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EVALUATION OF ADVANCED MATERIALS IN LABORATORY TESTS AND PILOT PLANT SERVICE FOR USE IN LIQUEFACTION LETDOWN VALVES

Final Report

By
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D12A-217
DT13-25
SP-25

May 1981

Work Performed Under Contract No. AC01-79ET13537

Battelle Columbus Laboratories
Columbus, Ohio

U. S. DEPARTMENT OF ENERGY

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FINAL REPORT

on

**EVALUATION OF ADVANCED MATERIALS IN LABORATORY
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J. H. Peterson, and W. E. Merz**

May, 1981

BATTELLE

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Abstract

The aim of this program was to obtain erosion data on a number of candidate valve materials under a range of slurry erosion conditions which would be useful to valve and process engineers involved in materials selection and valve design. The Battelle slurry erosion rig was used with reconstituted coal-derived slurries to erode candidate materials under a range of slurry velocity and impingement angle conditions.

The materials studied were the cemented tungsten carbides: K 701, KZ 701 and K 703; and the ceramics silicon carbide (in the reaction-bonded, CVD and sintered alpha forms) and hot-pressed boron carbide. Screening tests were performed on several cemented titanium diborides. For the cemented tungsten carbides, the reproducibility of the wear rates was good. No significant difference was found between the three grades at low impingement angles, but the low binder grade (K 703) was more resistant to erosion at higher angles ($> 50^\circ$). In contrast, the ceramics exhibited a range of wear rates. The boron carbide and reaction-bonded silicon carbide were comparable in erosion resistance to the cemented tungsten carbides, whereas the alpha and CVD silicon carbide versions showed significantly lower erosion rates.

The erosive nature of slurries from several different coals and from two processes, SRC-1, and H-Coal were also investigated. The size distribution of insoluble solid particles in the slurries examined showed fairly close similarity between different coals processed in one plant, and for a given coal slurry from the two processes

Service trials with a reaction-bonded silicon carbide valve stem in a cemented tungsten carbide seat resulted in what was classified as a premature failure, but provided quite revealing data. The two materials had eroded in the same mode and at the same relative rates as observed in the laboratory rig tests. Analysis of the parts suggested that, in fact, the failure may have resulted from the contour to which the stem was machined rather than from poor materials erosion performance.

EXECUTIVE SUMMARY

The aim of this program was to establish erosion data on a number of candidate valve materials under a range of slurry erosion conditions which would be useful to valve and process engineers involved in materials selection and valve design. The approach was to use the existing Battelle slurry erosion rig with reconstituted coal-derived slurries to erode candidate materials under a range of slurry velocity and impingement angle conditions. An analysis of the erosion kinetics and examination of the erosion damage provided information on the mode of erosion of the different materials and hence on routes to obtaining improved service life through modification of the materials or appreciation of the effects of process variables.

During the course of the program, extensive efforts were made to characterize the erosive nature of slurries from several different coals and from two processes, SRC-1 and H-Coal. Effective techniques for separating the insoluble solids from the slurries, and for conducting particle size analyses were evolved. The size distribution of insoluble solid particles in the slurries examined showed fairly close similarity between different coals processed in one plant, and for a given coal slurry from the two processes. In the laboratory test rig, some reduction in particle size occurred with time of use, and a slurry rejuvenation technique was developed to provide a practically constant condition of slurry erosivity.

The materials studied were the cemented tungsten carbides: K 701, KZ 701 and K 703; and the ceramics silicon carbide (in the reaction-bonded, CVD and sintered alpha forms) and hot-pressed boron carbide. Screening tests were performed on several cemented titanium diborides. For the cemented tungsten carbides, the reproducibility of the wear rates was good. No significant difference was found between the three grades at low impingement angles, but the low binder grade (K 703) was more resistant to erosion at higher angles (>50 degrees). In contrast, the ceramics exhibited a range of wear rates. The boron carbide and reaction-bonded silicon carbide were comparable in erosion resistance to the cemented tungsten carbides, whereas the alpha and CVD silicon carbide versions showed significantly lower erosion rates. There was in general no change in ranking of the materials as a function of slurry

impingement angle. The velocity exponents of the erosion rates (expressed as thickness of material removed per volume of impacting slurry) were the same for the cemented carbides K 701 and KZ 701 at 2.5, a value typical of those reported in the literature for gas-borne particle erosion. The K 703 grade exhibited a high value of 3.1, while hot-pressed boron carbide showed the lowest exponent, 1.4.

The dominant mode of erosion loss of the cemented tungsten carbides was preferential removal of the binder phase with subsequent liberation of the tungsten carbide particles; the merit of lowest possible amount of binder phase is obvious, provided mechanical properties are adequate. Boron carbide eroded by an apparently ductile erosion mechanism and showed enhanced loss around sites of porosity. The results for the various forms of silicon carbide revealed the excellent intrinsic erosion resistance of single crystals of this material. Deterioration of the practical forms studied was as a result of microporosity effects (in CVD), grain boundary impurity effects (alpha), or a more susceptible phase (free silicon in the reaction-bonded material).

Examination of the feasibility of using a synthetic slurry composed of low-hazard, readily available materials indicated that a commercially available dolomite product might provide a suitable substitute erodent. Initial tests with water as the carrier revealed problems of settling out of the erodent, which could be resolved by increased agitation in the slurry reservoir, or by using light oil with suitable viscosity-temperature characteristics.

Service trials with a reaction-bonded silicon carbide valve stem and a cemented tungsten carbide seat resulted in what was classified as a premature failure, but provided quite revealing data. The two materials had eroded in the same mode and at the same relative rates as observed in the laboratory rig tests. Analysis of the parts suggested that, in fact, the failure may have resulted from inadequate design and fabrication of the stem, rather than from poor materials erosion performance.

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I. INTRODUCTION

One of the critical materials problems hindering the development of coal liquefaction technology is the erosive wear of such equipment as pumps, valves and piping used to handle flowing coal slurries. The problem is particularly severe in valves used to "letdown" the process stream from the high-pressure side of the valve to the low-pressure side. The slurry stream attains high velocities in the narrow channels of the valves designed to maintain the pressure drop. The rapid acceleration of the slurry is also promoted by the expansion of the dissolved gases in the stream. The inorganic material and undissolved coal in the resulting high-velocity slurry stream severely erode the letdown valve internal surfaces with which they come into contact. Current practice is to use replaceable trim for the critical internal components such as the valve stem and seat. Even with these modifications, nominal wear lives as short as 14 days have been reported for letdown valves used in some of the liquefaction facilities.(1,2)

The high hardness and chemical inertness of ceramics make them attractive candidate materials for erosive wear applications that do not demand high strengths. However, the inherent brittleness or low fracture toughness of ceramics tend to make them susceptible to erosion by brittle chipping(3), so that improved performance of ceramic materials in a given erosive wear application cannot, therefore, be presumed. Experimental programs have been conducted at Battelle's Columbus Laboratories in which the coal slurry erosive wear behavior of a number of advanced ceramics was evaluated under conditions similar to those experienced by the letdown valve trims.(1,4,5) The results obtained to date have identified a number of ceramics/preparation techniques that have the potential to significantly improve the service life of the valve trim.

This report discusses (a) a comparative evaluation of the performance of the ceramics and the conventional valve trim materials -cemented carbides, (b) the dependence of the erosion rates of selected target materials on the velocity and the impingement angle of the slurry jet, and (c) the material microstructural effects on erosive wear as inferred from Scanning Electron

Microscope (S.E.M.) characterization of the eroded surfaces. The results of the present study are also examined in the light of the predictions of erosion models that are based on partial impact damage.

II. APPROACH

The approach in this program was to establish a research and data base in five interrelated areas; screening of candidate materials, study of erosion mechanisms, characterization of coal-derived slurries, development of a reproducible synthetic slurry, and service trials of a candidate valve trim material.

A number of commercially available and laboratory candidate materials were screened, including cemented tungsten carbides, boron carbide, different silicon carbide materials, and titanium diboride-nickel composites. Some of these materials, such as the $\text{TiB}_2 + \text{Ni}$ materials were subjected only to the standard screening test conditions used at Battelle. The others were subjected to more extensive experimentation, including the effect of impingement velocity and angle for elucidation of the erosion mechanisms of these materials. The erosion behavior of the cemented tungsten carbides K701 and KZ701 was evaluated for the entire range of erosion conditions and all the slurries used in this program to establish baseline laboratory properties for a material having service experience.

