mullite. Since the aluminosilicate foam inherently has low strength, further efforts are required to demonstrate the ability of the foam to retain its structural integrity during exposure at filter conditions. Assuming that the foam possesses adequate strength, complete coating of the glass fibers would be essential in order to prevent reaction with alkali which would lead to the formation of soda-aluminosilicate compositions which have eutectic temperatures of approximately $1050^{\circ}C$ ($1795^{\circ}F$). Devitrification of the glass fiber is expected as a result of sodium attack, causing shrinkage and cracking of the fibers, and ultimately failure of the filter structure.

In the fabrication of reaction bonded silicon nitride (RBSN), silicon is nitrided in the presence of iron, forming a microstructure in which Si_3N_4 grains are directly bonded to each other. A glassy grain boundary phase should not exist in this material, making it unique from the materials previously discussed. During exposure to oxidizing combustion gas environments, an amorphous and/or crystalline SiO_2 phase is expected to form on the external and internal surfaces of the filter material. Because the RBSN filters are not expected to experience temperatures $>1000^{\circ}C$ ($>1830^{\circ}F$), the rate of oxidation will be slow.

This rate increases in the presence of alkali, steam, and HCl. As a result of the low oxidation temperatures [$<1000^{\circ}\text{C}$ ($<1830^{\circ}\text{F}$)], the external surface should not be sealed by an SiO_2 layer. Consequently, oxidation occurs throughout the filter, and over long-term exposure (>1000 - 5000 hours) a significant weight gain in the filter material is expected to result. Because of the increase in molar volume (SiO_2 is approximately 80% larger than Si_3N_4), small pores and pore channels can be closed, and large pores and pore channels can be reduced in size. This is expected to lead to a significant reduction in filter permeability and an increased operating pressure drop. Similarly, if crystallization occurs during thermal cycling in the SiO_2 phase, a thermal expansion mismatch in the microstructure could result, leading to cracking in the SiO_2 layer, and further oxidation of subsurfaces.

3.2.3 Summary

Figures 3.66 through 3.69 present an assessment of the ceramic cross-flow filter material stability for each process in terms of

- Thermal degradation
- Chemical degradation - alkali
- Char/ash fines interaction
- Phase composition - crystallization.

Based on our current understanding of candidate cross-flow materials, Figures 3.70 and 3.71 were constructed in an attempt to assess the mechanical properties of material strength, and thermal shock resistance with respect to thermal cycling for each material under each set of process conditions.

Process (Filter Temp.)	Thermal Degradation				
	Alumina / Mullite	Cordierite	Aluminosilicate Foam	Cordierite/ Si ₃ N ₄	Reaction Bonded Si ₃ N ₄
	None				
	Fixed-Bed Gasification (590 °C)				
	Fluid-Bed Gasification (700 °C)				
	Entrained-Bed Gasification (870 °C)				
Direct Coal Fired Turbine (980 °C)					
Pressurized Fluidized-Bed Combustion (870 °C)	<div><div>• Oxidation of Grain Boundary Forming Si₃N₄ Forming SiO₂ / Si₂ON₂</div><div>• Oxidation of Pores Forming SiO₂ / Si₂ON₂ Layer</div></div>				

(W)

Figure 3.66 - Long-Term Ceramic Material Assessment - Thermal Degradation

	Chemical Degradation-Alkali				Reaction Bonded Si ₃ N ₄
Process (Filter Temp.)	None				Cordierite/ Si ₃ N ₄
Fixed-Bed Gasification (590 °C)	None				Aluminosilicate Foam
Fluid-Bed Gasification (700 °C)	Limited Glassy Grain Boundary Phase Reactions				Cordierite
Entrained-Bed Gasification (870 °C)	<ul style="list-style-type: none"> • Reaction with Grain Boundary Glass Phases • Dissolution of Adjacent Grains • Loss of Material Strength 	<ul style="list-style-type: none"> • Reaction with Uncoated Glass Fibers 	<ul style="list-style-type: none"> • Reaction with Grain Boundary Glass Phases • MgSiAlON Stabilizes Grain/Glass interface 	<ul style="list-style-type: none"> • Reaction with SiO₂ / Si₂ON₂ Layer • Small Pore Closure 	Alumina / Mullite
Direct Coal Fired Turbine (980 °C)					
Pressurized Fluid- ized Bed Com- bustion (870 °C)					

(W)

Figure 3.67 - Long-Term Ceramic Material Assessment - Chemical Degradation (Alkali)

Process (Filter Temp.)	Char / Ash Fines Degradation				
	Alumina / Mullite	Cordierite	Aluminosilicate Foam	Cordierite / Si ₃ N ₄	Reaction Bonded Si ₃ N ₄
Fixed-Bed Gasification (590 °C)	None				
Fluid-Bed Gasification (700 °C)	<ul style="list-style-type: none"> Adherence Along Glassy Grain Boundary Phase 	<ul style="list-style-type: none"> Adherence Along Glassy Grain Boundary Phase 			
Entrained-Bed Gasification (870 °C)	<ul style="list-style-type: none"> Adherence Along Glassy Grain Boundary Phase Basic Attack Dissolution of Adjacent Grains Loss of Material Strength 	<ul style="list-style-type: none"> Adherence Along Glassy Grain Boundary Phase Basic Attack MgSIALON Stabilizes Grain / Glass Interface 			
Direct Coal Fired Turbine (980 °C)		<ul style="list-style-type: none"> Adherence Along Glassy Grain Boundary Phase Basic Attack Limited Adherence Along Pore Glassy Layer Basic Attack 			
Pressurized Fluid- ized Bed Com- bustion (870 °C)					

WI

Figure 3.68 - Long-Term Ceramic Material Assessment - Char/Ash Fines Degradation

Process (Filter Temp.)	Phase Change/Crystallization				
	Alumina/Mullite	Cordierite	Aluminosilicate Foam	Cordierite/ Si ₃ N ₄	Reaction Bonded Si ₃ N ₄
Fixed-Bed Gasification (590 °C)	None				
Fluid-Bed Gasification (700 °C)					
Entrained-Bed Gasification (870 °C)					
Direct Coal Fired Turbine (980 °C)					
Pressurized Fluid- ized Bed Com- bustion (870 °C)					
	<ul style="list-style-type: none"> • Crystallization of Anorthite • Absorption of Alkal in Glassy Phase; Lowered Viscosity; Lowered Strength 	<ul style="list-style-type: none"> • Absorption of Alkal in Glassy Phase; Lowered Viscosity; Lowered Strength 		<ul style="list-style-type: none"> • Formation of SiO₂/Si₂ON₂ Along Grain Boundary (CSN) or Pore Surface (RBSN) • Crystallization of SiO₂ • Thermal Expansion Mismatch on Thermal Cycling 	

(W)

Figure 3.69 - Long-Term Ceramic Material Assessment - Phase Change/Crystallisation

Process (Filter Temp.)	Mechanical Properties - Material Strength				
	Alumina / Mullite	Cordierite	Aluminosilicate Foam	Cordierite / Si ₃ N ₄	Reaction Bonded Si ₃ N ₄
Fixed-Bed Gasification (590° C)	Excellent				
Fluid-Bed Gasification (700° C)	Excellent-Good				
Entrained-Bed Gasification (870° C)	Good				
Direct Coal Fired Turbine (980° C)	Good-Fair				
Pressurized Fluid- ized Bed Com- bustion (870° C)					

(W)

Figure 3.70 - Long-Term Ceramic Material Assessment - Mechanical Properties (Material Strength)

Process (Filter Temp.)	Thermal Shock Resistance-Thermal Cycling				
	Alumina / Mullite	Cordierite	Aluminosilicate Foam	Cordierite / Si ₃ N ₄	Reaction Bonded Si ₃ N ₄
	Fixed-Bed Gasification (590 °C)	Good	Good - Fair	Excellent - Good	Excellent
	Fluid-Bed Gasification (700 °C)				
	Entrained-Bed Gasification (870 °C)				
	Direct Coal Fired Turbine (980 °C)				
Pressurized Fluid- ized Bed Com- bustion (870 °C)					

(12)

Figure 3.71 - Long-Term Ceramic Material Assessment - Thermal Shock Resistance (Thermal Cycling)

Synergistic thermal/chemical degradation mechanisms which have been identified principally include:

- Chemical reaction of alkali with ceramic grain boundary phases
- Oxidation of silicon nitride containing ceramics at elevated process temperatures
- Phase crystallization (i.e., anorthite in alumina/mullite; formation of SiO_2 in cordierite silicon nitride and reaction bonded silicon nitride)
- Possibly the influence of steam and/or thermal cycling
- Possibly the interaction of fines along the "glassy" or amorphous phase of each material.

The rate at which these reactions occur, and their influence on the change in material's properties (i.e., loss of strength) all remain to be determined, prior to projecting long-term high temperature ceramic filter element life at process conditions.

4. CONCLUSIONS

- Synergistic, long-term, high temperature degradation of ceramic cross-flow filter materials (i.e., alumina/mullite, cordierite, aluminosilicate foam, cordierite-silicon nitride, and reaction bonded silicon nitride) may be expected to result principally from:

- The reaction of volatile alkali species with grain boundary phases
- Oxidation of non-oxide ceramic phases at elevated temperatures
- Phase crystallization.

Each of these mechanisms could potentially introduce residual stresses within the porous ceramic matrix, particularly within the "glassy" grain boundary phases, that could lead to subsequent stress corrosion crack formation and flaw propagation. Ceramic cross-flow filter material degradation may also be influenced by:

- The interaction of the ceramic matrix with steam
- Possibly thermal cycling
- Possibly the interaction of fines which adhere to the "glassy" or amorphous phase present in each ceramic cross-flow filter material.

- Desirable physical properties [i.e., MOR: 2,000-9,000 psi; pressure drop of 10 in. water at gas flow rates of 10 ft/min at 815°C (1500°F)] have been demonstrated for the alumina/mullite and cordierite materials. Further development is needed to increase porosity within the cordierite-silicon nitride and reaction bonded silicon nitride materials. Because of the low strength of the aluminosilicate foam, its durability in cross-flow filter applications needs to be demonstrated.

- The alumina/mullite cross-flow material is formed in the green (unfired) state from alumina, silica, and pore formers, and when fired, generally contains mullite rods surrounded by a grain boundary "glassy" or amorphous phase. In the current production of the alumina/mullite cross-flow filter elements, the chemical composition of the resulting filter elements, and strength measurements both within the filter plates, as well as along the rib-to-plate bonds have been shown to vary within and between fabrication lots.
- Cordierite is formed in the green state from talc (hydrated magnesium silicates), alumina, and ball clay (impure hydrated aluminosilicates containing alkali, TiO_2 , etc.). During firing cordierite forms mullite, spinels, and corundum along with glass. Further analytical characterization of the currently produced cordierite filter elements is needed to identify potential variability in chemical composition and physical properties both within and between fabrication lots.
- The aluminosilicate foam consists principally of glass fibers that are coated and held together by mullite. Although filter elements have been produced, further development is required to significantly improve material strength.
- Cordierite-silicon nitride is initially formed from a mixture of cordierite and silicon nitride. X-ray diffraction analysis indicates the presence of β - Si_3N_4 , Si_2ON_2 , and α -cordierite in the cordierite-silicon nitride material after firing. Mg-SiAlON and a glass phase are also expected to be present in the resulting ceramic matrix. To date, the developmental cordierite-silicon nitride material has not been fabricated into a cross-flow filter element.
- In the fabrication of reaction bonded silicon nitride, silicon is nitrided in the presence of iron, forming a microstructure in which the Si_3N_4 grains are directly bonded to each other. In contrast to the alternate cross-flow filter materials, a glassy grain boundary phase is

not expected to exist in the reaction bonded silicon nitride matrix. Similar to cordierite-silicon nitride, reaction bonded silicon nitride has not been fabricated into a full-scale cross-flow filter element.

- The final firing temperatures which are used in the ceramic material formulation processes exceed the temperatures which the cross-flow filter elements will experience during particulate removal in either the gasification or combustion systems. Phase transitions or chemical reactions within the ceramic matrix are therefore not expected to result solely from exposure to process temperatures. Long-term high temperature exposure may introduce residual stress within the cross-flow materials, particularly within the "glassy" phases. Stress corrosion cracking of the porous matrices may result if flaws are generated within the filter element structure.

- At the elevated filter operating temperature in the entrained-bed gasification system, "active" oxidation (low oxygen partial pressure) of the non-oxide silicon-based ceramics (i.e., cordierite-silicon nitride; reaction bonded silicon nitride) could result, releasing gaseous silicon-containing phases. At the elevated filter operating temperature in the direct coal fired turbine and pressurized fluidized-bed combustion systems, "passive" oxidation (high oxygen partial pressures) of the non-oxide silicon-based ceramics could result, leading to the formation of a silica layer along the filter surface or within pores.

- In pressurized bench-scale tests conducted at 815°C (1500°F), the alumina/mullite cross-flow filter material has been shown to adsorb gas phase sodium (i.e., NaCl) principally as a condensed water soluble chloride phase. Increased reaction temperatures of 925°C (1700°F) tend to drive alkali from the water soluble condensed alkali chloride phase into an acid soluble/insoluble phase which is considered to be the amorphous or "glassy" grain boundary structure of the alumina/mullite matrix. These data therefore imply the relative inertness of the

alumina/mullite material to alkali degradation in the fixed- and fluid-bed gasification processes since alkali is expected to remain as a condensed solid chloride phase. These data also imply that absorption of alkali may be limited at entrained-bed gasification or pressurized fluidized-bed combustion filter operating conditions, but possibly accelerated in the direct coal fired turbine system, as a result of alkali absorption within the amorphous or "glassy" structure of the alumina/mullite matrix.

- Thermodynamic equilibrium estimates provide a first level approximation of the process gas chemistry, trace alkali and chloride emissions concentrations, and char or ash fines compositions that can be released into the effluent gas streams. Similar calculations can project the possible interaction of these species with the various phases present in the ceramic cross-flow filter materials. Feed material composition (i.e., coal, sulfur sorbents, alkali getters, etc.) and process configuration (i.e., oxygen- versus air-blown gasification; combustion) significantly impact the projected equilibrium gas, condensed, and solid phase concentrations, and therefore the extent of reaction with ceramic cross-flow filter materials.
- On-line process data which attempt to quantify the concentration of alkali released into the effluent gas streams are generally lower than the projected equilibrium concentrations. This could in part be due to the inhomogeneous release of alkali during coal gasification or combustion; variation in the process system operating parameters; condensation of volatile alkali species along cooler surfaces of components which would ultimately lower the expected alkali concentration; or to the sensitivity of the alkali sampling equipment and analytical capabilities.
- The alkali phase which will be carried to the ceramic cross-flow filter element surface is dependent on the composition of the feed and sorbent materials which are used in the specific process. Parametric

equilibrium calculations indicate that condensation and deposition of NaCl, KCl, and Na_2CO_3 are expected to occur at the cross-flow filter surface [i.e., 590°C (1095°F), 300 psig, with or without char] when 2 to 20 ppm total alkali is released into the fixed-bed gasifier effluent stream.