The erosion screening and mechanism studies were carried out in Battelle's erosion test rig. This rig uses reconstituted coal-derived slurries obtained from actual pilot plant operations and can also be adapted for synthetic slurries. Most of the tests in this program used coal slurry from the SRC plant at Wilsonville, Alabama. In addition, a number of tests on two different slurries from the H-coal process development unit at Lawrenceville, New Jersey were run to examine slurry dependence of erosion behavior.

The screening tests were performed at an impingement angle of 20 degrees and a letdown pressure of 13.8 MPa (2000 psi). These conditions were found in a previous program (4) to give the best correlation between ranking of materials in the laboratory test and in-service trials at the SRC pilot

plant at Wilsonville, Alabama. To develop the needed information on erosion mechanisms in candidate materials to guide optimization of their properties and microstructure, more extensive erosion testing was conducted on several materials, cemented tungsten carbide, B_4C (Norbide) and reaction bonded SiC (NC430). In this more extensive testing, the impingement angles were varied from 10 to 90 degrees and letdown pressures from 5.5 to 13.8 MPa (800 to 2000 psi), resulting in particle velocities up to about 100 m/sec. The eroded surfaces were characterized by optical and scanning electron microscopy. The shape, depth and volume of the craters were determined by a series of Talysurf profiles.

Before beginning the screening and detailed evaluation testing, it was necessary to determine an acceptable procedure for rejuvenating the slurry for use on a continuous basis rather than mixing a new batch for each test. This is particularly important because in practice the slurry passes through the valve only once, while for laboratory testing, continuous cycling is a more practical proposition. To do this, the erosion characteristics and insoluble particle size of the slurry were investigated during testing for long periods (slurry aging) and a rejuvenation procedure was developed to provide consistent results.

To properly interpret the erosion results, understand differences between slurries from different coals, and for guidance in synthesizing a substitute standard slurry, the nature of the coal-derived slurries must be known. The coal-derived slurries were well characterized by scanning electron microscopy, energy dispersion analysis of x-rays and particle size distribution. This analysis was performed on as-received solids, rejuvenated slurries and used slurries cycled through the test rig for increasing erosion times. Based on these results, a synthetic slurry was formulated and tried in the erosion rig.

To extend the number of candidate valve trim materials with service experience, reaction bonded SiC (NC430) and B_4C (Norbide) were selected for service trials. These materials were machined into the appropriate shape and placed in a valve at the H-Coal PDU during a trial run. Only the SiC material was able to be given a service exposure due to time and equipment constraints.

III. EXPERIMENTAL PROCEDURES

III.1 Materials Selection

III.1.1 Erosion-Resistant Materials

The materials selected for inclusion in the program were intended to represent the types available now, or with slight adaptation, for service in valves. Based on the results of earlier programs (1,2,4), the cemented tungsten carbide, Kennametal K701, was chosen as the standard for comparison. A modification of this material, designated KZ701 to signify that it was produced by a hot isostatic pressing (HIP) process and should therefore have close to theoretical density, was included together with a lower binder-content version, K703, reported to be somewhat more erosion-resistant. Most of the coal liquefaction pilot plants have experimented with the use of wear resistant valve inserts of K701, and some have tried K703.

Silicon carbide in its various forms is a ceramic material of promise in this application (4,5); three forms of this material were included in this program: reaction bonded, the alpha variety, and a single-phase CVD coating. Samples of reaction bonded silicon carbide gave good erosion results in our earlier screening program, while some samples of CVD SiC exhibited the lowest rates of erosion yet measured in the Battelle slurry erosion rig. One grade of boron carbide was selected as representative of the class of erosion-resistant single-phase materials available for use in the massive form. The sources, grades and compositions of these materials are listed in Table 1.

In addition to this main set of materials, standard comparison erosion tests were run on a number of samples of Ni-cemented TiB_2 produced by Oak Ridge National Laboratory. These materials are also listed in Table 1.

III.1.2 Erosive Slurries

The slurries selected for study were intended to be representative of the products of the SRC-1 (Wilsonville) and the H-Coal (Trenton/Lawrenceville)

TABLE 1. SOURCES, GRADES, COMPOSITION AND MECHANICAL PROPERTIES OF CANDIDATE VALVE MATERIALS

Valve Materials		Grade	Composition	Hardness† GPa	Fracture Toughness MPa·m ^{1/2}
Material	Source				
Cemented WC,	Kennametal	K701	10% Co, 4% Cr binder	16.3	10.5*
"	"	KZ701	10% Co, 4% Cr binder	17.5	9.5*
"	Kennametal	K703	5.5 % Co, Cr binder	17.5	9.5*
B ₄ C	Norton	Norbide	B ₄ C	30.5	
SiC	Battelle	CVD	SiC	32.5	3.5 - 4*
SiC	Carborundum	α-SiC	SiC	26.1	3.5 - 4.3
SiC	Norton	NC-430	88.5% SiC, 10.6% Si (Reaction-Bonded)		3.2
TiB ₂	ORNL	NT80C	20% Ni binder		
TiB ₂	ORNL	NT85C	15% Ni binder		
TiB ₂	ORNL	NT90C	10% Ni binder		
TiB ₂	ORNL	NT80G	20% Ni binder		
TiB ₂	ORNL	NT85G	15% Ni binder		
TiB ₂	ORNL	NT90G	10% Ni binder		
SiC	Norton	HX341		19	4.0*
Si ₃ N ₄	Norton	NC-132		14	3.5-4.
Al ₂ O ₃	GE	Lucalox		18.2	3.1

† Vickers hardness with indenter lead of 2500 gm.

* Estimated values suggested by literature(6,7).

processes, operated on a range of coals. Samples of actual process stream solids were obtained, in the form of unfiltered product (downstream of the letdown valve, upstream of the filter) from SRC-1, or vacuum bottoms from H-coal. These samples were supplied in 55 gallon drums; the coal-derived liquids contained were solids at room temperature. The identifications of the samples obtained are listed in Table 2.

Test slurries were made by dissolving the solidified plant samples in anthracene oil in proportions to provide the same concentration of insoluble solids as that found in the actual process streams fed to the letdown valves. In run No. 46 at SRC-1, conditions were such that the insoluble solids content of the process stream was approximately 8 weight percent. As a result, all of the initial laboratory erosion work was done with a reconstituted slurry containing 8 percent insoluble solids. Later process runs at SRC-1, and at H-coal, have produced levels of approximately 12 percent insoluble solids in the slurries fed to the letdown valves.

TABLE 2. SOURCES OF ACTUAL COAL-DERIVED SLURRIES OBTAINED

Process Feed Coal	Process Run No.	Sample No.	Weight % Insoluble Solids
(A) <u>Solvent Refined Coal, SRC-1</u> <u>Wilsonville</u>			
Illinois No. 6 (Monterey)	46	8-29/31-75	34.0
Kentucky No. 9 (Lafayette)	201	2-2-80, 22.55	-
(B) <u>Hydrocarbon Research Inc.,</u> <u>H-Coal, Trenton</u>			
Illinois No. 6	130-82-29A	LO-2083	34.7
Wyodak	130-83-16A	LO-2084	45.5
Kentucky No. 11	130-89-20A	LO-2085	-

III.2 Erosion Testing Procedures

III.2.1 Laboratory Test Rig

The erosion test apparatus used in this program was developed during previous programs conducted for the Electric Power Research Institute.(1,4,5) This equipment was designed to simulate as closely as possible the slurry letdown conditions at the Wilsonville, Alabama, SRC pilot plant with the result that reasonable correlation of the test results with actual operating experience was obtained in those programs. Before beginning the present program, operational and maintenance considerations prompted certain modifications to be made to the test apparatus. No changes were made, however, that would change the characteristics of the test or test results.

The erosion test system is shown schematically in Figure 1. The basic components of the test system (right to left in Figure 1) are a pumping system, a pressurized reservoir, a heating system, and a test chamber. The purpose of the pumping system is to maintain the desired fluid level and pressure within the reservoir. The reservoir feeds the test chamber with slurry which is driven by a pressurized gas head. The slurry is heated to the desired test temperature as it passes through resistance heated coils of tubing enroute to the test chamber. The temperature of the slurry is measured prior to entry into the test chamber. Before entering the test chamber, the heated slurry passes through a filter to avoid plugging of the orifice by oversize particles. The test chamber contains an orifice through which the slurry is let down into a low pressure chamber while being directed onto the specimen surface. From the low-pressure chamber, which is maintained at about 0.55 to 0.69 MPa (80 to 100 psi), the slurry is returned to the pump after passing through heat exchangers which cool it to allow reasonable life for the seals and fittings in the pump and other parts of the system.

The pumping system consists of two standard hydraulic cylinders coupled together. One of the cylinders is driven by a standard hydraulic pump. This cylinder operates the other cylinder which is the slurry pump. By the use of two check valves, the slurry pump is first filled with the low-pressure slurry from the low-pressure chamber, and then during the pumping stroke it discharges the slurry into the high-pressure reservoir. The level control for the system is on the low-pressure side of the system (far left in

FIGURE 1. SCHEMATIC OF SLURRY EROSION TEST SYSTEM

Operating conditions; coal-derived slurry,
343 C, 13.8 MPa hydrogen.

Figure 1). When the level of slurry within the low-pressure chamber beneath the orifice and the test specimen fills to a given level, the pump is activated and pumps slurry into the reservoir. The pressure on the low-pressure side is adequate to then fill the pump for the next pumping stroke. Because a known volume of slurry is delivered on each stroke, the volume of slurry passing through the orifice per unit of time is known and the velocity of the slurry on the test specimen surface can be estimated. The pressurizing gas in the reservoir is a mixture of approximately 80 percent hydrogen and 20 percent argon. Solution of hydrogen into the slurry will not be as great as in the actual pilot plant, since in the rig the hydrogen contacts essentially cold slurry in the pressure vessel. In this respect, the rig will not accurately simulate the condition of the slurry at letdown in typical liquefaction processing. The gas over-pressure was varied from 2.0 to 13.8 MPa (300 to 2000 psi) to obtain the desired range of slurry velocities investigated during this program. The arrangement of the orifice and the test specimen is shown in Figure 2. The orifice is made of tungsten carbide and the collimating section of the orifice is nominally 0.51 mm (0.02 in.) in diameter by 2.54 mm (0.10 in.) long. The surface of the test specimen can be oriented at angles ranging from 10 to 90 degrees to the impinging jet of slurry. The distance traversed by the slurry to the point of contact with the test surface was held constant at 2.8 mm (0.11 in.).

FIGURE 2. ARRANGEMENT OF ORIFICE AND IMPINGEMENT TEST SPECIMEN

III.2.2 Slurry Characterization Techniques

Characterization of the slurries from the erosion rig to determine the size distribution of the insoluble solids, and to determine predominant particle shapes and compositions, was hampered by the difficulties involved in separating the solids from the long-chain asphalt-related compounds in the oils to obtain clean, non-agglomerated samples. This agglomeration has apparently complicated previous efforts at proper solids size analysis.(6,7)

A technique to produce clean solids samples for optical and electron-optical analysis was eventually evolved based on a soxhlet extraction apparatus using pyridine as solvent. Cleaned samples were obtained by dissolving the solid product obtained from the pilot plants in pyridine, placing this in a paper thimble, and washing with pyridine in a soxhlet unit until the solution ran clear. Examination of the cleaned particles in the scanning electron microscope (SEM) showed evidence of agglomeration or attachment of small particles to the larger ones, in the as-prepared unfiltered product from SRC-1, but there was no indication of any associated organic material.

Several techniques were evaluated for determining the particle size distributions in the slurries. These were (i) the line intercept method on SEM micrographs, (ii) optical particle size analysis of SEM micrographs, (iii) the Coulter Counter, and (iv) laser particle analysis. Methods (i) and (ii) require placing soxhlet-separated solids on a surface and drying for examination in the SEM. The line intercept method involved placing a grid on the SEM micrographs and individually measuring the size of each particle intersected by a line. The optical particle size analysis consisted of enlarging SEM micrographs and measuring the size of each particle using the Quantimet Particle Size Analyzer. Methods (iii) and (iv) require the solids to be dispersed in a liquid, usually pyridine in this study. Both soxhlet-cleaned solids and directly dissolved, uncleaned slurry samples were examined with these techniques.

III.2.3 Specimen Preparation

With the exception of the cemented TiB₂ material, the erosion specimens were machined from the as-received material to dimensions of

nominally 5 x 5 mm by up to 25 mm long (0.2 x 0.2 by up to 1 inch long). The cemented TiB₂ specimens were cut to 6 x 5 x 5 mm (0.25 x 0.2 x 0.19 inch) size. The erosion test surface was finish ground with a 600 grit diamond wheel, to provide a standard reference surface. This was necessary for two reasons. Firstly, the reference surface profile trace is used as a baseline to measure the crater depth, and a 600 grit level finish was required to obtain the sensitivity of measurements for small wear rates. Secondly, initial erosion wear rates of target test materials showed some sensitivity to the surface roughness. The fine diamond wheel grinding of the test surfaces was used to normalize the initial erosion rates.

III.2.4 Characterization of Eroded Surfaces

The erosive wear produced on the test specimen surfaces of the candidate valve materials was characterized by (a) measuring the maximum depth of the crater produced on the test surface by the slurry jet using a Talysurf surface profilometer, and (b) examination of the eroded surface in a scanning electron microscope (SEM). The sensitivity of the Talysurf profilometer was 0.25 μ m (10 microinches). Elemental analysis of selected features of the eroded surfaces was performed in the SEM with energy dispersion analysis by x-rays (EDAX).

IV. RESULTS AND DISCUSSION

IV.1 Materials Characterization

Table I lists the sources, grades, compositions, and mechanical properties of the candidate valve materials erosion tested in this program. The hot-pressed grades of SiC (Norton HX-341) and Si₃N₄ (Norton NC-132) and the sintered alumina (GE Lucalox) were tested in an earlier program⁽¹⁾ and are included in Table I for purposes of comparison. The hardness values listed were obtained with a Vickers microhardness indenter at an indent load of 2500 gms. The fracture toughness values (K_{IC}) listed were either reported by the material suppliers or they were estimated from values reported in the literature for similar materials.^(3,8) There is no significant

difference in the fracture toughness values of the different ceramics. K_{IC} values are generally in the range 3 - 4.5 MPam^{1/2}. The cemented WC materials have approximately three times the fracture toughness of the ceramics. There is a more systematic variation in the microhardness of the ceramics. The chemically vapor deposited SiC exhibited the highest hardness as expected, due to the high purity of the SiC and the essentially theoretical density obtained by the CVD fabrication. The sintered SiC and the hot-pressed SiC (Norton HX 341) represent forms with increasing impurity levels and a corresponding decrease in hardness. Due to the coarse, two-phase microstructures of reaction bonded SiC (Norton NC-430) and the cemented TiB₂ (ORNL), Vickers hardness values representative of the average microstructure could not be obtained. Among the ceramics listed, the hot-pressed Si₃N₄ had the lowest hardness value. The cemented carbides have hardnesses comparable to the sintered alumina (Lucalox) and the hot-pressed SiC. The K 701 and KZ 701 grades of cemented carbides have identical compositions and differ only in their fabrication. The KZ 701 grade is subjected to hot, isostatic pressing as a final fabrication step to improve the density. The individual hardness values for the three grades suggest that the increase in hardness due to the improved fabrication (KZ 701 grade) is comparable to the increase due to the reduction in the binder level (K 703 grade).

The microstructures of the cemented carbides and the ceramics were characterized by conventional metallographic techniques or in some cases by an electron replica technique to resolve fine features. The essential microstructural features of the candidate valve materials tested in the current program are briefly described in the following sections.