- In fluid-bed gasification, alkali that is released at concentrations of 0.2-2 ppm into the gasifier outlet remains totally as gas phase species over the 700°C (1290°F), 300 psig ceramic cross-flow filter surface. With 20 ppm total alkali released into the effluent gas stream, the potential exists for condensation and deposition of sodium as Na_2CO_3 along the filter surface (with or without char).

- In the entrained-bed gasification system, alkali which is released into the effluent stream at concentrations ranging between 0.2-20 ppm is not projected to condense prior to contacting the 870°C (1600°F), 450 psig ceramic filter surface (with or without). Due to the porous nature of the char layer, gas phase alkali is expected to permeate through the ceramic filter matrix, principally as a volatile alkali species.

- In the direct coal fired turbine system, alkali which is released as a volatile species at concentrations >2 ppm, has the potential to condense as molten Na_2SO_4 and solid K_2SO_4 along the ceramic filter surface (with or without ash fines) of the 980°C (1800°F), 180 psig ceramic cross-flow filter. Accelerated alkali degradation of the ceramic matrix is expected in the presence of the molten sulfate phase.

- As in the direct coal fired turbine system, Na_2SO_4 and K_2SO_4 are projected to condense along the cross-flow filter surface (with or without ash fines) in the pressurized fluidized-bed combustion system. With 20 ppb total alkali released into the pressurized fluidized-bed combustion effluent stream, deposition of liquid Na_2SO_4 is projected to

occur. At alkali concentrations of 0.2-20 ppm, both liquid Na_2SO_4 and solid K_2SO_4 are likely to result along the 870°C (1600°F), 150 psig filter surface. Accelerated alkali degradation of the ceramic matrix is expected in the presence of the molten sulfate phase.

- Thermodynamic equilibrium calculations have demonstrated the affinity of each of the principal phases in the various cross-flow filter materials to react with gas phase alkali (i.e., NaCl), forming alkali aluminates (i.e., $\beta\text{-NaAlO}_2$ from alumina), aluminosilicates (i.e., $\text{Na}_2\text{Al}_2\text{Si}_6\text{O}_{18}$ from mullite or cordierite), and silicates (i.e., $\text{Na}_2\text{Si}_2\text{O}_5$ from oxidized Si_3N_4). Each material may therefore be susceptible to long-term, high temperature alkali degradation.

- Each of the ceramic cross-flow filter materials has been shown to initially contain, or is expected to form a "glassy" or an amorphous phase during filter operations. Reactions of alkali with the intergranular "glassy" phases that are present throughout the alumina/mullite, cordierite, and cordierite-silicon nitride structures have been proposed. Comparable reactions of alkali with the glass fibers in the aluminosilicate foam are also proposed. Based on the relatively clean grain boundaries consisting of silicon nitride-to-silicon nitride contacts in the reaction bonded silicon nitride material, oxidation is expected to result only on the external filter and internal pore surfaces. Since the oxidation kinetics of reaction bonded silicon nitride have been shown to be very slow at temperatures below 900°C (1650°F), reaction of alkali with reaction bonded silicon nitride is expected to be limited to within the reaction product silica layer, and not directly with the silicon nitride material. The effects of these reactions on material's durability remains to be demonstrated.

- Bench-scale testing and thermodynamic equilibrium projections indicate the affinity of alkali to react with the aluminosilicate lattice of the char or ash fines. The question which remains to be

resolved is whether these reactions are kinetically limited either during the short residence time that the gas and fines experience during passage from the gasifier or combustor outlet and collection at the filter surface, or during the time which the char or ash fines remain along the filter surface before pulse jet cleaning.

- The thermodynamic calculations performed during the course of this contract did not directly address the stability of the ceramic cross-flow filter materials to variable steam concentrations. The principal phase which is expected to undergo degradation in each of these materials is considered to be the "glassy" or amorphous phase(s). Performance of a parametric series of equilibrium calculations demonstrating the interaction of steam with the "glassy" phase(s) would be informative, provided that reliable thermodynamic data are available for these phases.

- Thermodynamic equilibrium calculations project the potential for the formation of gaseous sulfides and chlorides to be released from oxidized silicon nitride at the elevated filter operating temperatures in the entrained-bed gasification, direct coal fired turbine, and pressurized fluidized-bed combustion systems. Kinetics for these reaction is needed to identify potential loss of material during operation of filter elements which contain silicon nitride.

- Current ASTM procedures were used in defining the melt or fusion temperatures of the char or ash fines that would be carried to the cross-flow filter element surface. Deformation and fluid temperatures for these fines all exceed the projected filter operating temperature for either the fixed-bed, fluid-bed, or entrained-bed gasification, direct coal fired turbine, or pressurized fluidized-bed combustion systems. If the gasifier or combustor operates at temperatures as high as 1180°C (2155°F), and fines carryover to the filter is rapid, there exists the potential for deformed and/or even softened fines to impact and stick to the filter element surface.

- Due to the significant quantity of amorphous phases formed within char or ash fines during processing, detailed compositional analysis using x-ray diffraction techniques could not be used to support the complex set of compounds that are projected by the thermodynamic equilibrium models.
- Phase crystallization forming submicron particles of anorthite results within the amorphous phase of the alumina/mullite filter during short-term exposure to pressurized fluidized-bed combustion gases at the New York University combustor test rig.
- During operation of the alumina/mullite filter elements in the pressurized fluid-bed gasification (i.e., METC gasifier) and pressurized fluidized-bed combustion (i.e., NYU combustor) environments, entrained fines which are retained appear to adhere to the "glassy" amorphous phase of the ceramic filter matrix. Efforts to date have not been able to identify the nature of the bond at the fines/ceramic interface.
- Thermodynamic equilibrium calculations have demonstrated potential interactions of the char or ash constituents with the various principal phases that are present in each of the ceramic materials. Localized point-contact melts may result through the formation of liquid NaCl, $K_2Si_4O_9$, or $Na_2Si_2O_5$, particularly along cross-flow filters operating in the pressurized fluidized-bed combustion and direct coal fired turbine systems. Alternately, if equilibrium between the char or ash constituents and the ceramic matrices were achieved, complex calcium, magnesium, or iron aluminates, alkali aluminosilicates, calcium aluminosilicates, calcium-magnesium or magnesium silicates could be formed.
- Thermodynamic equilibrium calculations predict the formation of carbon at the gas/silicon nitride ceramic material interface under oxidizing conditions (i.e., gas shift reaction in direct coal fired

turbine or pressurized fluidized-bed combustion systems). Pore plugging along the external filter surface could result in the cordierite-silicon nitride or reaction bonded silicon nitride filter elements.

- Four-point bend strength data indicate the potential for reduction in strength of the alumina/mullite filter elements after short-term exposure in the New York University pressurized fluidized-bed combustion test rig. Data need to be generated which detail variation in strength within a given filter element, among filter elements in a fabrication lot, and between various fabrication lots.

- In developing the long-term, high temperature cross-flow filter element life performance models, the following critical issues have been identified:

- Definition of the alkali reaction(s) and kinetics for the various ceramic cross-flow filter material glass phases.
- Definition of the relationship between the alkali reaction and subsequent change in the ceramic material properties.
- Definition of an acceptable change or loss in the critical physical and mechanical properties that govern long-term cross-flow filter element integrity.

- With respect to identifying alternate materials for use as potential cross-flow filter materials, the following issues should be considered:

- Definition of an acceptable glass phase concentration in the ceramic filter materials which would permit alkali absorption but not material's or performance degradation.
- Definition of residual stress introduced within the filter as a result of process exposure.

5. RECOMMENDATIONS

- Conduct of experimental bench-scale tests is recommended in order to validate the proposed long-term high temperature degradation mechanisms in ceramic cross-flow filter materials. This effort is proposed through a series of:

- Flow-through tests which identify the rate of alkali absorption with the various ceramic materials, while simultaneously identifying any resulting change in material's chemical (i.e., phase or compound) or physical (i.e., strength) properties.
- Flow-through tests which attempt to identify synergistic effects of thermal cycling and alkali absorption on the durability of the ceramic cross-flow filter materials.
- Thermogravimetric analysis tests which demonstrate the possible influence of simulated oxidizing or reducing gas environments on the resulting microstructure of the ceramic cross-flow filter materials.
- Thermal exposure tests which explore the possible interaction of ash or char fines with the various ceramic cross-flow filter materials.

- Chemical and physical characterization of sample coupons or actual ceramic cross-flow filter elements which have been exposed to in-field sub-pilot-scale process environments are recommended to supplement the bench-scale data, and provide further insight into development of the filter life performance model(s).

- Identification of an acceptable change or loss in the critical physical and mechanical properties that govern long-term high temperature cross-flow filter material integrity is recommended.

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APPENDIX A

THERMODYNAMIC EQUILIBRIUM PROCESS CALCULATIONS

APPENDIX A

THERMODYNAMIC EQUILIBRIUM PROCESS CALCULATIONS

A first level approximation of the gas and solid phase composition formed at gasifier or combustor process condition can be generated using public domain thermodynamic equilibrium computer codes (i.e., NASA CET86; SOLGASMIX). During the Phase I effort of this contract, compositions for a fixed-bed gasifier, entrained-bed gasifier, and a pressurized fluidized-bed combustor effluent gas and solid stream were generated using the NASA CET86 program. These data, as well as data previously generated by Westinghouse for a fluid-bed gasification system and a direct coal fired turbine system are presented in the following Sections.

1.0 Fixed-Bed Gasification

Table A.1 illustrates the thermodynamic equilibrium product gas and solid compositions which are projected to result in the fixed-bed gasification system that is shown in Figure A.1. For a fixed-bed gasifier which operates at temperatures of 800°C (1100°F) and pressures of 20 atm, release of alkali is principally projected to be in the form of gaseous chlorides (i.e., 0.101 ppmv KCl; 0.016 ppmv K₂Cl₂; 0.389 ppbv NaCl). The composition of the resulting fixed-bed gasifier fines is projected to include C, SiO₂, Al₂SiO₅, FeS, CaAl₂Si₂O₈, K₂Al₂Si₂O₈, Na₂Al₂Si₂O₈, and CaMgSi₂O₆.

TABLE A.1

THERMODYNAMIC EQUILIBRIUM PRODUCT DISTRIBUTION
FORMED DURING FIXED-BED GASIFICATION OF A
PITTSBURGH SEAM COAL

Mole Fraction*

FORMALDEHYDE	7.3235-8
FORMIC ACID	2.3393-7
CH3	3.944-11
CH3CL	1.554-18
CH4	7.3447-2
METHANOL	2.8569-8
CO	1.6999-2
COS	5.7875-5
CO2	1.3788-1
CS2	5.8642-9
ACETYLENE	1.697-12
KETENE	1.264-18
METHYL CYANIDE	8.733-11
ETHYLENE	4.8643-8
ACETALDEHYDE	1.5449-9
ACETIC ACID	2.2476-9
ETHANE	4.8361-8
ETHANOL	3.988-11
PROPYLENE	1.218-18
PROPANE	9.775-10
FECL2	4.248-12
FE02H2	8.819-12
H	1.883-12
HCN	1.8737-8
HCL	3.8632-5
HNCO	1.6481-9
H2	6.1685-2
H2O	1.8541-1
H2S	6.5298-3
KCL	4.9685-8
KOH	3.511-12
K2CL2	7.8734-9
NH3	8.4782-5
N2	7.7498-3
NACL	1.886-18
SH	1.3898-9
SO2	3.115-11
S2	8.358-18
AL2SI05 (AN)	1.3548-3
C (GR)	5.8424-1
CAAL2SI208 (S)	4.4157-4
CAMGSI208 (S)	6.1394-6
FES (C)	1.6311-3
K2AL2SI208 (S)	4.1527-4
NA2AL2SI6016 (1)	2.7214-4
SI02 (HQZ)	2.6858-3

*NASA CET86 Projections.

2.0 Fluid-Bed Gasification

In 1983 Westinghouse performed a series of thermodynamic calculations which identified the equilibrium gas/solid products formed in the Westinghouse coal gasification PDU at Madison. The thermodynamically projected gas/solid compositions and concentrations formed from the gasification of Upper Freeport coal, Western Kentucky coal, Brookville coal, and North Dakota lignite are shown in Figures A.2 through A.5. (12)

The principal chemical constituents which were projected to be formed in each of the resulting ashes included:

- KAlSi_3O_8 , $\text{NaAlSi}_3\text{O}_8$, $\text{FeO} \cdot \text{Al}_2\text{O}_3$, and V_2O_5 .

Specific to each feed, additional phases were projected in the resulting ashes:

- SiO_2 , MgSiO_3 , FeS , and $\text{CaO} \cdot \text{MgO} \cdot \text{SiO}_2$ (Upper Freeport)
- SiO_2 , MgAl_2O_4 , FeS , and $\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ (Western Kentucky)
- SiO_2 , MgAl_2O_4 , FeS , and $\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ (Brookville)
- NaAlSiO_4 , CaSiO_3 , FeO , and $\text{CaO} \cdot \text{MgO} \cdot \text{SiO}_2$ (North Dakota lignite).

Several phase changes or transitions in the alkali content of the solids were projected during gasification. These included:

- An initial coexistence of solid NaCl and KCl and the alkali feldspar phases ($\text{NaAlSi}_3\text{O}_8$ and KAlSi_3O_8) of the Upper Freeport fines at temperatures between 127 and 227°C (261 and 441°F), prior to complete release or conversion into the feldspar phase.

- The formation of the alkali chloride phase with the ash matrix of the Western Kentucky coal below temperatures of 327 to 427°C (621 to 801°F). At higher gasification temperatures, the feldspar complexes were projected as the principal alkali phases.
- The presence of sodium as solid NaCl in the Brookville fines at temperatures below 427°C (801°F). Alkali were projected to exist as the feldspar complex at 227 to 982°C (441 to 1800°F).
- A significantly different reaction chemistry was projected for the alkali transitions in North Dakota lignite. Sodium was projected to exist as solid NaCl, Na₂CO₃, and NaAlSi₃O₈ at relatively low operating temperatures of 227°C (441°F). Complete removal of both NaCl and Na₂CO₃ resulted at gasification temperatures above 527°C (981°F). The reaction of the alkali chloride and carbonate with the ash matrix lead to the formation of the high temperature nepheline complex, NaAlSiO₄, in addition to the release of sodium as the volatile chloride or hydroxide. The sodium feldspar phase was projected as a stable solid over the entire gasification temperature range.