IV.1.1 Cemented Carbides (Kennametal K 701 and K 703)

The microstructures of the two grades of cemented WC, Kennametal grades K 701 and K 703, were examined by metallographic and optical techniques. Figures 3(a) and 4(a) show these microstructures for the two grades. The fine size of the carbides and the intercarbide binder could not be clearly resolved at normal magnifications available with the optical microscope. A transmission electron replica technique was, therefore, used to improve the resolution. Figures 9(b) and 10(b) show the electron replica

(a)

500X

(b)

6400X

FIGURE 3. MICROSTRUCTURE OF CEMENTED WC (KENNAMETAL GRADE K 701)

- (a) Optical Micrograph, Polished and Etched
- (b) Electron Replica of Etched Surface

(a)

500X

(b)

6400X

FIGURE 4. MICROSTRUCTURE OF CEMENTED WC (KENNAMETAL GRADE K 703)

- (a) Optical Micrograph, Polished and Etched
- (b) Electron Replica of Etched Surface

micrographs for the K 701 and K 703 grades of the cemented carbide, respectively. The particle size for the K 701 ranges up to the 2 μm size range. Whereas in the K 703 the particles range up to about 5 or 6 μm . The particle boundaries are somewhat diffuse and irregular due to the higher binder level in the K 701 grade. The particle boundaries are more clearly defined and are of angular shape in the K 703 grade. A contributing factor to the difference in the appearance of the etched boundaries could be that the Cr in the binder in the K 701 grade, due to its affinity to carbon, acts to form a better bond with the tungsten carbide surface and provides significant precipitation hardening of the binder phase with chromium carbides.

Microstructure of the KZ 701 grade was not evaluated; but it is expected that it should be very similar to the K 701 grade with the exception of a lower overall porosity due to the hot, isostatic pressing operation.

IV.1.2 B₄C - Norton Norbide

The microstructure of hot pressed boron carbide (Norton Norbide) is shown in Figure 5. It is a single-phase material with equiaxed grains in the size range 10-20 μm . The microstructure exhibits isolated grain boundary pores and it will be shown in a later section that these pores have a significant influence on the erosive wear behavior of this material. Twin boundaries are also apparent within some grains, which were probably induced mechanically during the surface preparation stage.

IV.1.3 CVD SiC (Battelle)

The chemically vapor deposited SiC, fabricated at Battelle's Columbus Laboratory, exhibited the most intriguing microstructure among all the materials investigated in the current program. It is characterized by "growth regions" in the plane of deposition (parallel to the substrate surface) and a uniform and alternating layered structure in the plane normal to the substrate. The "growth region" structure, as viewed normal to the substrate, is shown in Figure 6(a). These regions are approximately circular in cross section and are characterized by "rings" within each. The average diameter of

FIGURE 5. MICROSTRUCTURE OF HOT-PRESSED BORON CARBIDE (NORTON NORBIDE)

FIGURE 6. (a) MICROSTRUCTURE OF CVD SiC (BATTELLE) IN A PLANE PARALLEL TO THE SUBSTRATE SURFACE

the outermost ring is in the range 100-200 μm . The characteristic layered structure of the CVD SiC, in the plane normal to the substrate surface, is shown in Figure 6(b). The layered structure is typified by uniform and alternating bands; one set of the bands is devoid of any structure (appears as white bands in Figure 6(b)) while the adjacent set of bands exhibits some structure (appears as dark bands in Figure 6(b)). The spacing of these bands is very uniform and approximately equal to 4 μm .

To relate the ring-like structure of Figure 6(a) to the layer structure of Figure 6(b) a specimen was prepared in such a way that both the surfaces could be observed simultaneously. Figure 6(c) shows the edge of such a specimen where the two surfaces of interest meet. A careful examination of the microstructure of the material, especially near the edge where the two surfaces meet, reveals the following explanation for the ring structures of the growth regions. During chemical vapor deposition the material deposits in periodic layers. The deposited surface is, however, not flat but consists of "humps" of varying sizes. These humps are essentially the growth regions. The rings are the "contour lines" of the growth layers in the humps in the plane of polishing in Figure 6(a). Near the centers of the growth regions the surface of the deposit is more nearly parallel to the plane of polish than at the boundary. As a result of this the rings are more closely spaced near the boundaries of the growth regions than at the center.

To investigate the nature and origin of the layered structure, the transverse structure of the material was examined in a scanning electron microscope at high magnification. Figure 6(d) shows the polished and etched surface of the CVD material in the transverse plane. The alternating bands are not physically distinct phases. Instead, it appears that the characteristics of material deposition and nucleation of SiC crystals change periodically. This results in a band where deposited SiC is homogeneous and the crystal size is extremely fine and not resolved in Figure 6(d). After a certain period, another band forms where the deposition and nucleation characteristics change and physically distinct crystals emerge in the size range 0.2-0.4 μm . Many of these crystals are elongated in the direction normal to the substrate surface. Associated with the formation of the crystals is microporosity distributed between the crystals. The porosity is

FIGURE 6. (b) MICROSTRUCTURE OF CVD SiC (BATTELLE) IN A PLANE NORMAL TO THE SUBSTRATE SURFACE

FIGURE 6. (c) MICROSTRUCTURE OF CVD SiC (BATTELLE) SHOWING THE RELATION OF RING STRUCTURE OF THE PLANE OF DEPOSITION (FIG. 6 (a)) AND THE LAYER STRUCTURE OF THE TRANSVERSE PLANE (FIG. 6 (b))

FIGURE 6. (d) LAYER STRUCTURE OF CVD SiC (BATTELLE) IN A PLANE NORMAL TO THE SUBSTRATE SURFACE

FIGURE 7. TYPICAL MICROSTRUCTURE OF SINTERED ALPHA SILICON CARBIDE, FROM KRAFT AND COPPOLA (9)

maximum at the interface between the homogeneous band and the crystalline band. The physical origin of the periodic variation in the deposition characteristics was not ascertained. But it is suspected that either the substrate temperature or the flow of methylchlorosilane, the organic source of Si and C, were oscillating in some periodic manner and affecting the deposition and nucleation characteristics of SiC.

IV.1.4 α -SiC (Carborundum)

The microstructure of sintered alpha SiC could not be revealed by normal etchants like 10 percent oxalic acid (electroetching) and hot orthophosphoric acid. The etchant recommended by Carborundum Co., molten salt consisting of equal weights of KOH and KNO₃, was also tried but was not successful. The microstructure reported by E. H. Kraft and J. A. Coppola of Carborundum Company⁽⁹⁾ for nominally the same material is shown in Figure 7. The material has fairly uniform grains in the size range 5-10 μ m. Some grain boundary porosity is also noted in the microstructure. This is consistent with the reported density: 98 percent theoretical.

IV.1.5 Reaction-bonded SiC (Norton Noralide NC-430)

The reaction-bonded SiC, obtained from Norton Company (Noralide NC-430), is a two-phase, duplex microstructure ceramic. The typical microstructure reflects the fabrication process of this ceramic which consists of mixing SiC grains with carbon and an organic binder and forming a "green" body by one of the conventional methods. The green body is then cured and fired to carbonize the resin binder and drive-off the volatiles. The porous body is then infiltrated with liquid Si at high temperatures, causing a reaction with the carbon present to form SiC, thus bonding the existing SiC grains together. The result of this process is a microstructure consisting of preexistent alpha SiC grains (large gray areas in Figure 8(a)) of average size 100 μ m surrounded by reaction product SiC (mottled gray areas in Figure 8(b)) and free Si (mottled bright areas in Figure 8(b)). The microstructure of Norton NC-430 grade reaction-bonded SiC has roughly 88.5 percent SiC and 10.6 percent Si.

100X

(a)

500X

(b)

FIGURE 8. MICROSTRUCTURE OF REACTION-BONDED SiC (NORTON NC-430)

IV.1.6 Cemented TiB_2 (Oak Ridge National Laboratory)

The cemented TiB_2 , subjected to the screening test only, is a developmental material obtained from Oak Ridge National Laboratory. Six grades of this material, with the Ni binder level ranging from 10 to 20 percent, were received and erosion tested. The microstructure of only one grade, NT90G, was evaluated and is shown in Figure 9. Figure 9(a) is an optical micrograph of the etched surface. The grain sizes are nonuniform and some porosity is evident at the boundaries. Figure 9(b) shows an as-polished surface of the specimen. The presence of the Ni binder phase is more clearly apparent on this unetched surface.

IV.2 Slurry Characterization

IV.2.1 Evaluation of Slurry Characterization Techniques

Before extensive characterization of the coal-derived slurries was undertaken it was necessary to evaluate techniques for preparing the samples and for measuring the particle size distributions. This task was hampered, as discussed in Section III.2.2, by difficulties involved in separating the solids from the long-chain asphalt-related compounds in the slurries to obtain clean, non-agglomerated samples.(6,7)

Figure 10 shows particles separated from the as-prepared unfiltered product from SRC-1. While many of the smaller particles still appeared agglomerated or attached to larger particles, there was no indication of any associated organic material which might have caused bonding. SEM examination of the walls of the paper thimbles which were used in the soxhlet extraction indicated that some of the smaller insoluble particles had become entrapped in the thimble, Figure 11. This suggests that the population of unattached small particles in the slurry was greater than views like Figure 10 would indicate. Although this loss of some small particles is undesirable, on balance this cleaning process provides the best samples obtained so far for subsequent particle analysis.

500X

(a)

1000X

(b)

FIGURE 9. MICROSTRUCTURE OF CEMENTED TiB₂ (ORNL NT90G)

(a) Optical Micrograph - Etched Surface

(b) Scanning Electron Micrograph - Polished Surface

.00X

FIGURE 10. SCANNING ELECTRON MICROGRAPH OF INSOLUBLE SOLIDS SEPARATED FROM UNFILTERED PRODUCT FROM SRC-1 (Illinois No. 6, Run 46)

400X

FIGURE 11. SEM MICROGRAPH OF SURFACE OF PAPER THIMBLE USED IN SEPARATION TECHNIQUE, SHOWING ENTRAPPED SMALL PARTICLES FROM COAL SLURRY

IV.2.2 Slurry Aging

IV.2.2.1 Aging of SRC-1/Illinois No. 6 Slurry

The solids separation technique described above was used to prepare samples from slurry extracted from the slurry aging run (Section IV.3.1), to allow an investigation of the change in particle size and shape with time of use in the erosion rig. The sequence of SEM micrographs in Figure 12 shows the general change in particle makeup with time for up to 3.24×10^4 sec (9h) in the erosion test. As shown in Figures 10 and 12(a), the initial slurry consisted of a number of smooth, regular-shaped particles of size 20-50 μm , together with numerous smaller particles of 4 μm and less in size which were attached to the larger particles or agglomerated together. In addition, numerous particles of apparently fossilized cellular origin were present, with forms ranging from circular sponge-like structures, to long, thin stem types, (Figure 10). The major change observed in the appearance of the insoluble particles with time of use was the increase in population of the smaller particles adhering to or embedded in the larger particles, or agglomerated together. Even after 3.24×10^4 sec (9h) of testing, 20 to 40 μm size particles were still evident, while few of the fossilized cellular structures were observed after only 2.4×10^3 sec (0.67h) of use. The source of the increased numbers of small particles is probably from breakup of the larger regular-shaped particles, and from the destruction of the cellular particles. One inference which might be drawn is that the process of breaking up of the fossil-like particles is likely to lead to the production of an increased number of smaller particles which are likely to be sharp-edged until they finally degenerate to smaller sizes and rounded edges.

Samples of these same separated solids were also subjected to a number of particle size analysis techniques. Figures 13 and 14 show the particle size distributions of the 600 sec (10 min) and 2.4×10^3 sec (40 min) samples, obtained from line intercepts, optical particle analysis, Coulter Counter, and laser particle analysis techniques. The first two techniques used SEM photographs of the soxhlet-separated solids, while the latter two used the same solids redispersed in pyridine. The results of the

(a) Start

400X

(b) 600 Sec (0.17 h)

400X

(c) 2.4×10^3 Sec (0.67 h) (d) 6.01×10^3 Sec (1.67 h)

400X

FIGURE 12. SCANNING ELECTRON MICROGRAPHS OF INSOLUBLE SOLIDS
SEPARATED FROM TEST SLURRY (ILLINOIS NO. 6, SRC-1)
AFTER STATED TIMES OF OPERATION

(e) 9.61×10^2 Sec (2.67 h) 400X

(f) 1.68×10^4 Sec (4.67 h) 400X

(g) 2.37×10^4 Sec (5.67 h) 400X

(h) 6.01×10^3 Sec 400X

FIGURE 13. SIZE DISTRIBUTION OF SRC NO. 6 SLURRY
BY FOUR TECHNIQUES, SLURRY AGE IS 600 SEC
(10 MIN)

FIGURE 14. SIZE DISTRIBUTION OF SRC-1/ILLINOIS NO. 6
SLURRY BY 4 TECHNIQUES, SLURRY AGE IS 2.4×10^3 SEC (40 MIN)

two optical techniques agree quite well, and suggest that the general size consist of the solids is finer than that indicated by the Coulter Counter or laser methods.

Further investigation of the laser technique was made to try to discover the reasons for its recording a size distribution so different from the other techniques. In order to avoid the problems and losses involved in sampling reconstituted slurry from the erosion rig, a sample of solidified product from Wilsonville was dissolved directly in pyridine, and subjected to the size analyzer. Simultaneously, another sample of the same solid product was processed in the soxhlet extraction apparatus with pyridine, and the solids so obtained were redispersed in pyridine and analyzed by the laser technique. The results of these analyses are shown in Figure 15. The soxhlet-extracted material exhibited the same characteristic size-distribution curve as those for similarly treated aged material in Figures 13 and 14. The directly dissolved material, on the other hand, gave a size distribution very similar to those obtained by optical methods. These results indicated direct solution of the particle samples in pyridine is required to obtain consistent results with the laser analysis technique.

A further point of interest is the shift in size distribution obtained for the soxhlet-extracted material immediately after the suspension was ultrasonically agitated. The shift towards smaller particle sizes suggests that the soxhlet-extracted material does not redisperse well in pyridine, and the laser identified agglomerated particles instead of individuals.

Although the direct solution/laser analysis technique appeared most promising, access to this device was limited. Therefore, most particle size analyses on the aged slurries were made using the soxhlet-Coulter Counter method. The preferable route for determining insoluble particle size distributions in these slurries appears to be by the optical methods, but these are very time-consuming and require extraction of the solids. Direct solution of the coal-derived material in pyridine coupled with laser size analysis is probably the cleanest and simplest technique when comparing numerous different samples.

FIGURE 15. COMPARISON OF EFFECTS OF SAMPLE PREPARATION ON LASER SIZE ANALYSIS RESULTS (SRC-1, ILLINOIS NO. 6).

The sets of size distribution data presented in Figures 16 and 17 were obtained by Coulter Counter analysis of the soxhlet-extracted samples shown in Figure 12. The conventional Coulter Counter plot in Figure 16 suggests that no drastic change in size distribution occurs over the 2.04×10^4 sec (5.67 hr) of the slurry aging test. Replotting these results as a function of time for each size fraction reported, however, shows a possible trend with time in the relative populations of the particles in sizes 6 to 31 μ m. The populations of small particles (3.8 and 4.6 μ m) and the largest observed particles (38 to 62 μ m) did not change much with time.

Significantly, there is a general decrease in particle size of the population of particles in the size range 6 to 31 μ m in the first 600 sec (0.17 hr) of the test. In the next 1.8×10^3 sec (0.5 hr) the data suggest that the average size of particles in this size range increased, followed by another decrease in average size over the next 7.2×10^3 sec (2 hr), and finally a further increase over the next 10.8×10^3 sec 3 hr. Such oscillations in particle size distribution are confusing, and may result from artefacts of the techniques used. However, these results, combined with the SEM/optical information, suggest that during the aging test, there is an initial breaking up of some of the friable initial particles or edges and tips from the larger particles. This is followed by regrouping and rearrangement, as the smaller particles become associated together or embedded in larger particles, resulting in larger apparent particles, or as further size reduction occurs by collision of these larger particles with each other and the equipment.

The slurry as a whole appears to exhibit its most stable size distribution in the period 600 to 16.8×10^3 sec (0.17 to 4.67 hr). Replenishment with original slurry at some point in this time frame might be expected to cause the least change in overall size distribution, while introducing fresh erodent shapes.