The thermodynamic equilibrium calculations indicate that the gaseous alkali chlorides are the species which form with the highest partial pressures of all minor or trace constituents over the solid gasifier products. In each set of projections (Figures A.2 through A.5), the partial pressures for the various alkali species, as well as, the percentage of the feed alkali present within the volatile phase are shown as a function of temperature. Estimates of the released equilibrium concentrations of gaseous NaCl, KCl, and HCl are shown in Table A.2. The calculated thermodynamic equilibrium concentration of alkali released at the gasifier freeboard is greater than the

PROJECTED EQUILIBRIUM GAS COMPOSITION AT
GASIFIER OUTLET USING UPPER FREEPORT COAL
(TP-032-2-1A 5/21/82)

Figure A.2 - Thermodynamic Equilibrium Projections Illustrating the Composition of the Gas/Solid Phases Released during Fluid-Bed Gasification of Upper Freeport Coal

PROJECTED EQUILIBRIUM SOLIDS FORMED AS A FUNCTION OF TEMPERATURE
AT 16.78 ATM DURING THE GASIFICATION OF UPPER FREEPORT COAL IN
THE WESTINGHOUSE PDU GASIFIER (TP-032-2-1A 5/21/82)

— No Fines Recycle —

Temperature Compound	500 K	600 K	700 K	800 K	900 K	1000 K	1200 K	1281 K
C	✓	✓	✓	✓	✓	✓		
MgCO ₃	✓							
KAISI ₃ O ₈	✓	✓	✓	✓	✓	✓	✓	✓
CaO · MgO · 2 SiO ₂	✓	✓	✓	✓	✓	✓	✓	✓
Al ₂ SiO ₅	✓							
SiO ₂	✓	✓	✓	✓	✓	✓	✓	✓
FeS ₂	✓	✓						
V ₂ O ₃	✓	✓	✓	✓	✓	✓	✓	✓
KCl	✓							
NaCl	✓	✓	✓					
FeO · Al ₂ O ₃		✓	✓	✓	✓	✓	✓	✓
MgSiO ₃		✓	✓	✓	✓	✓	✓	✓
NaAlSi ₃ O ₈			✓	✓	✓	✓	✓	✓
FeS			✓	✓	✓	✓	✓	✓

ESTIMATED GAS AND SOLIDS FLOW FROM THE PDU GASIFIER USING
UPPER FREEPORT COAL
(TP-032-2-1A 5/21/82)

—No Fines Recycle—

Effluent Gas Composition, Mole % at 1281 K, 16.78 atm		Mole $\times 10^4$ (lb/hr) Gas	
51.875	CO	0.1268 -1	CH ₄ (4.4847)
20.029	H ₂	0.1775 -4	HCN (0.0106)
10.306	H ₂ O	0.1982 +1	CO ₂ (1922.9682)
16.084	CO ₂	0.4904 -2	COS (6.5014)
0.103	CH ₄	0.1135 -2	HCl (0.9123)
1.098	N ₂	0.6393 +1	CO (3947.7057)
0.453	H ₂ S	0.2824 -5	CS ₂ (0.0047)
0.009	HCl	0.2525 -3	NH ₃ (0.0948)
0.039	COS	0.1270 +1	H ₂ O (504.3882)
		0.5579 -1	H ₂ S (41.9163)
		0.2468 +1	H ₂ (109.6888)
		0.1354	N ₂ (83.6220)
		0.1484 -4	KCl (0.0244)
		0.2881 -4	NaCl (0.0371)
		0.2519 -5	S ₂ (0.0036)
			(6622.3628 lb/hr)
Moles $\times 10^4$ (lb/hr) Solids			
0.7476 -3	KAISi ₃ O ₈	(4.5873)	
0.8422 -3	NaAISi ₃ O ₈	(4.8688)	
0.3775 -3	CaO · MgO · 2SiO ₂	(1.8022)	
0.1489 -1	FeO · Al ₂ O ₃	(57.0540)	
0.6507 -5	V ₂ O ₃	(0.0215)	
0.4441 -1	SiO ₂	(58.8256)	
0.1094 -1	FeS	(21.2025)	
0.6658 -3	MgSiO ₃	(2.4736)	
		(149.8355 lb/hr)	

PROJECTED PARTIAL PRESSURES AND PERCENT FEEDSTOCK
CONCENTRATION OF ALKALI FORMED IN THE WESTINGHOUSE
PDU GASIFICATION OF UPPER FREEPORT COAL
(TP-032-2-1A 5/21/82)

-No Fines Recycle -

Temperature, K	pNaCl (atm)	Percent Feedstock Na	pKCl (atm)	Percent Feedstock K
1281	0.3923 -4	3.3080	0.2071 -4	1.9468
1200	0.1637 -4	1.3703	0.8333 -5	0.7966
1000	0.1083 -5	0.0708	0.5253 -6	0.0392
900	0.1727 -6	0.0102	0.8050 -7	5.4076 -3
800	0.1685 -7	9.3974 -4	0.7424 -8	4.7313 -4
700	0.7222 -9	3.9411 -5	0.2937 -9	1.8307 -5
600	0.1186 -11	6.4189 -8	0.7619 -12	4.7088 -8
500	0.1394 -15	7.5191 -12	0.7713 -15	4.7513 -11
Temperature, K	pNa ₂ Cl ₂ (atm)	Percent Feedstock Na	pK ₂ Cl ₂ (atm)	Percent Feedstock K
1281	0.5429 -7	9.1545 -3	0.1040 -7	2.0038 -3
1200	0.3286 -7	5.9003 -3	0.5586 -8	1.0680 -3
1000	0.7544 -8	9.8641 -4	0.8609 -9	1.2858 -4
900	0.2723 -8	3.2018 -4	0.2348 -9	3.1543 -5
800	0.7220 -9	8.0563 -5	0.4329 -10	5.5189 -6
700	0.9727 -10	1.0616 -5	0.3593 -11	4.4794 -7
600	0.8221 -13	8.8953 -9	0.4921 -14	6.0824 -10
500	0.3648 -17	3.9350 -13	0.8862 -17	1.0918 -12
Temperature, K	pNaOH (atm)	Percent Feedstock Na	pKOH (atm)	Percent Feedstock K
1281	0.2249 -6	1.8962 -2	0.1105 -6	1.0645 -2
1200	0.3443 -7	2.8813 -3	0.1689 -7	1.6141 -3
1000	0.2164 -9	1.4146 -5	0.1044 -9	7.7969 -6
900	0.6780 -11	3.9873 -7	0.3213 -11	2.1583 -7
800	0.7637 -13	4.2606 -9	0.3514 -13	2.2395 -9
700	0.2278 -15	1.2432 -11	0.1000 -15	6.2364 -12
600	0.2634 -19	1.4253 -15	0.1911 -19	1.1809 -15
500	0.5477 -25	2.9536 -21	0.3641 -24	2.2430 -20
Temperature, K	pNa ₂ SO ₄ (atm)	Percent Feedstock Na	pK ₂ SO ₄ (atm)	Percent Feedstock K
1281	0.3122 -18	5.2648 -14	0.6438 -18	1.2402 -13
1200	0.9356 -20	1.5658 -15	0.2408 -19	4.6043 -15
1000	0.3992 -22	5.2188 -18	0.2024 -21	3.0228 -17
900	0.1543 -23	1.8142 -19	0.1208 -22	1.6232 -18
800	0.1862 -25	2.0780 -21	0.2474 -24	3.1527 -20
700	0.6186 -28	5.7513 -24	0.1589 -26	1.9817 -22
600	0.2027 -32	2.1938 -28	0.3883 -30	4.8003 -26
500	-	-	0.1799 -34	2.2160 -30

PROJECTED EQUILIBRIUM GAS COMPOSITION AT
GASIFIER OUTLET USING WESTERN KENTUCKY COAL
(TP-032-2-MOD-3A-1 5/24/82)

Figure A.3 - Thermodynamic Equilibrium Projections Illustrating the Composition of the Gas/Solid Phases Released during Fluid-Bed Gasification of Western Kentucky Coal

PROJECTED EQUILIBRIUM SOLIDS FORMED AS A FUNCTION OF TEMPERATURE
AT 16.7 ATM DURING THE GASIFICATION OF WESTERN KENTUCKY COAL
IN THE WESTINGHOUSE PDU GASIFIER (TP-032-2-MOD-3A-1 5/24/82)

Temperature Compound	500 K	600 K	700 K	800 K	900 K	1000 K	1200 K	1249 K
C	✓	✓	✓	✓	✓			
MgCO ₃	✓							
CaO · MgO · 2SiO ₂	✓	✓	✓	✓				
Al ₂ SiO ₅	✓	✓						
SiO ₂	✓	✓	✓	✓	✓	✓	✓	✓
FeS ₂	✓	✓						
V ₂ O ₃	✓	✓	✓	✓	✓	✓	✓	✓
KCl	✓	✓						
NaCl	✓	✓	✓					
FeO · Al ₂ O ₃			✓	✓	✓	✓	✓	✓
MgAl ₂ O ₄		✓			✓	✓	✓	✓
KAlSi ₃ O ₈			✓	✓	✓	✓	✓	✓
FeS			✓	✓	✓	✓	✓	✓
MgSiO ₃			✓	✓		✓		
NaAlSi ₃ O ₈				✓	✓	✓	✓	✓
CaO · Al ₂ O ₃ · 2SiO ₂					✓	✓	✓	✓

ESTIMATED GAS AND SOLIDS FLOW FROM THE PDU GASIFIER USING
WESTERN KENTUCKY COAL
(TP-032-2-MOD-3A-) 5/24/82)

Effluent Gas Composition, Mole % at 1249 K, 16.7 atm		Moles $\times 10^4$ (lb/hr) Gas	
53.386 CO		0.9969 -1 CH ₄	(35.2585)
29.447 H ₂		0.3705 -4 HCN	(0.0221)
6.803 H ₂ O		0.9179 CO ₂	(890.5613)
8.034 CO ₂		0.4580 -2 COS	(6.0657)
0.872 CH ₄		0.4880 -2 HCl	(3.9226)
0.718 N ₂		0.6099 +1 CO	(3766.1594)
0.653 H ₂ S		0.5305 -5 CS ₂	(0.0089)
0.043 HCl		0.3839 -3 NH ₃	(0.1441)
0.040 COS		0.7774 H ₂ O	(308.7491)
		0.7459 -1 H ₂ S	(56.0412)
		0.3365 +1 H ₂	(149.5556)
		0.8198 -1 N ₂	(50.6302)
		0.3776 -4 KCl	(0.0621)
		0.7363 -4 NaCl	(0.0949)
		0.1459 -5 S ₂	(0.0021)
			(5267.2778 lb/hr)
Moles $\times 10^4$ (lb/hr) Solids			
0.8020 -3 KAISi ₃ O ₈	(4.9212)		
0.1848 -2 NaAISi ₃ O ₈	(10.6834)		
0.2420 -3 CaO · Al ₂ O ₃ · 2SiO ₂	(1.4843)		
0.8930 -2 FeO · Al ₂ O ₃	(34.2171)		
0.1224 -2 MgAl ₂ O ₄	(3.8392)		
0.9649 -5 V ₂ O ₃	(0.0319)		
0.4398 -1 SiO ₂	(58.2561)		
0.4680 -2 FeS	(9.0702)		
	(122.5034 lb/hr)		

PROJECTED PARTIAL PRESSURES AND PERCENT FEEDSTOCK
CONCENTRATION OF ALKALI FORMED IN THE WESTINGHOUSE
POU GASIFICATION OF WESTERN KENTUCKY COAL
(TP-032-2-M00-3A-1 5/24/82)

Temperature, K	pNaCl (atm)	Percent Feedstock Na	pKCl (atm)	Percent Feedstock K
1249	0.1076 -3	3.8317	0.5519 -4	4.4967
1200	0.6280 -4	2.1939	0.3196 -4	2.5546
1000	0.4178 -5	0.1175	0.2025 -5	0.1303
900	0.6863 -6	0.0158	0.3199 -6	0.0168
800	0.6664 -7	1.4469 -3	0.2937 -7	1.4593 -3
700	0.7222 -9	1.5272 -5	0.8521 -9	4.1231 -5
600	0.1186 -11	2.4807 -8	0.4803 -11	2.2980 -7
500	0.1394 -15	2.9061 -12	0.7713 -15	3.6782 -11
Temperature, K	pNa ₂ Cl ₂ (atm)	Percent Feedstock Na	pK ₂ Cl ₂ (atm)	Percent Feedstock K
1249	0.6551 -6	4.6651 -2	0.1199 -6	1.9551 -2
1200	0.4435 -6	3.3778 -2	0.8218 -7	1.3137 -2
1000	0.1122 -6	6.3088 -3	0.1280 -7	1.6473 -3
900	0.4298 -7	1.9777 -3	0.3707 -8	3.9025 -4
800	0.1130 -7	4.9075 -4	0.6777 -9	6.7397 -5
700	0.9727 -10	4.1137 -6	0.3025 -10	2.9276 -6
600	0.8221 -13	3.4377 -9	0.1956 -12	1.8713 -8
500	0.3648 -17	1.5208 -13	0.8862 -17	8.4524 -13
Temperature, K	pNaOH (atm)	Percent Feedstock Na	pKOH (atm)	Percent Feedstock K
1249	0.6263 -7	2.2299 -3	0.3076 -9	2.5059 -3
1200	0.2039 -7	7.1217 -4	0.9997 -8	7.9912 -4
1000	0.5936 -10	1.6690 -6	0.2864 -10	1.8427 -6
900	0.6530 -11	1.5024 -7	0.3094 -11	1.6288 -7
800	0.7329 -13	1.5915 -9	0.3373 -13	1.6756 -9
700	0.7562 -16	1.9991 -12	0.9636 -16	4.6626 -12
600	0.3808 -20	7.9616 -17	0.1741 -19	8.3301 -16
500	2.1633 -26	4.5074 -23	0.1438 -25	6.8559 -22
Temperature, K	pNa ₂ SO ₄ (atm)	Percent Feedstock Na	pK ₂ SO ₄ (atm)	Percent Feedstock K
1249	0.3890 -20	2.7702 -16	0.8730 -20	1.4225 -15
1200	0.6559 -21	4.5825 -17	0.1688 -20	2.6989 -16
1000	0.5407 -24	3.0408 -20	0.2742 -23	3.5279 -19
900	0.9459 -24	4.3526 -20	0.7409 -23	7.8003 -19
800	0.1123 -25	4.8779 -22	0.1492 -24	1.4824 -20
700	0.4318 -29	1.8264 -25	0.9343 -27	9.0416 -23
600	0.2087 -34	8.7272 -31	0.1588 -30	1.5202 -26
500	-	-	-	-