IV.2.2.2 Aging of Slurry Based on H-Coal/Wyodak Coal Product. The slurry samples from this aging run were simply diluted with pyridine after sampling, and then analyzed using the laser particle size analyzer, which was available during this stage of the program. This was considered to be

FIGURE 16. COULTER COUNTER SIZE DISTRIBUTION FOR SRC (ILLINOIS NO. 6) SLURRY AGING TESTS

FIGURE 17. CHANGE IN THE SIZE DISTRIBUTION OF SRC-1 (ILLINOIS NO. 6) SLURRY IN SLURRY AGING TESTS

probably the most error-free technique available. The resulting size distributions as a function of slurry life are shown in Figure 18. A major feature of these data is that the Wyodak slurry has in general a smaller particle size than the Illinois No. 6 slurry, the average particle sizes being, respectively, approximately 5 μm and 8 to 15 μm . In addition, the change with time of use of the Wyodak slurry is a slight but orderly trend to smaller particle sizes; the only perturbation is the appearance of a small number of particles larger than 22 μm after 13.2×10^3 sec (3.67 hr.).

Since the degradation behavior of this slurry appears very well controlled, replenishment procedures can be arranged to maintain the particle size distribution within tight limits.

IV.2.3 Characterization of Slurry from Different Coals and Processes

Samples of each of the as-received solidified coal liquefaction products listed in Table 2 were dissolved in pyridine and analyzed in the laser particle size analyzer. The results in terms of relative volume of particles in given size fractions are shown in Figure 19, and the standard size distribution plots are shown in Figure 20. The size distribution of insoluble particles in these slurries appears to be remarkably similar for the range of coals in a given process, and for the two processes. The average particle size in the SRC-1 slurries ranged from 5.4 to 7.5 μm , while the range in the H-coal slurries was 6.5 to 8.0 μm . The average particle size for Illinois No. 6 processed by SRC-1 was 5.4 μm , compared to 6.5 μm for the H-coal processed material.

Figures 21 to 25 illustrate the appearance of the insoluble particles separated from these same samples, together with representative EDAX analyses of different particles. The original intent of correlating the particle size and shape characteristics in terms of typical chemical composition proved to be too complicated to be resolved within the resources of this program. However, some generalizing comments in this direction can be made. The cellular particles appeared to be predominantly Si-rich, probably silica. Many of the larger, smooth, angular particles were unreacted carbon containing some Si

FIGURE 18. LASER/PYRIDINE SIZE DISTRIBUTION FOR H-COAL (WYODAK)
SLURRY AGING TESTS

FIGURE 19. PARTICLE SIZE DISTRIBUTION OF INSOLUBLE PARTICLES IN THE PRODUCTS FROM SRC-1 AND H-COAL (LASER ANALYSIS, PRODUCTS DISSOLVED IN PYRIDINE)

FIGURE 20. COULTER COUNTER ANALYSES OF THE INSOLUBLE SOLIDS SEPARATED FROM THE VARIOUS COAL-DERIVED SLURRIES

400X

FIGURE 21. SEM VIEW OF INSOLUBLE PARTICLES FROM SRC-1 PRODUCT USING ILLINOIS NO. 6 COAL

EDAX ANALYSES: 1: Si >> S, Ca, Fe
 2: Si >> Al > S, Ca, K, Fe
 3: Si, Fe > K, Ca, S
 4: Cu >> S, Si, Fe

400X

FIGURE 22. INSOLUBLE PARTICLES FROM SRC-1 PRODUCT FROM KENTUCKY NO. 9 COAL

EDAX ANALYSIS: 3: Unreacted C 8: Si, Al, S, C, Fe
 6: Al, Si, S, Fe 9: Si >> S
 7: Si, Al, S, K 10: Si

FIGURE 23. INSOLUBLE PARTICLES FROM H-COAL PRODUCT USING ILLINOIS NO. 6 COAL

EDAX ANALYSES:

1: Si, S, Al, Ca, Fe	5: Si >> Al, S > Fe, K > Ca
2: Ti > Si > S, Al, Fe, Ti, Ca	6: Fe, Ca, Ti, S, Si
3: Si, Fe > Al, S > Ca, Ti	7: Si > K, Al >> Ca, Fe, S
4: Si >> Al. > S > K, Ca > Fe, Ti	8: Fe > Si > S, Al > K, Ca, Ti

FIGURE 24. INSOLUBLE PARTICLES FROM H-COAL PRODUCT FROM KENTUCKY NO. 11 COAL

EDAX ANALYSIS:

1: Fe > K > Ca, Mo, Mn	6: Ca, S >> Si, Al, Fe, P
2: Fe	7: Fe, Si, > S, Al > K, Ca, Ti
3: Fe > Co > Si	8: Fe
4: Fe, Si, S > Al >> K, Ca, Ti	9: Fe >> S, Ca, Si, K
5: Fe >> Si, Al, K	

400X

FIGURE 25. INSOLUBLE SOLIDS FROM H-COAL PROCESS USING WYODAK COAL

EDAX ANALYSIS: 1: Al, Si, S, Mo, Ca
2: Ca > Si, Al, S, C
3: Ca > Al, Si, > S, K, Fe, Mg, Ti, V

and S, or were mixtures such as Al, Si, or Si, Al, K or Si, Fe. The large, loosely-packed agglomerations often contained iron, and were mixtures of Fe, Si, Al, S or Fe, K, Ca, or Fe, S, Ca, while some were Al, Si, S mixtures. The clean-appearing, small, regular particles were often pieces of heavy metals, such as Fe, Cu or Fe, Ca, whereas the smaller spheres were often Ca or Si. Extensive electron microprobe X-ray mapping showed that Al was often associated with O and Si, presumably indicating the clay-like compounds often found in coal. Iron was often associated with S and sometimes with Si, suggesting pyrites-derived material, while the Ca and S maps also sometimes coincided. Where detected, Cl appeared to be associated with Si, whereas no particular association was evident for K. Trends with the various coal types could not be attempted from these results.

IV.3 Erosion Studies

The erosion testing consisted of two integrated activities, examination of slurry aging and investigations of erosion behavior of the aging slurry. Before extensive experimentation on the effects of material and erosion parameters on the erosion behavior of these materials, it was necessary to establish an acceptable procedure for permitting continued use of the experimental slurry for a series of tests without mixing a new batch each time. After the slurry aging characteristics were determined and an acceptable slurry rejuvenation procedure was developed, the more basic and extensive studies of the effect of various erosion parameters, such as jet velocity and impingement angle, were initiated.

These results are discussed in this section.

IV.3.1 Erosion During Slurry Aging Studies

The continued recycling of the same slurry in the Battelle slurry erosion test rig can lead to disintegration of the suspended solids and make the slurry less effective in erosion and nonrepresentative of service conditions. This is referred to as slurry aging. In a systematic evaluation of candidate valve materials or when examining the influence of such variables

as impingement angle and velocity of the jet, it is necessary to maintain a near-uniform slurry condition representative of slurries in service conditions. The observed variations in the target erosion rates can then be attributed to the material of the test variables alone.

Before establishing a reproducible slurry condition, the erosive characteristics of slurries during aging were examined for three different slurries prepared from a) high ash-content SRC (Wilsonville)/Illinois No. 6 coal product, b) H-Coal product derived from Wyodak coal, and c) H-Coal product derived from Illinois No. 6 coal. The slurry aging was monitored by measuring the erosion rates, expressed as the depths of the crater produced per unit time, as a function of the total time of use of the slurry. For these tests, the Kennametal cemented carbide grades K 701 and KZ 701 were used as the reference test materials, since these grades are frequently used in letdown valve trim and provide a suitable laboratory baseline material. The erosion tests were run under the following fixed conditions: jet impingement angle of 20 degrees, slurry pressure 13.8 MPa (2000 psi), temperature 343 C (650 F), hydrogen plus argon atmosphere. The majority of the tests were run for a duration of 3.6×10^3 sec (1 hour) each. Two initial tests on a new slurry were run for durations of 600 sec (10 minutes) and 1.8×10^3 sec. (30 minutes), respectively. All the erosion depths were normalized to a one hour test period to calculate an erosion rate for evaluating the slurry aging characteristics.

The preparation and the aging test results for the slurries prepared from the three coal-derived products are discussed individually in the following sections.

IV.3.1.1 Erosion by SRC-1/Illinois No. 6 Slurry. The coal slurry that was used in the majority of the erosion tests in the current program was prepared from an unfiltered SRC product (Wilsonville, Alabama facility) derived from Monterey, Illinois No. 6 coal. The product was reported to nominally contain approximately 8 percent ash. The insoluble solids in the product, consisting of ash plus undissolved coal (determined by solution of the organic material in pyridine and filtering), was found to be 34 percent by weight. The slurry used in the erosion testing was prepared by dissolving 24

weight percent of the solid product in anthracene oil, which was selected as a suitably representative solvent.