PROJECTED EQUILIBRIUM GAS COMPOSITION AT
GASIFIER OUTLET USING BROOKVILLE COAL
(TP-03)-1-2A 8/12/87

Figure A.4 - Thermodynamic Equilibrium Projections Illustrating the Composition of the Gas/Solid Phases Released during Fluid-Bed Gasification of Brookville Coal

PROJECTED EQUILIBRIUM SOLIDS FORMED AS A FUNCTION OF TEMPERATURE
AT 16.7 ATM DURING THE GASIFICATION OF BROOKVILLE COAL IN THE
WESTINGHOUSE PDU GASIFIER (TP-033-1-2A 8/12/82)

Temperature Compound	500 K	700 K	800 K	900 K	1000 K	1200 K	1223 K
C	✓	✓	✓	✓	✓		
K AlSi ₃ O ₈	✓	✓	✓	✓	✓	✓	✓
NaAlSi ₃ O ₈	✓	✓	✓	✓	✓	✓	✓
CaO · MgO · 2 SiO ₂	✓	✓	✓	✓	✓		
Al ₂ SiO ₅	✓						
SiO ₂	✓	✓	✓	✓	✓	✓	✓
FeS ₂	✓						
V ₂ O ₃	✓	✓	✓	✓	✓	✓	✓
NaCl	✓						
CaCO ₃	✓						
CaO · Al ₂ O ₃ · 2 SiO ₂		✓	✓	✓	✓	✓	✓
FeO · Al ₂ O ₃		✓	✓	✓	✓	✓	✓
FeS		✓	✓	✓	✓	✓	✓
Mg Al ₂ O ₄						✓	✓

ESTIMATED GAS AND SOLIDS FLOW FROM THE PDU GASIFIER USING
BROOKVILLE COAL
(TP-033-1-2A 8/12/82)

Effluent Gas Composition, Mole % at 1223 K, 16.7 atm		Moles $\times 10^4$ (lb/hr) Gas	
57.295	CO	0.7608 -1	CH ₄ (26.0981)
22.139	H ₂	0.2771 -4	HCN (0.0165)
6.607	H ₂ O	0.1388 +1	CO ₂ (1346.6599)
11.906	CO ₂	0.6214 -2	COS (8.2297)
0.653	CH ₄	0.1576 -3	HCl (0.1267)
0.734	N ₂	0.6680 +1	CO (4124.9295)
0.609	H ₂ S	0.6458 -5	CS ₂ (0.0108)
0.001	HCl	0.2896 -3	NH ₃ (0.1087)
0.053	COS	0.7704	H ₂ O (305.9691)
		0.7107 -1	H ₂ S (53.3965)
		0.2581 +1	H ₂ (114.7111)
		0.8554 -1	N ₂ (52.8289)
		0.9405 -6	KCl (0.0015)
		0.1841 -5	NaCl (0.0024)
		0.1584 -5	S ₂ (0.0022)
			(6033.9016 lb/hr)
Moles $\times 10^4$ (lb/hr) Solids			
0.2796 -2	KAISi ₃ O ₈	(17.1565)	
0.7896 -2	NaAISi ₃ O ₈	(45.6472)	
0.2194 -2	CaO · Al ₂ O ₃ · 2 SiO ₂	(13.4568)	
0.1263 -1	FeO · Al ₂ O ₃	(48.3944)	
0.1085 -2	MgAl ₂ O ₄	(3.4032)	
0.9236 -5	V ₂ O ₃	(0.0305)	
0.2387 -1	SiO ₂	(31.6183)	
0.1231 -1	FeS	(23.8577)	
		(183.5646 lb/hr)	

PROJECTED PARTIAL PRESSURES AND PERCENT FEEDSTOCK
CONCENTRATION OF ALKALI FORMED IN THE WESTINGHOUSE
PDU GASIFICATION OF BROOKVILLE COAL
(TP-033-1-2A 8/12/82)

Temperature, K	pNaCl (atm)	Percent Feedstock Na	pKCl (atm)	Percent Feedstock K
1223	0.2637 -5	0.0233	0.1347 -5	0.0336
1200	0.2029 -5	0.0178	0.1033 -5	0.0256
1000	0.1351 -6	8.7360 -4	0.6549 -7	1.1965 -3
900	0.2155 -7	1.2530 -4	0.1005 -7	1.6487 -4
800	0.2104 -8	1.1593 -5	0.9271 -9	1.4435 -5
700	0.1079 -9	5.8114 -7	0.4386 -10	6.6755 -7
500	0.1394 -15	7.4194 -13	0.4198 -16	6.3106 -13
Temperature, K	pNa ₂ Cl ₂ (atm)	Percent Feedstock Na	pK ₂ Cl ₂ (atm)	Percent Feedstock K
1223	0.5882 -9	1.0401 -5	0.1037 -9	5.1769 -6
1200	0.3046 -9	8.8654 -6	0.8577 -10	4.2569 -6
1000	0.1173 -9	1.5170 -6	0.1338 -10	4.8901 -7
900	0.4299 -10	4.9292 -7	0.3656 -11	1.2008 -7
800	0.1126 -10	1.2411 -7	0.6752 -12	2.1024 -8
700	0.2169 -11	2.3380 -8	0.8015 -13	2.4397 -9
500	0.3648 -17	3.8828 -14	0.2626 -19	7.8938 -16
Temperature, K	pNaOH (atm)	Percent Feedstock Na	pKOH (atm)	Percent Feedstock K
1223	0.3533 -7	3.1232 -4	0.1734 -7	4.3300 -4
1200	0.2025 -7	1.7788 -4	0.9929 -8	2.4643 -4
1000	0.1829 -9	-1829 -6	0.8826 -10	1.6124 -6
900	0.5739 -11	3.3363 -8	0.2719 -11	4.4659 -8
800	0.6471 -13	3.5661 -10	0.2977 -13	4.6355 -10
700	0.1934 -15	1.0421 -12	0.8494 -16	1.2928 -12
500	0.1022 -23	5.4381 -21	0.3698 -24	5.5587 -21
Temperature, K	pNa ₂ SO ₄ (atm)	Percent Feedstock Na	pK ₂ SO ₄ (atm)	Percent Feedstock K
1223	0.3959 -20	7.0000 -17	0.9544 -20	4.7669 -16
1200	0.1524 -20	2.6773 -17	0.3922 -20	1.9468 -16
1000	0.3753 -22	4.8537 -19	0.1903 -21	6.9527 -18
900	0.1451 -23	1.6869 -20	0.1136 -22	3.7323 -19
800	0.1749 -25	1.9285 -22	0.2324 -24	7.2357 -21
700	0.5797 -28	6.2464 -25	0.1489 -26	4.5339 -23
500	0.1838 -36	1.9557 -33	0.3599 -34	1.0819 -30

PROJECTED EQUILIBRIUM GAS COMPOSITION AT
GASIFIER OUTLET USING NORTH DAKOTA LIGNITE
(TP-033-1-3A-1 8/21/82)

Figure A.5 - Thermodynamic Equilibrium Projections Illustrating the Composition of the Gas/Solid Phases Released during Fluid-Bed Gasification of North Dakota Lignite

PROJECTED EQUILIBRIUM SOLIDS FORMED AS A FUNCTION OF TEMPERATURE AT
16.7 ATM DURING THE GASIFICATION OF NORTH DAKOTA LIGNITE IN THE
WESTINGHOUSE PDU GASIFIER (TP-033-1-3A-1 8/21/82)

Temperature Compound	500 K	600 K	700 K	800 K	900 K	1000 K	1078 K	1100 K	1200 K	1223 K
C	✓	✓	✓	✓	✓	✓	✓	✓		
MgCO ₃	✓									
KAISi ₃ O ₈	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
NaAISi ₃ O ₈	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
FeO · Al ₂ O ₃	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
MgAl ₂ O ₄	✓									
FeS ₂	✓									
V ₂ O ₃	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
NaCl	✓	✓	✓							
CaCO ₃	✓	✓								
NaCO ₃	✓	✓								
CaO · MgO · 2SiO ₂		✓	✓	✓	✓	✓	✓	✓	✓	✓
FeS		✓	✓	✓	✓	✓	✓			
NaAISiO ₄			✓	✓	✓	✓	✓	✓	✓	✓
CaSiO ₃			✓	✓	✓	✓	✓	✓	✓	✓
NaCl				✓						
FeO								✓	✓	✓

ESTIMATED GAS AND SOLIDS FLOW FROM THE PDU GASIFIER USING
NORTH DAKOTA LIGNITE (TP-033-1-3A-1 8/21/82)

Effluent Gas Composition, Mole % at 1078 K, 16.7 atm		Moles $\times 10^4$ (lb/hr) Gas	
29.869	CO	0.4861	CH ₄ (171.9246)
23.810	H ₂	0.2818	-4 HCN (0.0168)
14.227	H ₂ O	0.2381	+1 CO ₂ (2310.0844)
19.336	CO ₂	0.7614	-3 COS (1.0084)
3.948	CH ₄	0.1407	-3 HCl (0.1131)
8.641	N ₂	0.3678	+1 CO (2271.1812)
0.147	H ₂ S	0.5653	-7 CS ₂ (0.0001)
0.001	HCl	0.2445	-2 NH ₃ (0.9180)
0.006	COS	0.1752	+1 H ₂ O (695.8175)
		0.1811	-1 H ₂ S (13.6065)
		0.2932	+1 H ₂ (130.3111)
		0.1064	+1 N ₂ (657.1185)
		0.3355	-5 KCl (0.0055)
		0.6764	-5 NaCl (0.0087)
		0.7665	-8 S ₂ (0.0000)
			(6252.1144 lb/hr)
Moles $\times 10^4$ (lb/hr) Solids			
0.8837-2	NaAlSiO ₄	(27.6747)	
0.4072-2	KAlSi ₃ O ₈	(24.9862)	
0.1200-1	NaAlSi ₃ O ₈	(69.3726)	
0.2859-2	CaO · MgO · 2 SiO ₂	(13.6489)	
0.7426-2	FeO · Al ₂ O ₃	(28.4542)	
0.1575-4	V ₂ O ₅	(0.0520)	
0.7608-2	FeS	(14.7449)	
0.1107-1	CaSiO ₃	(0.2835)	
		(179.2170 lb/hr)	

PROJECTED PARTIAL PRESSURES AND PERCENT FEEDSTOCK
CONCENTRATION OF ALKALI FORMED IN THE WESTINGHOUSE
POU GASIFICATION OF NORTH DAKOTA LIGNITE
(TP-033-1-3A-1 8/21/82)

Temperature, K	pNaCl (atm)	Percent Feedstock Na	pKCl (atm)	Percent Feedstock K
1223	0.2458 -4	0.1005	0.1256 -4	0.2625
1200	0.2246 -4	0.0911	0.1143 -4	0.2371
1100	0.1084 -4	0.0397	0.5404 -5	0.1012
1000	0.5492 -5	1.7339 -2	0.2663 -5	4.2991 -2
900	0.1431 -5	4.0753 -3	0.6667 -6	9.7132 -3
800	0.8483 -7	2.2851 -4	0.3739 -7	5.1505 -4
700	0.7222 -9	1.8956 -4	0.2937 -9	3.9417 -6
600	0.1186 -11	3.0781 -9	0.4283 -12	5.6829 -9
500	0.1394 -15	3.4031 -13	0.4198 -16	5.5480 -13
Temperature, K	pNa ₂ Cl ₂ (atm)	Percent Feedstock Na	pK ₂ Cl ₂ (atm)	Percent Feedstock K
1223	0.5110 -7	4.1779 -4	0.9005 -8	3.7648 -4
1200	0.6184 -7	5.0165 -4	0.1051 -7	4.3605 -4
1100	0.8677 -7	6.3550 -4	0.1235 -7	4.6251 -4
1000	0.1939 -6	1.2242 -5	0.2212 -7	7.1438 -4
900	0.1864 -6	1.0641 -5	0.1611 -7	4.6927 -4
800	0.1831 -7	9.8652 -5	0.1098 -8	3.0254 -5
700	0.3593 -11	5.1059 -7	0.9727 -10	9.6455 -8
600	0.8221 -13	4.2655 -10	0.1555 -14	4.1266 -11
500	0.3648 -17	1.8856 -14	0.2626 -19	6.9397 -16
Temperature, K	pNaOH (atm)	Percent Feedstock Na	pKOH (atm)	Percent Feedstock K
1223	0.7079 -6	2.8939 -3	0.3475 -6	7.2635 -3
1200	0.4785 -6	1.9409 -3	0.2347 -6	4.8676 -3
1100	0.7297 -7	2.6719 -4	0.3558 -7	6.6634 -4
1000	0.1128 -7	3.5604 -5	0.5441 -8	8.7852 -5
900	0.5623 -9	1.6018 -6	0.2664 -9	3.8815 -6
800	0.1342 -10	3.6162 -8	0.6177 -11	8.5089 -8
700	0.9269 -13	2.4329 -10	0.4071 -13	5.4638 -10
600	0.3478 -16	9.0226 -14	0.1418 -16	1.8815 -13
500	0.3508 -21	9.0654 -19	0.1269 -21	1.6775 -18
Temperature, K	pNa ₂ SO ₄ (atm)	Percent Feedstock Na	pK ₂ SO ₄ (atm)	Percent Feedstock K
1223	0.2719 -18	2.2230 -15	0.6555 -18	2.7405 -14
1200	0.1512 -18	1.7266 -15	0.3892 -18	1.6146 -14
1100	0.1973 -19	1.4451 -16	0.6941 -19	2.9997 -15
1000	0.1524 -19	9.6243 -17	0.7729 -19	2.4957 -15
900	0.1027 -20	5.8485 -18	0.8039 -20	2.3425 -16
800	0.5333 -22	2.8735 -19	0.7083 -21	1.9517 -17
700	0.8911 -24	4.6779 -21	0.2289 -22	6.1472 -19
600	0.3565 -27	1.8497 -24	0.2158 -25	5.7261 -22
500	0.1027 -32	5.3064 -30	0.2011 -30	5.3144 -27

TABLE A.2

THERMODYNAMIC ESTIMATES OF ALKALI AND CHLORIDE
RELEASE CONCENTRATIONS AT THE FLUID-BED GASIFIER OUTLET

Feed Coal	Gasifier Temp., °C	Gasifier Press., atm	ppm NaCl	ppm KCl	ppm HCl
Upper Freeport Coal	1008	18.8	2.349	1.204	92.13
Western Kentucky Coal	976	18.7	6.443	3.305	427.13
Brookville Coal	950	18.7	0.158	0.081	13.52
North Dakota Lignite	805	18.7	0.549	0.272	11.43

analytically determined alkali concentrations which reached the high temperature probe. Condensation of the volatile release alkali may have resulted in transit from the freeboard to the sampling probe, forming solid deposits. Adherence and/or reaction by chemisorption of the volatile alkali along the surface of the entrained fines may have also occurred.