Figure 26 shows the results of the slurry aging tests using the K 701 target. Two different series of tests were run on the same test piece with two differently-finished surfaces; a surface ground with a 320 grit diamond wheel and a lapped surface. In the test series using the 320 grit ground surface, the majority of the tests were run on the longitudinal faces of the test pieces while two tests were run on the end faces. The tests on the lapped surface were all on the same longitudinal face. All the erosion rates plotted are from separate test sites on the target surface. The following features of the test results are noteworthy:

- (i) A transient regime is observed for approximately 10.8×10^3 sec (3 hours) of test time on the slurry; beyond this period the erosion rates are approximately constant or decreasing very gradually and are independent of the initial surface condition.
- (ii) The characteristics of the initial transient are dependent upon the initial surface roughness; the erosion rates monotonically decrease from an initial high value to a steady state value in the case of the 320 grit ground surface. The lapped surface, on the other hand, shows an initial increase and then a decrease in the erosion rates. A result of this difference in the characteristics of the transients is that the initial erosion rates are three to four times higher for the ground surface in relation to the lapped surface.
- (iii) The K701 grade of cemented carbide exhibits anisotropy in its erosion resistance. Tests run on the end faces of the piece indicate higher erosion rates relative to the longitudinal faces.

Several factors contribute to the occurrences of the transients in the slurry aging results of Figure 26. There is, of course, a direct effect of the disintegration of the suspended particles. Evidence for particle breakup was noted both in size analyses as well as in SEM characterization of the inorganic solid particles from the used slurry. Reduction of the erosion rates from particle size reduction is counteracted to some degree by the

FIGURE 26. EFFECT OF SLURRY AGING ON THE EROSION RATES. THE EROSION RATES, AS INDICATED BY THE NORMALIZED MAXIMUM DEPTH OF THE EROSION CRATER, PLOTTED AS A FUNCTION OF THE CUMULATIVE TEST TIME ON THE SLURRY; TARGET MATERIAL: K 701

increase in the number or concentration of the particles in the slurry. In addition to these erodent effects, the initial wear rates are also influenced by the surface finish. Erosion of an initially smooth lapped surface leads to an initial roughening of the surface and a consequent initial increase in the erosion rates. Starting with a rougher surface (320 grit) apparently results in initial smoothening due to erosion by rapid wear of the grinding ridges. The effect of the surface finish cannot, however, be simply accounted for by the difference in the initial surface profiles. The average amplitude of the surface roughness on a 320 grit ground surface of cemented carbide (K 701) specimen is approximately $0.5 \mu\text{m}$ (20 min). The corresponding value for the lapped surface is very much smaller. The difference in the initial erosion rates noted in Figure 25 is greater than can be accounted for directly from the difference in the amplitudes of the surface roughness. Some additional difference in the subsurface material, such as a damage zone, may also influence the effect of the surface roughness.

Based on this evidence it was decided to normalize the initial surface condition to the same degree of roughness for all specimens in this investigation. Grinding with a 600 grit diamond wheel provided a convenient, smooth reference surface while not requiring the cost and the time involved in the lapping process.

IV.3.1.2 Erosion by H-Coal/Wyodak Coal Slurry. The test slurry used in evaluating the aging characteristics of H-Coal product derived from Wyodak coal was initially prepared by dissolving 37 percent by weight of the product in anthracene. The solids content of the Wyodak product, determined using a Soxhlet extraction apparatus with pyridine as solvent, was 45.5 percent. This results in 16.6 percent of the suspended solids in the test slurry, a value typical of the process stream loading at H-Coal.*

The aging characteristics of the Wyodak slurry were evaluated using a cemented carbide (Kennametal KZ 701) target finish ground with a 600 grit

*More recent information from H-Coal concerning the conditions during the service trial run in their PDU performed during this program indicated a total solids content of 28 to 30 percent, including 13 percent ash in the letdown slurry.

diamond wheel. The results of these tests are shown in Figure 27. The first five tests in the series were run at a suspended solids concentration of 16.6 weight percent. Experimental difficulties necessitated the reduction of the solids concentration to 13 percent for the last three tests in the series. The characteristics of aging of the Wyodak slurry are qualitatively similar to those of the Wilsonville SRC product; however, the magnitudes of the erosion rates are significantly higher for the test series on the Wyodak slurry. This increase is due to both the increased concentration of the undissolved solids in the slurry (17 and 13 percent versus 8 percent for the Wilsonville product), and to the different jet orifice employed in this test series. The characteristics of slurry flow through nominally identical orifices can be significantly different and can lead to differences in erosion rates. In critical evaluations of the influence of material and test variables on erosion rates, therefore, the same orifice was used to normalize the conditions of jet flow.

IV.3.1.3 Erosion by H-Coal/Illinois No. 6 Coal Slurry. The test slurry used to evaluate aging H-Coal product derived from Illinois No. 6 coal was prepared by dissolving 24.5 weight percent in anthracene oil. This corresponds to 8.5 percent of undissolved solids in the slurry based on solids content of 34.7 percent, determined by the soxhlet extraction method using pyridine as the solvent.

Figure 28 shows the result of the aging tests on the Illinois No. 6 coal slurry using a cemented carbide (KZ701) target. Two series of tests were conducted. Tests 1 through 4 indicate aging effects of one batch of slurry. A new batch was used for Tests 5 through 7. In addition, Test 5 was conducted at the same test site as Test 4, whereas Tests 6 and 7 were on new sites. The characteristics of the initial transient in the aging curve for the Illinois No. 6 coal are different from those of the Wyodak slurry. There is a monotonic decrease in the erosion rates without any evidence of an initial increase. Repeated tests at new sites with similar slurries yielded reproducible wear rates as indicated by Tests 2 and 6 and 3 and 7. But a test conducted with a new slurry on an old test site (Test 5 on Site 4) does not reproduce the result of new slurry on new site (Test 1). A contributing factor to the low wear rate observed in Test 5 may be offered as follows.

FIGURE 27. EFFECT OF SLURRY AGING ON THE EROSION RATES FOR A WYODAK COAL PRODUCT H COAL.
 TARGET MATERIAL: KZ701

NOTE THE DIFFERENCE IN THE CONCENTRATION OF THE SUSPENDED SOLIDS AFTER 4 HOURS OF TEST
 TIME ON THE SLURRY

FIGURE 28. EFFECT OF SLURRY AGING ON THE EROSION RATES FOR AN ILLINOIS-6 COAL PRODUCT (H-COAL)
TARGET MATERIAL: KZ701

FIGURE 29. EFFECT OF PERIODIC SLURRY ADDITION ON THE EROSION RATES. NORMALIZED MAXIMUM DEPTH OF EROSION CRATERS PLOTTED AS A FUNCTION OF THE CUMULATIVE TEST TIME ON THE SLURRY; TARGET MATERIAL K701

During the course of Test 4 the effective angle of jet impingement decreases due to continued wear of the impingement site. Test 5 is, therefore, started at a jet angle somewhat less than the nominal value of 20 degrees which can result in a lower erosion rate (see Section IV.3.4.3). In addition to the complexities of the initial transient, the wear rates were also unexpectedly high for the Illinois No. 6 slurry with a solids content of only 8.5 percent.

The results of the aging studies on the three types of slurries pointed out the need for controlling the slurry condition in comparative evaluation of erosion rates. A procedure developed to meet those requirements is discussed in the following section.

IV.3.1.4 Effects of Slurry Rejuvenation. To avoid the expense of using new slurry for each test, but to provide relatively constant, reproducible slurry conditions for each test, a periodically rejuvenated slurry might be used. To establish a reference slurry condition to yield reproducible erosion rates, a procedure involving periodic partial replacement of slurry with fresh slurry was examined, using the SRC-derived slurry. The new slurry was prepared from the SRC product in the same manner as that used in the slurry aging studies. The erosion tests were conducted on K701 cemented carbide material with a 600 grit ground surface. Approximately 25 percent by volume of the test slurry was replaced by fresh slurry at intervals of 3 hours, i.e., following completion of three individual tests.