3.0 Entrained-Bed Gasification

Table A.3 illustrates the thermodynamic equilibrium product gas and solid compositions which are projected to result in the entrained-bed gasification system that is shown in Figure A.6. For an entrained-bed gasifier which operates at temperatures of 1300°C (2370°F) and pressures of 30 atm, release of alkali is principally projected to be in the form of gaseous chlorides (i.e., 22.13 ppmv KCl; 13.40 ppmv NaCl; 6.12 ppmv NaCN; 2.59 ppmv KCN; 2.19 ppmv KOH; 1.42 ppmv NaOH; 0.404 ppmv NaH; 0.063 ppmv KH; 0.016 ppm K₂Cl₂; 0.006 ppmv Na₂Cl₂). The composition of the resulting entrained-bed gasifier fines is projected to consist of solid C, SiO₂, Fe, Al₆Si₂O₁₃, CaAl₂Si₂O₈, and MgAl₂O₄, and liquid K₂Si₄O₉, FeS, and Na₂Si₂O₅.

TABLE A.3

THERMODYNAMIC EQUILIBRIUM PRODUCT DISTRIBUTION
FORMED DURING ENTRAINED-BED GASIFICATION OF A
PITTSBURGH SEAM COAL

Mole Fraction*

ALOH	6.381-12	H2	2.3786-1
CH2	1.981-11	H2O	5.8883-3
FORMALDEHYDE	3.7883-8	H2S	3.9132-3
FORMIC ACID	4.8196-8	K	8.5242-8
CH3	1.2688-8	KCN	1.9871-8
CH3CL	5.417-11	KCL	1.6948-6
HYDROXYMETHYLENE	3.855-11	KH	4.8831-8
CH4	4.1288-3	KOH	1.8788-8
METHANOL	1.3378-8	K2	1.238-11
CN	5.424-12	K2C2N2	1.494-11
CO	5.8846-1	K2CL2	1.2422-8
COCL	1.819-12	K2O2H2	2.878-12
COS	2.8146-4	MO	8.236-18
CO2	3.7181-3	MOCL2	1.336-12
CS	5.5559-7	MGM	2.222-11
CS2	5.8583-8	MGMH	7.287-11
C2H RAD	8.388-11	MGO2H2	2.218-18
ACETYLENE	5.8882-8	MGS	1.423-11
KETENE	4.8858-7	NH	1.586-12
C2H3 RAD	5.3228-9	NH2	4.878-18
METHYL CYANIDE	4.8248-8	NH3	1.1882-6
CH3CO RAD	3.883-18	NO	3.384-12
CH2CHO RAD	1.379-11	N2	2.4988-3
ETHYLENE	8.8851-8	NA	1.7323-6
ACETALDEHYDE	9.8883-9	NACN	4.8843-8
ACETIC ACID	4.283-11	NACL	1.8288-6
ETHYL RAD	2.8888-9	NAH	3.8988-7
ETHANE	3.2113-7	NAOH	1.8848-8
ETHANOL	9.888-12	NA2	3.841-18
CYANOGEN	2.468-11	NA2C2N2	3.588-18
CCO RAD	1.797-12	NA2CL2	4.8822-9
C3H3 RAD	5.384-18	NA2O2H2	3.289-12
ALLENE	4.8111-9	OH	2.4692-9
CYCLOPROPENE	2.821-12	S	1.4541-8
PROPYNE	8.7775-9	SH	1.8479-6
C3H5 RAD	8.822-18	SN	5.728-11
CYCLOPROPANE	1.289-11	SO	2.7179-9
PROPYLENE	8.2821-9	SO2	2.542-18
PROPANE	8.533-11	S2	1.8112-8
CARBON SUBOXIDE	3.463-18	S2O	8.283-11
BUTADIENE	1.828-11	SIO	1.4236-8
BUTAN-1EN-3YN	1.828-11	SIS	1.9378-8
2-BUTYNE	2.148-12	AL6SI2O13(S)	6.5835-4
1-BUTENE	1.336-12	C(GR)	2.2738-1
ISOBUTENE	1.282-12	CAAL2SI2O8(S)	5.1128-4
BENZENE	7.936-12	FE(C)	1.5832-3
CAO2H2	1.515-12	FE(L)	1.5584-4
CL	2.978-11	K2SI4O9(L)	4.8871-4
FE	1.8879-8	MAL2O4(S)	8.2794-6
FECL2	2.893-11	NA2SI2O5(L)	2.5999-4
FE0	1.911-12	SIO2(HCR)	3.8788-3
FE02H2	7.8494-9		
FES	2.8844-9		
H	3.1488-8		
HCN	4.1429-6		
HCO RAD	7.3858-8		
HCL	2.8223-8		
HNCO	8.5434-8		

*NASA CET86 Projections.

Figure A.6 - Entrained-Bed Gasification

Coal: Pittsburgh Seam, Wt %			
C	74.45	Moisture	2.21
H	4.97	SiO ₂	3.781
O	6.17	Al ₂ O ₃	2.145
S	3.00	Fe ₂ O ₃	1.103
N	1.51	CaO	0.239
Na	0.106	MgO	0.021
K	0.275		
Cl	0.009		

4.0 Direct Coal Fired Turbine

In the direct coal fired turbine study⁽²⁾ conducted by Westinghouse, the baseline slurry-fired power plant consisted of a slurry preparation plant, a gas turbine cycle, and a steam turbine cycle. The slurry preparation plant converted Pittsburgh No. 8 lump coal, as delivered to the plant, into a micronized, physically beneficiated coal/water slurry.

The baseline plant contained two gas turbines and one reheat steam turbine. The energy in the exhaust from the two gas turbines is used to make steam in a single heat recovery steam generator. The steam is expanded in the reheat steam turbine to generate power, and then passed to a condenser that is cooled by circulating water from a forced-draft wet cooling tower.

In each gas turbine, the slurry is burned in an external combustor vessel that uses pressurized air from the compressor. Sulfur is removed from the products of combustion by a fluidized-bed desulfurizer with dolomite as its sorbent. The particulate matter is removed by a ceramic cross-flow filter. The filtered products of combustion enter an expander that is similar to commercially available expanders. No steam or water is injected into the combustor because the coal/water slurry already contains enough water for NO_x control.

Pittsburgh No. 8 coal was used as the reference coal in order to project the composition of the hot coal-gas and coal/water slurry. The composition of the gases at various points in the system shown in Figure A.7 are identified in Table A.4. The hot gas delivered to the

Figure A.7 - Schematic of the Coal Gasification System that Supplies Hot Coal Gas to the Gas Turbine

TABLE A.4

GAS COMPOSITION AT VARIOUS LOCATIONS IN
THE DIRECT COAL FIRED TURBINE SYSTEM

<u>Gas</u>	<u>Gasifier Exit</u>	<u>Desul- furizer Water Spray Exit</u>	<u>Combustor Exit Temperature</u>		
			<u>1600°F</u>	<u>1800°F</u>	<u>2000°F</u>
H ₂ , Mole%	24.04	20.79	---	---	---
CO	44.69	38.43	---	---	---
H ₂ O	11.80	23.40	5.56	6.63	7.74
CO ₂	17.59	16.18	6.30	7.57	8.94
CH ₄	0.94	0.66	---	---	---
N ₂	0.56	0.49	71.91	70.62	69.26
O ₂	---	---	16.26	15.16	14.00
H ₂ S, ppmv	3455	421	---	---	---
COS	216	26	---	---	---
HCl	137	84	12	14	17
NH ₃	31	25	---	---	---
SO ₂	---	---	33	54	72
SO ₃	---	---	20	14	8
NO	---	---	19	19	19
NaCl	0.37	0.10	0.02	0.07	0.24
KCl	0.40	0.23	0.01	0.03	0.06
Gas HHV (LHV), BTU/SCF		200(188)			

combustion turbine contains approximately 0.32 weight percent solids. The projected gas compositions provided in Table A.4 suggest that gasification of Pittsburgh No. 8 coal results in a fuel containing 3455 ppmv H_2S , 216 ppmv COS , and 31 ppmv NH_3 . Processing this gas in a fluidized-bed at $900^\circ C$ ($1650^\circ F$) and 15 atm with dolomite, and then spray cooling the product gas to $850^\circ C$ ($1200^\circ F$), results in a hot coal gas containing 421 ppmv H_2S , 26 ppmv COS , and 25 ppmv NH_3 . Firing this fuel in a combustion turbine at 13 atm with $370^\circ C$ ($700^\circ F$) air to obtain a combustor outlet temperature of $1093^\circ C$ ($2000^\circ F$) results in a flue gas containing 80 ppmv SO_x , and 0.29 weight percent particulates.

5.0 Pressurized Fluidized-Bed Combustion

Table A.5 illustrates the thermodynamic equilibrium product gas and solid compositions which are projected to result in the pressurized fluidized-bed combustion system that is shown in Figure A.8. If the coal-sorbent mixture was permitted to come to equilibrium at process conditions, the calcium and magnesium present in the sorbent would be projected to react with aluminum and silicon in the coal ash, forming stable solid aluminosilicate complexes. Since within the actual process the sorbent calcines and/or reacts with sulfur, the pressurized fluidized-bed combustion thermodynamic projections were divided into two calculations - one which illustrates the release of volatiles and solid phase formation as a result of the coal combustion; and the second which considers the reaction of dolomite with combustion gas (C, H, N, O, S, Cl, Na, and K).

With 13,000 lb/hr air entering the combustor, coal is partially combusted, leading to the production of an ash-char which consists of solid C, SiO_2 , Al_2SiO_5 , $FeAl_2O_4$, FeS , $Na_2Al_2Si_6O_{16}$, and liquid KCl. For the Kittanning coal, potassium appears to be completely released from the ash aluminosilicate structure, resulting in the formation of either gas phase species (i.e., KCl or K_2Cl_2), or the liquid chloride phase.

TABLE A.5

THERMODYNAMIC EQUILIBRIUM PRODUCT DISTRIBUTION
FORMED DURING PRESSURIZED FLUIDIZED-BED COMBUSTION OF A
KITTANNING COAL

Mole Fraction*

Coal		Sorbent	
FORMALDEHYDE	4.2686-8	FORMALDEHYDE	4.5129-8
FORMIC ACID	2.8389-9	FORMIC ACID	3.1275-9
CH3	5.165-10	CH3	5.228-10
CH3CL	2.541-10	CH3CL	7.757-11
CH4	1.3844-4	CH4	1.3923-4
METHANOL	8.853-11	METHANOL	8.447-11
CO	9.1159-2	CO	9.7586-2
COCL	1.369-12	CO3	5.5513-7
CO3	1.5731-6	CO2	7.4256-3
CO2	8.8545-3	CS	3.864-12
CS	9.885-11	CS2	9.918-12
CS2	8.8851-9	ACETYLENE	1.1218-9
ACETYLENE	1.1839-9	KETENE	8.295-10
KETENE	7.832-10	METHYL CYANIDE	6.512-10
METHYL CYANIDE	6.498-10	ETHYLENE	8.8823-9
ETHYLENE	8.8167-9	ACETALDEHYDE	2.335-11
ACETALDEHYDE	2.226-11	ETHANE	7.588-10
ETHANE	7.538-10	CACL2	1.3848-7
CL	4.345-11	CAO2H2	2.188-12
FECL2	1.1954-8	CL	1.335-11
FECL3	1.672-11	H	2.7618-9
FE02H2	8.755-11	HCN	3.3485-8
FE2CL4	3.695-11	HCO RAD	5.618-11
H	2.7858-9	HCL	8.8279-6
HCN	3.3678-6	HNCO	2.3163-8
HCO RAD	5.278-11	H2	1.5981-2
HCL	2.8862-4	H2O	1.5339-3
HNCO	2.1945-8	H2S	2.8631-6
H2	1.5737-2	K	1.9998-9
H2O	1.4482-3	KCN	6.3915-9
H2S	8.5451-6	KCL	1.2919-4
K	5.845-10	KH	1.292-12
KCN	1.8839-9	KOH	3.2187-9
KCL	1.2599-4	K2CL2	5.6474-6
KOH	9.864-10	MGCL2	5.231-10
K2CL2	5.5872-6	NH2	1.776-12
NH2	1.764-12	NH3	6.8471-6
NH3	6.8341-6	N2	2.5289-1
N2	2.5878-1	NA	5.7884-9
NA	4.868-11	NACN	1.8264-8
NACN	1.485-10	NACL	5.8488-6
NACL	1.5711-6	NAH	1.453-11
NAOH	1.153-11	NAOH	1.4844-9
NA2CL2	1.3548-8	NA2CL2	1.8252-6
OH	1.759-12	OH	1.872-12
S	2.161-12	SH	4.739-10
SH	1.4878-8	S2	1.524-12
SO	3.538-12	C (GR)	6.1538-1
SO2	5.728-12	CACL2 (L)	8.2328-6
S2	1.3852-9	CAMG02 (S)	5.8328-3
AL2SiO5 (AN)	1.5348-3	CAO (S)	2.5813-3
C (GR)	6.2725-1	CAS (S)	3.4853-4
FEAL2O4 (S)	5.8981-4	KCL (L)	2.1539-6
FES (C)	2.4788-4		
KCL (L)	3.4799-6		
NA2AL2Si6O18 (2)	4.7988-6		
SiO2 (HCR)	3.8877-3		

*NASA CET86 Projections.

Figure A.8 - Pressurized Fluidized-Bed Combustion

Coal: Kittanning, Wt % (Eastern Bituminous)				Dolomite: Ohio Lime, Wt %	
C	73.07	SiO ₂	2.87	CaCO ₃	64.01
H	4.75	Al ₂ O ₃	1.79	MgCO ₃	35.86
O	13.60	Fe ₂ O ₃	0.51	Cl	0.13
S	1.49	CaO	0.103		
N	1.46	MgO	0.05		
Na ₂ O	0.026				
K ₂ O	0.109				
Cl	0.17				

Conversely, sodium which is present in coal, is partitioned between the solid sodium aluminosilicate structure and the gaseous chloride species. The estimated release of approximately 500 ppmv mono- and dimeric gaseous KCl represents equilibrium over liquid KCl, while the estimated 4.3 ppmv mono- and dimeric gaseous NaCl represents equilibrium with the alkali aluminosilicate ash.

Similarly, with 13,000 lb/hr air, Ohio lime is projected to calcine, forming $\text{CaO} \cdot \text{MgO}$. The excess calcium present in the Ohio lime forms CaO, or reacts to form solid CaS or liquid CaCl_2 .

5.1 Pressurized Fluidized-Bed Combustion Trace and Minor Element Release

Effort has been devoted to projecting the phase and concentration of alkali released during coal combustion or gasification. In addition to alkali emissions from coal, sulfur sorbent materials as dolomite or limestone can also contribute to the overall total alkali emissions concentration. Table A.6 and Figures A.9 and A.10 illustrate the concentration of alkali within various U.S. sorbent materials, as well as release concentrations that have been experimentally determined as a function of temperature.⁽¹⁴⁾

Similarly, trace and minor elements present in the feed and sorbents can also be released during combustion or gasification. Release depends not only on the affinity, concentration, and distribution of each trace or minor element within the inorganic or organic-associated matrix, but also on process conditions such as temperature, heating rate, exposure time at elevated temperature, and localized reducing or oxidizing environments surrounding the coal particles.

Previous efforts at Westinghouse have identified the fate and concentration of twenty-seven trace and minor elements which are released during pressurized fluidized-bed combustion (PFBC) operations.⁽¹⁴⁾ The approach used in this study focused on generating the equilibrium gas, liquid, or condensed phase concentrations for species containing fluorine, beryllium, mercury, lead, cobalt, chromium, iron, molybdenum, manganese, nickel, titanium, sodium, potassium, bromine, boron, phosphorous, copper, vanadium, zinc, antimony, tin, zirconium, arsenic, cadmium, selenium, gallium, and germanium at PFBC conditions. The equilibrium compositions of the trace and minor element species were calculated using Geometric programming techniques in which the Gibbs Free energy of the polyphase system was minimized while satisfying the mass constraints for the system. The thermodynamic

TABLE A.6

CONCENTRATION OF Ca, Mg, Na, K, and Cl IN SULFUR SORBENT MATERIALS

Concentration, Weight %										
Sorbent	Location	Ca	Mg	Na			K			Cl
				Soluble *	Insoluble *	Total	Soluble	Insoluble	Total	
Canaan	Conn.	21. 91	12. 56	0. 0023	0. 0014	0. 0037	0. 0088	0. 0070	0. 0158	
Lehigh	Ill.	18. 07	10. 87	0. 0164	0. 0080	0. 0244	0. 0379	0. 6333	0. 6712	0. 028
Mt. Carroll	Ill.	21. 07	12. 32	0. 0158	0. 215	0. 0373	0. 0026	0. 2200	0. 2226	0. 078
Thornton	Ill.	21. 44	12. 83	0. 2000	0. 0002	0. 2002	0. 0175	0. 0240	0. 0415	0. 120
Geneva	Ind.	21. 76	11. 61	0. 0167	0. 0010	0. 0177	0. 0038	0. 0178	0. 0216	0. 017
Salamonie	Ind.	21. 61	12. 97	0. 0163	0. 0005	0. 0168	0. 0069	0. 0051	0. 0120	
Cedarville	Mich.	21. 59	12. 73	0. 0325	0. 0006	0. 0331	0. 0258	0. 0168	0. 0426	0. 229
Drummond	Mich.	20. 95	12. 80	0. 0193	0. 0010	0. 0203	0. 0263	0. 0850	0. 1113	0. 098
Maybee	Mich.	18. 80	11. 32	0. 0216	0. 0012	0. 0228	0. 0213	0. 0340	0. 0553	
Ottawa Lake	Mich.	21. 07	12. 80	0. 0224	0. 0064	0. 0288	0. 0182	0. 1150	0. 1332	0. 033
Tymochtee	Ohio	19. 81	11. 80	0. 0179	0. 0150	0. 0329	0. 0450	0. 3250	0. 3700	0. 042
Glasshouse #10	Ohio	21. 08	12. 49	0. 0175	0. 0005	0. 0180	0. 0075	0. 0175	0. 0250	
General Portland	Texas	37. 5	—	0. 0058	0. 0016	0. 0074	0. 0221	0. 0372	0. 0593	
Parker Bros	Texas	37. 0	—	0. 0032	0. 0012	0. 0044	0. 0028	0. 0059	0. 0087	
McDonough Bros	Texas	38. 4	—	0. 0021	0. 0008	0. 0029	0. 0025	0. 0033	0. 0058	

• Alkali Soluble Phases - Chlorides, Carbonates, Water Glasses, Aluminosilicates and Feldspars.
Sorbents are treated on a 1:1 Volumetric basis with HCl, followed by heating for one hour, then filtered

• Alkali Insoluble Phases - Amorphous Clays. Residue is heated in alcohol, followed by the addition of HF, heated for one hour, then perchloric acid is added and the entire sample brought to fuming

Curve 723289-C

Figure A.9 - Release of Sodium from Sulfur Sorbent Materials as a Function of Temperature

Figure A.10 - Release of Potassium from Sulfur Sorbent Materials as a Function of Temperature

database used in this study contained approximately 2000 species. The projected equilibrium product distributions which resulted were considered as first-level estimates of the gas/solid chemistry that would result within high temperature systems.

In an attempt to identify a possible upper limit of the trace and minor element concentrations released during combustion, equilibrium projections were generated for the various elements which reflected their reactions with only the principal constituents of the bulk gas phase (i.e., C, H, N, O, S, Cl). How the trace and minor elements would react with the aluminosilicate structure of the coal ash, or with the calcium and/or magnesium contained within the sulfur sorbents was not addressed in the initial series of equilibrium projections. Table A.7 summarizes this phase of the study, presenting the concentration of the various elements in a typical U.S. mean coal,⁽⁶⁸⁾ and projecting the condensed and volatile phases at PFBC process conditions. In addition estimates of the percent volatilization for the trace and minor elements from the feed matrix is presented for PFBC operating temperatures of 1025°C (1880°F) and pressures of 1 and 15 atm. Tables A.8 and A.9 illustrate the percent distribution of the element between the various emissions phases for two process operating conditions. The data presented for the alkali species reflect only the reactions with the bulk gas phase (C, H, N, O, S, and Cl), and do not account for the interactions that are likely to occur with the aluminosilicate structure of the ash.

Independent of system operating pressure, the trace and minor elements were classified as constituents that:

- Volatilized completely: Be, F, Hg, Pb, Mo, Br, B, P, Cu, As, Cd, and Se
- Volatilized partially: Co, Cr, Mn, Ni, and Sn
- Remained as stable solid complexes: Fe, Ti, Al, Si, V, Zn, Zr, and Ga.

TABLE A.7

**SUMMARY OF TRACE AND MINOR ELEMENT REACTIONS IN
FLUIDIZED-BED COMBUSTION SYSTEMS**

Element	Coal, ppm	Condensed Phases	Volatile Phases	Percent Volatilization	
				101 kPa	1520 kPa
Be	1.81	BeSO ₄	Be(OH) ₂	100	100
F	80.94	--	HF, HSO ₃ F	100	100
Hg	0.20	--	Hg, HgCl ₂ , HgO, Hg ₂ , HgCl	100	100
Pb	34.78	--	PbCl ₄ , PbCl ₂ , PbO, PbCl	100	100
Co	9.57	CoSO ₄ , Co ₃ O ₄ , CoO	CoCl ₂ , CoCl ₃ , Co ₂ Cl ₄ , CoCl	26	27
Cr	13.75	Cr ₂ O ₃	CrO ₄ H ₂ , CrO ₂ Cl ₂ , CrO ₂ OH, CrO ₃ , CrO ₂ , Cr CrCl ₃ , CrCl, CrCl ₂ , CrO ₄ CrCl	28-100	25-100
Fe	1.92%	Fe ₂ O ₃ Fe ₂ (SO ₄) ₃	FeCl ₂ , Fe(OH) ₂ , FeCl ₃ , FeO, Fe ₂ Fe ₂ Cl ₄ , FeCl, Fe ₂ Cl ₆	0	0
Mo	7.54	MoO ₃	MoO ₄ H ₂ , MoO ₂ Cl ₂ , MoO ₃ , MoO ₂ , MoCl ₄ , MoO, MoCl ₅ , MoCl ₆	100	100
Mn	49.40	MnSO ₄ , Mn ₂ O ₃ , Mn ₃ O ₄	MnCl ₂ , MnCl, MnO, Mn	8-12	5-8
Ni	21.07	NiSO ₄ NiO	NiCl ₂ , Ni(OH) ₂ , NiCl, NiO, Ni, NiH	13	13
Ti	0.07%	TiO ₂	TiOCl ₂ , TiCl ₃ , TiCl ₂ , TiCl, TiCl ₄ , TiOCl, TiO ₂ , TiO	0	0
Al	1.29%	Al ₂ O ₃ ,	AlCl ₃ , AlOCl,	0	0

TABLE A.7 (continued)

		$\text{Al}_2(\text{SO}_4)_3$	AlCl_2 , AlOH , AlCl , AlO , Al_3Cl_8		
Si	2.49	SiO_2	SiCl_4 , SiCl_3 , SiCl_2 , SiCl , SiO_2 , SiO	0	0
Br	15.42	--	BrH , Br_2 , Br , BrCl , BrO , NOBr	100	100
B	102.21	H_3BO_3 , HBO_2	BHO_2 , H_3BO_3 , $(\text{HBO}_2)_3$, BO_2	100	100
P	71.10	H_3PO_4	$(\text{P}_2\text{O}_5)_2$, PO_2	100	100
Cu	15.16	CuO , CuSO_4	CuCl , CuO , Cu_2Cl_2 , Cu , Cu_2 , CuS , CuH	100	100
V	32.71	V_2O_5	VOCl_3 , VO , VCl_4 , VO , 2V , VN	0.03	0.03
Zn	272.29	ZnSO_4 , $\text{ZnSO}_4 \cdot \text{H}_2\text{O}$, $\text{ZnSO}_4 \cdot \text{ZnO}$	Zn , ZnCl , Zn_2 , ZnS , ZnH	0.3-0.5	0.01-0.1
Sb	1.26	SbO_2	SbCl , SbCl_3 , Sb	100	3-5
Sn	4.79	SnO_2	SnO , SnCl_2 , SnCl_4	2-3	0.1-0.3
Zr	72.46	ZrO_2	ZrCl_4	0	0
As	14.02	As_2O_5	AsCl , AsO , AsN , AsCl_3	100	100
Cd	2.52	CdSO_4	CdO , Cd , CdCl	100	100
Se	2.08	--	SeO	100	100
Ga	3.12	Ga_2O_3	GaCl	0.5-0.6	0.03-0.04
Ge	6.59	GeO_2	GeO	100	2-4

TABLE A.8
PERCENT DISTRIBUTION OF TRACE AND MINOR ELEMENTS
IN 10% EXCESS AIR, 0% SULFUR REMOVAL,
FLUIDIZED BED COMBUSTION SYSTEMS

COMPOUND	1100K		//	1200K		//	1300K	
	// 1ATM	/ 15ATM		// 1ATM	/ 15ATM		// 1ATM	/ 15ATM
BeO (S)	// 97.92	/ 97.92	//	89.62	/ 89.62	//	---	/ ---
Be(OH) ₂ (G)	// 2.08	/ 2.08	//	10.38	/ 10.38	//	99.99	/ 99.99
BeCl ₂ (G)	// ---	/ ---	//	---	/ ---	//	0.01	/ 0.01
HF (G)	// 100.	/ 100.	//	100.	/ 100.	//	100.	/ 100.
HgO (G)	// 1.12	/ 3.98	//	0.94	/ 3.50	//	0.80	/ 3.02
HgCl ₂ (G)	// 0.09	/ 4.91	//	0.01	/ 0.47	//	---	/ 0.06
Hg (G)	// 98.79	/ 91.11	//	99.05	/ 96.03	//	99.20	/ 96.92
HgCl (G)	// ---	/ ---	//	---	/ ---	//	---	/ ---
PbO (G)	// ---	/ ---	//	0.60	/ ---	//	23.03	/ 0.21
PbCl ₄ (G)	// 99.61	/ 99.99	//	83.64	/ 99.67	//	11.47	/ 91.87
PbCl ₂ (G)	// 0.39	/ 0.01	//	15.34	/ 0.33	//	56.82	/ 7.77
PbCl (G)	// ---	/ ---	//	0.42	/ ---	//	8.53	/ 0.15
Pb (G)	// ---	/ ---	//	---	/ ---	//	0.15	/ ---
Co ₃ O ₄ (S)	// 92.61	/ ---	//	---	/ ---	//	---	/ ---
CoO (S)	// ---	/ ---	//	84.77	/ 84.76	//	73.56	/ 73.31
Co ₂ O ₃ (S)	// ---	/ 97.80	//	---	/ ---	//	---	/ ---
CoCl ₂ (G)	// 7.39	/ 2.20	//	15.23	/ 15.23	//	26.44	/ 26.69
Cr ₂ O ₃ (S)	// 97.15	/ 96.64	//	91.91	/ 92.51	//	72.12	/ 75.65
CrO ₃ (G)	// ---	/ ---	//	0.02	/ 0.01	//	0.12	/ 0.06
CrO ₂ Cl ₂ (G)	// 0.23	/ 1.73	//	0.17	/ 1.24	//	0.13	/ 0.96
CrO ₄ H ₂ (G)	// 1.99	/ 1.00	//	4.40	/ 2.23	//	8.66	/ 4.39
CrO ₂ OH (G)	// 0.63	/ 0.63	//	4.00	/ 3.99	//	18.97	/ 18.94
Fe ₂ O ₃ (S)	// 100.	/ 100.	//	100.	/ 100.	//	100.	/ 100.
MoO ₂ Cl ₂ (G)	// 0.71	/ 0.71	//	0.30	/ 0.03	//	0.14	/ 0.15
MoO ₃ (G)	// ---	/ ---	//	0.01	/ ---	//	0.03	/ ---
H ₂ MoO ₄ (G)	// 99.29	/ 99.29	//	99.69	/ 99.70	//	99.83	/ 99.85
Mn ₂ O ₃ (S)	// ---	/ 99.20	//	---	/ ---	//	---	/ ---
Mn ₃ O ₄ (S)	// 98.60	/ ---	//	95.43	/ 97.08	//	87.85	/ 92.18
MnCl ₂ (G)	// 1.40	/ 0.80	//	4.57	/ 2.92	//	12.15	/ 7.82
NiO (S)	// 98.19	/ 98.19	//	94.91	/ 94.91	//	86.61	/ 86.52
Ni(OH) ₂ (G)	// 0.10	/ 0.10	//	0.73	/ 0.73	//	3.92	/ 3.92
NiCl ₂ (G)	// 1.71	/ 1.71	//	4.36	/ 4.36	//	9.46	/ 9.56
NiCl (G)	// ---	/ ---	//	---	/ ---	//	0.01	/ ---
TiO ₂ (C)	// 100.	/ 100.	//	100.	/ 100.	//	100.	/ 100.
Na ₂ SO ₄ (C)	// 98.63	/ 100.	//	81.34	/ 100.	//	---	/ 93.67
NaCl (G)	// 1.37	/ ---	//	18.66	/ ---	//	100.	/ 6.33
Na ₂ Cl ₂ (G)	// ---	/ ---	//	---	/ ---	//	---	/ ---
Na ₂ SO ₄ (G)	// ---	/ ---	//	---	/ ---	//	---	/ ---
NaOH (G)	// ---	/ ---	//	---	/ ---	//	---	/ ---
K ₂ SO ₄ (S)	// 98.21	/ 100.	//	74.49	/ 99.06	//	---	/ 89.54
KCl (S)	// ---	/ ---	//	---	/ ---	//	---	/ ---
K ₂ Cl ₂ (G)	// ---	/ ---	//	---	/ ---	//	---	/ ---
KCl (G)	// 1.79	/ ---	//	21.45	/ 0.94	//	73.60	/ 8.13
K ₂ SO ₄ (G)	// ---	/ ---	//	4.06	/ ---	//	26.07	/ 2.33
KOH (G)	// ---	/ ---	//	---	/ ---	//	0.33	/ ---
Al ₂ O ₃ (S)	// 100.	/ 100.	//	100.	/ 100.	//	100.	/ 100.
SiO ₂ (C)	// 100.	/ 100.	//	100.	/ 100.	//	100.	/ 100.

TABLE A.8 (continued)

PERCENT DISTRIBUTION OF TRACE AND MINOR ELEMENTS
IN 10% EXCESS AIR, 0% SULFUR REMOVAL,
FLUIDIZED BED COMBUSTION SYSTEMS

BRH (G)	//	53.28	/	64.25	//	47.19	/	62.76	//	41.87	/	41.97
BR0 (G)	//	0.01	/	0.03	//	0.01	/	0.03	//	0.02	/	0.02
BRCL (G)	//	0.94	/	4.49	//	0.33	/	1.71	//	0.14	/	0.14
BR (G)	//	45.69	/	28.77	//	52.45	/	35.38	//	57.97	/	58.13
BR2 (G)	//	0.04	/	0.23	//	0.01	/	0.04	//	---	/	---
NOBR (G)	//	---	/	0.01	//	---	/	0.01	//	---	/	---
HM0213 (G)	//	0.05	/	0.06	//	0.01	/	0.05	//	---	/	0.03
H3B03 (G)	//	84.87	/	98.77	//	52.41	/	94.20	//	20.73	/	79.62
BM02 (G)	//	13.72	/	1.07	//	47.19	/	5.65	//	79.24	/	20.29
BO2 (G)	//	---	/	---	//	---	/	---	//	---	/	---
IP20512 (G)	//	99.98	/	99.98	//	99.93	/	99.97	//	98.83	/	99.90
PO2 (G)	//	---	/	---	//	0.05	/	0.03	//	1.15	/	0.08
CU3CL3 (G)	//	11.00	/	27.40	//	0.14	/	17.90	//	---	/	0.60
CUCI (G)	//	89.00	/	27.40	//	99.85	/	82.08	//	99.76	/	99.28
CU0 (G)	//	---	/	---	//	0.01	/	0.02	//	0.24	/	0.12
V205 (L)	//	99.98	/	99.73	//	99.99	/	99.75	//	99.98	/	99.77
VOCL3 (G)	//	0.02	/	0.09	//	0.01	/	0.05	//	0.01	/	0.03
VO2 (G)	//	---	/	---	//	---	/	---	//	0.01	/	---
ZNO (S)	//	99.99	/	---	//	99.99	/	99.99	//	99.56	/	99.99
ZNS04 (S)	//	---	/	100.	//	---	/	---	//	---	/	---
ZN (G)	//	---	/	---	//	0.01	/	---	//	0.43	/	---
ZNCL (G)	//	---	/	---	//	---	/	---	//	---	/	---
SB02 (S)	//	99.59	/	99.26	//	96.69	/	98.66	//	---	/	95.12
SBO (G)	//	0.01	/	---	//	1.63	/	0.03	//	75.23	/	1.77
SBCL3 (G)	//	0.38	/	0.74	//	0.65	/	1.28	//	0.72	/	1.98
SBCL (G)	//	0.02	/	---	//	1.03	/	0.03	//	24.04	/	1.12
SB (G)	//	---	/	---	//	---	/	---	//	0.01	/	---
SN02 (S)	//	99.99	/	100.	//	99.96	/	99.97	//	97.10	/	99.72
SNCL2 (G)	//	0.01	/	---	//	0.01	/	0.03	//	0.95	/	0.25
SNO (G)	//	---	/	---	//	0.03	/	---	//	1.95	/	0.03
ZR02 (S)	//	100.	/	100.	//	100.	/	100.	//	100.	/	100.
AS205 (S)	//	---	/	79.08	//	---	/	---	//	---	/	---
ASO (G)	//	4.93	/	10.51	//	14.21	/	7.73	//	30.83	/	18.38
ASCL3 (G)	//	0.08	/	0.95	//	0.01	/	0.32	//	---	/	0.03
ASCL (G)	//	94.99	/	19.46	//	85.78	/	91.95	//	69.16	/	81.59
ASN (G)	//	---	/	---	//	---	/	---	//	0.01	/	---
CDO (G)	//	97.14	/	98.92	//	93.93	/	98.11	//	88.60	/	96.58
CDCL (G)	//	0.19	/	0.37	//	0.14	/	0.29	//	0.11	/	0.24
CD (G)	//	2.67	/	0.71	//	5.93	/	1.60	//	11.29	/	3.18
SEO (G)	//	100.	/	100.	//	100.	/	100.	//	100.	/	100.
GA203 (S)	//	100.	/	100.	//	99.97	/	100.	//	99.34	/	99.96
GACL (G)	//	---	/	---	//	0.03	/	---	//	0.66	/	0.04
GE02 (S)	//	99.97	/	100.	//	96.80	/	99.94	//	---	/	97.33
GE0 (G)	//	0.03	/	---	//	3.20	/	0.06	//	100.	/	2.67

TABLE A.9
PERCENT DISTRIBUTION OF TRACE AND MINOR ELEMENTS
IN 300% EXCESS AIR, 99% SULFUR REMOVAL,
FLUIDIZED BED COMBUSTION SYSTEMS

COMPOUND	1100K		//	1200K		//	1300K	
	// 1ATM	/ 15ATM		// 1ATM	/ 15ATM		// 1ATM	/ 15ATM
BeO (S)	// 97.92	/ 97.92	//	89.62	/ 89.62	//	---	/ ---
Be(OH) ₂ (G)	// 2.08	/ 2.08	//	10.38	/ 10.38	//	99.99	/ 99.99
BeCl ₂ (G)	// ---	/ ---	//	---	/ ---	//	0.01	/ 0.01
Hf (G)	// 100.	/ 100.	//	100.	/ 100.	//	100.	/ 100.
HgO (G)	// 2.95	/ 10.16	//	2.46	/ 8.88	//	2.11	/ 7.71
HgCl ₂ (G)	// 0.07	/ 3.57	//	0.01	/ 0.03	//	---	/ 0.05
Hg (G)	// 96.98	/ 86.27	//	97.53	/ 90.79	//	97.89	/ 92.24
HgCl (G)	// ---	/ ---	//	---	/ ---	//	---	/ ---
PbO (G)	// ---	/ ---	//	2.56	/ ---	//	52.15	/ 3.92
PbCl ₄ (G)	// 99.51	/ 99.99	//	78.08	/ 99.58	//	5.44	/ 89.01
PbCl ₂ (G)	// 0.49	/ 0.01	//	18.76	/ 0.42	//	36.03	/ 9.85
PbCl (G)	// ---	/ ---	//	0.60	/ ---	//	6.25	/ 0.22
Pb (G)	// ---	/ ---	//	---	/ ---	//	0.13	/ ---
Co ₃ O ₄ (S)	// 94.68	/ 94.61	//	---	/ 87.79	//	---	/ ---
CoO (S)	// ---	/ ---	//	84.77	/ ---	//	74.08	/ 73.31
CoSO ₄ (S)	// ---	/ ---	//	---	/ ---	//	---	/ ---
CoCl ₂ (G)	// 5.32	/ 3.39	//	15.23	/ 12.21	//	25.92	/ 26.69
Cr ₂ O ₃ (S)	// 87.11	/ 84.74	//	59.76	/ 64.53	//	---	/ ---
CrO ₃ (G)	// 0.02	/ 0.01	//	0.25	/ 0.13	//	1.37	/ 0.79
CrO ₂ Cl ₂ (G)	// 1.01	/ 7.67	//	0.73	/ 5.55	//	0.40	/ 3.52
CrO ₄ H ₂ (G)	// 8.70	/ 4.42	//	19.25	/ 9.78	//	28.01	/ 16.13
CrO ₂ H ₂ (G)	// 3.16	/ 3.16	//	20.01	/ 20.01	//	70.22	/ 79.56
Fe ₂ O ₃ (S)	// 100.	/ 100.	//	100.	/ 100.	//	100.	/ 100.
MoO ₂ Cl ₂ (G)	// 0.71	/ 0.71	//	0.30	/ 0.30	//	0.14	/ 0.14
MoO ₃ (G)	// ---	/ ---	//	0.02	/ ---	//	0.12	/ 0.01
H ₂ MoO ₄ (G)	// 99.29	/ 99.29	//	99.68	/ 99.70	//	99.74	/ 99.85
Mn ₂ O ₃ (S)	// 99.04	/ 99.51	//	---	/ 98.17	//	---	/ 94.49
Mn ₃ O ₄ (S)	// ---	/ ---	//	96.71	/ ---	//	91.41	/ ---
MnCl ₂ (G)	// 0.96	/ 0.49	//	3.29	/ 1.83	//	8.59	/ 5.51
NiO (S)	// 98.19	/ 98.19	//	94.91	/ 94.91	//	86.79	/ 86.52
Ni(OH) ₂ (G)	// 0.10	/ 0.10	//	0.73	/ 0.73	//	3.92	/ 3.92
NiCl ₂ (G)	// 1.71	/ 1.71	//	4.36	/ 4.36	//	9.28	/ 9.56
NiCl (G)	// ---	/ ---	//	---	/ ---	//	0.01	/ ---
TiO ₂ (C)	// 100.	/ 100.	//	100.	/ 100.	//	100.	/ 100.
Na ₂ SO ₄ (C)	// 48.22	/ 57.99	//	---	/ 58.00	//	---	/ 8.38
NaCl (G)	// 51.78	/ 38.44	//	100.	/ 42.00	//	100.	/ 91.62
Na ₂ Cl ₂ (G)	// ---	/ 3.57	//	---	/ ---	//	---	/ ---
Na ₂ SO ₄ (G)	// ---	/ ---	//	---	/ ---	//	---	/ ---
NaOH (G)	// ---	/ ---	//	---	/ ---	//	---	/ ---
K ₂ SO ₄ (S)	// 29.58	/ 29.58	//	---	/ 29.58	//	---	/ 9.70
KCl (S)	// ---	/ ---	//	---	/ ---	//	---	/ ---
K ₂ Cl ₂ (G)	// ---	/ 20.16	//	---	/ 6.26	//	---	/ ---
KCl (G)	// 70.42	/ 50.26	//	91.53	/ 64.16	//	97.62	/ 82.13
K ₂ SO ₄ (G)	// ---	/ ---	//	8.47	/ ---	//	2.38	/ 8.17
KOH (G)	// ---	/ ---	//	---	/ ---	//	---	/ ---
Al ₂ O ₃ (S)	// 100.	/ 100.	//	100.	/ 100.	//	100.	/ 100.
SiO ₂ (C)	// 100.	/ 100.	//	100.	/ 100.	//	100.	/ 100.

TABLE A.9 (continued)

PERCENT DISTRIBUTION OF TRACE AND MINOR ELEMENTS
IN 300% EXCESS AIR, 99% SULFUR REMOVAL,
FLUIDIZED BED COMBUSTION SYSTEMS

BRM (G)	//	27.17	/	39.59	//	22.65	/	35.48	//	19.09	/	31.37
BRO (G)	//	---	/	0.12	//	---	/	0.16	//	0.06	/	0.19
BRCL (G)	//	1.27	/	7.18	//	0.42	/	4.11	//	0.16	/	1.04
BR (G)	//	71.36	/	52.83	//	77.03	/	60.19	//	80.88	/	67.54
BR2 (G)	//	---	/	0.44	//	---	/	---	//	---	/	---
NOBR (G)	//	---	/	0.04	//	---	/	---	//	---	/	---
HM0213 (G)	//	0.75	/	0.17	//	0.05	/	0.12	//	---	/	0.03
H3803 (G)	//	62.35	/	95.81	//	24.05	/	82.31	//	6.96	/	52.79
BHO2 (G)	//	35.39	/	3.63	//	75.81	/	17.30	//	93.12	/	47.11
B02 (G)	//	---	/	---	//	---	/	---	//	0.03	/	---
IP20512 (G)	//	99.97	/	99.99	//	99.87	/	99.95	//	98.16	/	99.83
PO2 (G)	//	---	/	---	//	0.08	/	0.01	//	1.79	/	0.12
CU3CL3 (G)	//	0.08	/	46.01	//	0.01	/	2.26	//	---	/	0.05
CUCL (G)	//	99.91	/	53.99	//	99.88	/	97.65	//	99.30	/	99.57
CU0 (G)	//	0.01	/	---	//	0.11	/	0.09	//	0.70	/	0.38
V205 (L)	//	99.99	/	99.95	//	99.99	/	99.97	//	99.99	/	99.98
VOCL3 (G)	//	0.01	/	0.05	//	0.01	/	0.03	//	0.01	/	0.02
V02 (G)	//	---	/	---	//	---	/	---	//	---	/	---
ZNO (S)	//	100.	/	99.99	//	99.99	/	100.	//	99.44	/	99.99
ZNSO4 (S)	//	---	/	---	//	---	/	---	//	---	/	---
ZN (G)	//	---	/	---	//	0.01	/	---	//	0.05	/	0.01
ZNCL (G)	//	---	/	---	//	---	/	---	//	---	/	---
SB02 (S)	//	99.84	/	99.76	//	97.21	/	99.53	//	---	/	96.56
SBO (G)	//	0.02	/	---	//	2.14	/	0.37	//	90.44	/	2.32
SBCL3 (G)	//	0.12	/	0.24	//	0.21	/	0.42	//	0.21	/	0.65
SBCL (G)	//	---	/	---	//	0.44	/	0.02	//	9.35	/	0.48
SB (G)	//	---	/	---	//	---	/	---	//	---	/	---
SN02 (S)	//	100.	/	100.	//	99.93	/	99.99	//	97.09	/	99.87
SNCL2 (G)	//	---	/	---	//	0.04	/	0.01	//	0.35	/	0.09
SNO (G)	//	---	/	---	//	0.03	/	---	//	2.56	/	0.04
ZR02 (S)	//	100.	/	100.	//	100.	/	100.	//	100.	/	100.
AS205 (S)	//	---	/	94.39	//	---	/	---	//	---	/	---
ASO (G)	//	13.70	/	0.41	//	33.64	/	20.44	//	57.94	/	40.81
ASCL3 (G)	//	0.06	/	0.19	//	---	/	0.21	//	---	/	0.02
ASCL (G)	//	86.24	/	5.01	//	66.36	/	79.35	//	42.06	/	59.17
ASN (G)	//	---	/	---	//	---	/	---	//	---	/	---
COO (G)	//	98.86	/	99.49	//	97.60	/	99.20	//	95.38	/	96.63
CDCL (G)	//	0.12	/	0.24	//	0.10	/	0.20	//	0.08	/	0.16
CD (G)	//	1.02	/	0.26	//	2.30	/	0.60	//	4.56	/	1.21
SEO (G)	//	100.	/	100.	//	100.	/	100.	//	100.	/	100.
GA203 (S)	//	100.	/	100.	//	99.98	/	100.	//	99.54	/	99.97
GACL (G)	//	---	/	---	//	0.02	/	---	//	0.46	/	0.03
GE02 (S)	//	99.96	/	100.	//	95.81	/	99.93	//	---	/	96.51
GE0 (G)	//	0.04	/	---	//	4.19	/	0.07	//	100.	/	3.49

The resulting Na, K, Sb, and Ge phases were shown to be dependent on system operating pressure. An example of how operating temperature influences the emissions concentration of Br, F, Be, Hg, and Pb is illustrated in Figure A.11.

The thermodynamic model which was developed utilized the assumption that at high temperature, equilibrium would be attained in the bed, and the projected gas phase would represent the process gas chemistry. With this approach, further reaction of the process gas with either entrained fines, or mechanisms that would lead to the condensation of materials along system components were not realized. For example, volatile Be, F, Pb, Mo, B, P, Cu, As, Cd, Se, Na, K, Sb, and Ge species were considered to have the potential to condense at lower process operating temperatures, while Hg and Br species were expected to remain as volatiles.

In addition to the simple reactions which may result between the trace and minor elements and the bulk gases, additional interactions are likely to result in the fluidized-bed between these elements and the aluminosilicate structure of the coal ash, as well as the calcium and magnesium constituents of the sorbent material. Figure A.12 illustrates the numerous pathways which the trace or minor elements may react with or repartition within the ash or sorbent structures during combustion. Tables A.10 through A.13 are provided to illustrate the range in the projected trace and minor element species emission concentration that may result during the combustion of eastern and western coals.

System:

Composition: C, H, N, O, S, Cl, K, Na
Al, Si, Br, F, Be, Hg, Pb

90% Sulfur Removal

100% Excess Air

1013 kPa

Curve 72379-C

Figure A.11 - Partial Pressure of Volatile Equilibrium Phases Formed in Pressurized Fluidized-Bed Combustion Systems

TABLE A.10

PFBC PROJECTIONS FOR EASTERN COALS CONTAINING
LOW TRACE AND MINOR ELEMENT CONCENTRATIONS

C	83%
H	4%
N	0.94%
O	2.5%
S	0.56%
Cl	0.01%

ELEMENT	CONCENTRATION IN COAL (%, ppm)	PROJECTED PHASES AND PERCENT DISTRIBUTION AT 300K	PROJECTED PHASES AND PERCENT DISTRIBUTION AT 1300K FOR 100% EXCESS AIR, 90% SULFUR REMOVAL 1013kPa OPERATIONS
Si	1.0%	99.99 SiO ₂ , 2.31 KAlSi ₃ O ₈ 0.81 2Na ₂ O·SiO ₂	49.77 SiO ₂ , 38.74 3Al ₂ O ₃ ·2SiO ₂ , 12.88 KAlSi ₃ O ₈ , 0.81 2Na ₂ O·SiO ₂
Al	1.1%	99.71 Al(OH) ₃ , 2.11 KAl(SO ₄) ₂ ·12H ₂ O, 0.99 KAlSi ₃ O ₈ , 0.22 AlF ₃	96.25 3Al ₂ O ₃ ·2SiO ₂ , 3.75 KAlSi ₃ O ₈
K	0.06%	99.04 KAl(SO ₄) ₂ ·12H ₂ O, 25.58 KAlSi ₃ O ₈ , 18.38 KCl	99.62 KAlSi ₃ O ₈ , 0.38 KCl(g)
Na	0.01%	100 2Na ₂ O·SiO ₂	100 2Na ₂ O·SiO ₂
Pb	1.0 ppm	100 PbCl ₂ (s)	97.14 PbO (g), 1.81 PbCl ₂ (g), 1.13 PbCl (g), 0.02 PbCl ₄ (g), 0.10 (Pb, PbF, PbF ₂ , PbF ₄) (g)
Hg	0.05 ppm	100 HgCl ₂ (g)	94.81 Hg (g), 5.19 HgO (g)
F	50 ppm	100 AlF ₃	100 HF (g)
Ba	0.23 ppm	100 Ba(OH) ₂ (l)	100 Ba(OH) ₂ (g)
As	1.8 ppm	100 As ₂ O ₃	93.33 AsO (g), 6.60 AsCl (g), 0.07 AsF ₃ (g)
Cd	0.10 ppm	100 CdCl ₂	98.18 CdO (g), 1.82 Cd (g)
Se	1.1 ppm	100 SeO (g)	100 SeO (g)

* SOLID UNLESS OTHERWISE INDICATED

TABLE A.11

PFBC PROJECTIONS FOR EASTERN COALS CONTAINING
HIGH TRACE AND MINOR ELEMENT CONCENTRATIONS

C	80%
H	6.0%
N	1.5%
O	18%
S	5.0%
Cl	0.80%

ELEMENT	CONCENTRATION IN COAL (%, ppm)	PROJECTED PHASES AND PERCENT DISTRIBUTION AT 300K AND 1013kPa	PROJECTED PHASES AND PERCENT DISTRIBUTION AT 1300K FOR 100% EXCESS AIR, 90% SULFUR REMOVAL 1013kPa OPERATIONS
Si	6.3%	99.22 SiO ₂ [*] , 0.78 2Na ₂ O.SiO ₂	62.01 SiO ₂ , 22.66 KAlSi ₃ O ₈ , 14.85 3Al ₂ O ₃ .2SiO ₂ , 0.78 2Na ₂ O.SiO ₂
Al	3.1%	92.98 Al(OH) ₃ , 6.78 KAl(SO ₄) ₂ .12H ₂ O, 0.23 AlF ₃	86.21 3Al ₂ O ₃ .2SiO ₂ , 14.76 KAlSi ₃ O ₈ , 0.04 BeAl ₂ O ₄
K	0.68%	55.12 KCl, 44.88 KAl(SO ₄) ₂ .12H ₂ O	97.49 KAlSi ₃ O ₈ , 2.51 KCl(g)
Na	0.08%	100 2Na ₂ O.SiO ₂	100 2Na ₂ O.SiO ₂
Pb	18 ppm	100 PbCl ₄ (g)	98.69 PbCl ₄ (g), 3.22 PbCl ₂ (g), 0.06 PbO (g), 0.03 PbCl ₂ (g)
Hg	0.47 ppm	100 HgCl ₂ (g)	94.85 Hg (g), 4.99 HgO (g), 0.16 HgCl ₂ (g)
F	150 ppm	100 AlF ₃	99.18 HF(g), 0.81 AlF ₃ O (g), 0.01 (AsF ₃ , BeF ₂ , BeClF, CoF ₂) (g)
Be	2.6 ppm	100 Be(OH) ₂ (s)	83.18 BeAl ₂ O ₄ , 16.89 Be(OH) ₂ (g), 0.01 (BeCl ₂ , BeClF, BeF ₂) (g)
As	100 ppm	100 As ₂ O ₅	80.76 AsCl(g), 19.24 AsO(g)
Cd	0.60 ppm	100 CdCl ₂	97.56 CdO (g), 1.91 Cd (g), 0.23 CdCl (g)
Se	8.1 ppm	100 SeO (g)	100 SeO (g)

* SOLID UNLESS OTHERWISE INDICATED

TABLE A.12

PFBC PROJECTIONS FOR WESTERN COALS CONTAINING
LOW TRACE AND MINOR ELEMENT CONCENTRATIONS

C	58%
H	3.8%
N	0.59%
O	8.8%
S	0.34%
Cl	0.01%

ELEMENT	CONCENTRATION IN COAL (%, ppm)	PROJECTED PHASES AND PERCENT DISTRIBUTION AT 300K AND 1013kPa	PROJECTED PHASES AND PERCENT DISTRIBUTION AT 1300K FOR 100% EXCESS AIR, 90% SULFUR REMOVAL 1013kPa OPERATIONS
Si	0.38%	98.38 SiO_2^s , 1.61 $2\text{Na}_2\text{O} \cdot 0.5\text{SiO}_2$	85.16 SiO_2 , 27.89 $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$, 5.54 KAISi_3O_8 , 1.61 $2\text{Na}_2\text{O} \cdot 0.5\text{SiO}_2$
Al	0.31%	94.30 $\text{Al}(\text{OH})_3$, 3.18 $\text{Al}_2(\text{SO}_4)_3$, 2.23 KAISi_3O_8 , $12\text{H}_2\text{O}$, 0.29 AlF_3	97.82 $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$, 2.18 KAISi_3O_8
K	0.01%	100 KAISi_3O_8 , $12\text{H}_2\text{O}$	97.73 KAISi_3O_8 , 2.27 $\text{KCl}(\text{g})$
Na	0.01%	100 $2\text{Na}_2\text{O} \cdot 0.5\text{SiO}_2$	100 $2\text{Na}_2\text{O} \cdot 0.5\text{SiO}_2$
Pb	0.70 ppm	100 $\text{PbCl}_4(\text{g})$	96.75 $\text{PbO}(\text{g})$, 1.89 $\text{PbCl}_2(\text{g})$, 1.24 $\text{PbCl}(\text{g})$, 0.10 $\text{Pb}(\text{g})$, 0.02 $\text{PbCl}_4(\text{g})$
Hg	0.02 ppm	100 $\text{HgCl}_2(\text{g})$	94.90 $\text{Hg}(\text{g})$, 5.10 $\text{HgO}(\text{g})$
F	19 ppm	100 AlF_3	99.83 $\text{HF}(\text{g})$, 0.16 $\text{AlF}_3\text{O}(\text{g})$, 0.01 $(\text{H}_2\text{SO}_4\text{F}, \text{ONF}, \text{SiF}_4, \text{AsF}_3, \text{BeF}_2)(\text{g})$
Ba	0.10 ppm	100 $\text{BaSO}_4(\text{s})$	100 $\text{Ba}(\text{OH})_2(\text{g})$
As	0.01 ppm	100 As_2O_5	92.81 $\text{AsO}(\text{g})$, 7.19 $\text{AsCl}(\text{g})$
Cd	0.10 ppm	100 CdSO_4	98.72 $\text{CdO}(\text{g})$, 1.28 $\text{Cd}(\text{g})$
Se	0.40 ppm	100 $\text{SeO}(\text{g})$	100 $\text{SeO}(\text{g})$

* SOLID UNLESS OTHERWISE INDICATED

TABLE A.13

PFBC PROJECTIONS FOR WESTERN COALS CONTAINING
HIGH TRACE AND MINOR ELEMENT CONCENTRATIONS

C	74%
H	5.8%
N	1.5%
O	22%
S	1.9%
Cl	0.13%

ELEMENT	CONCENTRATION IN COAL (%, ppm)	PROJECTED PHASES AND PERCENT DISTRIBUTION AT 300K AND 1013kPa	PROJECTED PHASES AND PERCENT DISTRIBUTION AT 1300K FOR 100% EXCESS AIR, 90% SULFUR REMOVAL 1013kPa OPERATIONS
Si	4.7%	89.38 SiO_2 , 7.80 $2\text{Na}_2\text{O} \cdot \text{SiO}_2$, 2.82 KAlSi_3O_8	83.03 SiO_2 , 14.82 $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$, 14.55 KAlSi_3O_8 , 7.80 $2\text{Na}_2\text{O} \cdot \text{SiO}_2$
Al	2.2%	94.14 $\text{Al}(\text{OH})_3$, 3.83 $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$, 1.83 KAlSi_3O_8 , 0.30 AlF_3	90.02 $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$, 9.95 KAlSi_3O_8 , 0.03 BeAl_2O_4
K	0.32%	44.58 KCl , 35.20 $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$, 19.21 KAlSi_3O_8	99.16 KAlSi_3O_8 , 0.84 KCl (g)
Na	0.60%	100 $2\text{Na}_2\text{O} \cdot \text{SiO}_2$	100 $2\text{Na}_2\text{O} \cdot \text{SiO}_2$
Pb	9.0 ppm	100 PbCl_2 (s)	39.15 PbCl_2 (s), 35.35 PbCl_2 (g), 22.70 PbO (s), 2.78 PbCl (g), 0.02 Pb (g)
Hg	0.83 ppm	100 HgCl_2 (s)	96.08 Hg (s), 4.91 HgO (s), 0.01 HgCl_2 (g)
F	140 ppm	100 AlF_3	98.21 HF (g), 0.78 AlF_3 (s), 0.01 (BeClF , PbF_2 , PbF , AsF_3 , BeF_2 , CdF) (g)
Be	1.4 ppm	100 $\text{Be}(\text{OH})_2$ (s)	89.56 BeAl_2O_4 , 30.43 $\text{Be}(\text{OH})_2$ (s), 0.01 (BeCl_2 , BeClF , BeF_2) (g)
As	0.07 ppm	100 As_2O_3	57.17 AsO (g), 42.38 AsCl (g), 0.45 AsF_3 (g)
Cd	0.60 ppm	100 CdCl_2	98.01 CdO (g), 1.95 Cd (g), 0.04 CdCl (g)
Se	2.7 ppm	100 SeO (g)	100 SeO (g)

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