The results are summarized in Figure 29. The erosion rates in terms of normalized maximum depth of craters is plotted as a function of the cumulative test time on the slurry. Two results are significant in Figure 29. Consistent and measurable increases in erosion rates are observed following each fresh slurry addition. This confirms that some slurry rejuvenation does take place by the partial replenishing of the slurry. Secondly, the overall differences in the erosion rates between successive tests using a given rejuvenated batch of slurry decreases with each additional two cycles in Figure 29. This is indicative of a stabilization of the slurry in terms of its erosive capability.

The successive small differences in erosion rates between successive cycles and rejuvenated slurries are in general much smaller than the

differences in rates observed for changes in materials or erosion parameters. Based on these results, a three hour interval, quarter volume replacement procedure was adopted as a standard to maintain a uniform slurry condition.

IV.3.2 Erosive Wear Rates of Cemented Carbides and Ceramics

The erosive wear rates of the three grades of cemented tungsten carbides and the ceramics at three slurry jet impingement angles are listed in Table 3. The other test conditions used are also indicated in Table 3. The slurry used in these tests was prepared from the Wilsonville (SRC) product derived from the Illinois No. 6 coal, using anthracene as the solvent. The inorganic solids content of the slurry was 8 weight percent and the slurry condition was maintained stable by the periodic rejuvenation procedure. For the majority of the materials only one test was run under a given set of conditions. For the cemented carbides some of the tests were repeated as part of the investigation of the slurry velocity and angle effects. These duplicate test results of wear rates are also included in Table 3. The reproducibility of wear rates is generally quite good.

There is no significant difference in the wear rates among the three cemented carbide grades at low angles of jet impingement; the low binder grade, however, shows better erosion resistance at higher angles. Improved wear resistance with decreasing binder level is the common trend observed in cemented carbides both in laboratory evaluations as well as in service(1,2).

In relation to the cemented tungsten carbides, the ceramics exhibited a range of wear rates. Two ceramics, the chemically vapor deposited (CVD) SiC (Battelle) and the α -SiC (Carborundum), showed significantly lower erosion rates. In particular, the wear rate for the CVD SiC at the 20 degree jet angle was almost an order of magnitude smaller than the wear rates for the cemented carbides. The sintered α -SiC also performed well and its superior wear resistance is especially noticeable at the 50 degree and 90 degree jet angles. The erosive wear rates for the B₄C (Norton Norbide) and the reaction-bonded SiC (Norton Noralide NC-430) were comparable to the wear rates of the cemented carbides. The six grades of cemented TiB₂ (ORNL) had wear

TABLE 3. EROSION WEAR RATES FOR CANDIDATE VALVE MATERIALS
 TEST TEMPERATURE = 343 C, DURATION = 1 HR.
 SLURRY JET VELOCITY = 100 m/second

Target Material	Erosive Wear Depths, at Different Jet Impingement Angles 2 μ m		
	(20°)	(50°)	(90°)
Cemented WC, Kennametal K 701	7	30, 41	55, 55
Cemented WC, Kennametal KZ 701	6	31, 37	56, 56
Cemented WC, Kennametal K 703	9	31, 26	39, 35
B ₄ C, Norton Norbide	11	28	47
CVD SiC, Battelle	0.8	10	10
α -SiC, Carborundum	6	20	26
RB SiC, Norton NC-430	12		
TiB ₂ , Oak Ridge Lab., NT 80C	33		
TiB ₂ , Oak Ridge Lab., NT 85C	42		
TiB ₂ , Oak Ridge Lab., NT 90C	28		
TiB ₂ , Oak Ridge Lab., NT 90G	31		
TiB ₂ , Oak Ridge Lab., NT 85G	26		
TiB ₂ , Oak Ridge Lab., NT 90G	43		
SiC, Hot Pressed, Norton HX 341	70	200*	
Si ₃ N ₄ , Hot Pressed, Norton NC-132		241*	
Al ₂ O ₃ , Lucalox, GE		152*	

*Normalized wear rates from Reference (1).

rates 4-6 times those of the cemented carbides. No consistent correlation was noted with the Ni binder content of the different grades of TiB_2 . The hot-pressed grades of SiC (Norton HX-341) and Si_3N_4 (Norton NC-132), and the sintered alumina (GE Lucalox), exhibited very poor resistance to erosion. The wear rates for the hot-pressed SiC and Si_3N_4 were almost an order of magnitude higher than the rates for the cemented carbides.

In general, there was no major difference in the rankings of the materials in terms of their wear rates at the three different angles of jet impingement. The K703 grade of cemented carbide, the B_4C and the reaction-bonded SiC did show improvements in their rankings at a 90 degree angle of jet impingement. A qualitative rationale for the observed differences in the wear rates of the different types and grades of ceramics, based on characterization of the eroded surfaces by scanning electron microscopy, will be discussed in the next section.

Examination of the erosive wear rates of Table 3 and the mechanical properties of the candidate valve materials listed in Table 1 reveals several interesting features. There is no apparent relation between fracture toughness of the target materials and their wear rates. This is evidenced by the widely differing erosion rates among the ceramics with little difference in the fracture toughness values. This is especially apparent for the generic material, SiC. The CVD and the hot-pressed forms have approximately the same fracture toughness values while their erosion rates differ by two orders of magnitude. Conversely, the cemented carbides, with fracture toughness values approximately three times the ceramic values, exhibit intermediate erosion rates. It can, therefore, be concluded that there is no simple correlation between the bulk fracture toughness of the target materials and their erosive wear rates.

The Vickers microhardnesses listed in Table 1 do show some approximate correlation with the wear rates of Table 3. The erosive wear rates decrease with increasing hardness. To further investigate this dependence on hardness, the wear rates were plotted against the inverse of the microhardness values as shown in Figure 30. Approximate linear relations are noted between erosion rates and hardness values among a limited number of materials. The notable exception in Figure 30 is the hot-pressed B_4C which shows a higher

FIGURE 30. EROSION RATE-MICROHARDNESS CORRELATIONS FOR CANDIDATE VALVE MATERIALS AT JET IMPINGEMENT ANGLES OF 20 and 90 DEGREES

wear rate relative to its hardness. Similarly, the hot-pressed SiC and Si₃N₄, and the sintered alumina (Lucalox) show wear rates much higher than the values expected from the correlation of Figure 30 (these wear rates are not plotted in Figure 30). These deviations may be significant in that they could be indicative of a difference in erosion wear mechanism caused by the material microstructure. This interaction between the material microstructure and the erosive wear mechanisms is discussed in the next section.

IV.3.3 Relationships of Microstructures to Erosion Behavior

The eroded surfaces of selected specimens of the candidate valve materials were examined in a scanning electron microscope to evaluate the mechanisms of material removal and to assess the influence of the material microstructure on the erosive wear process. For purposes of comparison of the different target materials, eroded surfaces obtained under the following reference conditions are presented and discussed: jet angle = 20 degrees, test duration = 3.6×10^3 sec (1 hr), jet velocity 100 m/second*, test temperature = 343 C and a slurry derived from the Wilsonville (SRC) Illinois No. 6 coal product containing 8 percent insoluble solids. Eroded surfaces were also characterized on specimens tested under different conditions, but these are presented and discussed only when they show a significant difference in relation to the reference conditions. In each figure, a low magnification view of the crater produced on the test surface is presented in Part (a) and a higher magnification picture, Part (b), shows details of the damage in the center of the crater. Occasionally the structure of the as-ground surface (Part (c)) is also presented to contrast with the eroded surface.

IV.3.3.1 Cemented Carbides. The eroded surfaces for the three grades of the cemented carbide material, K701, KZ701, and K703, are shown in Figures 31, 32 and 33, respectively. The three grades of the cemented

*The jet velocity is calculated from the volume flow of the slurry through the orifice and the orifice diameter.

(a)

100X

(b)

1500X

FIGURE 31. ERODED SURFACE ON CEMENTED WC (KENNOMETAL K701)

(a)

100X

(b)

1500X

FIGURE 32. ERODED SURFACE ON CEMENTED WC (KENNAMETAL KZ701)

(a)

75X

(b)

1500X

FIGURE 33. ERODED SURFACE ON CEMENTED WC (KENNOMETAL K703)

1500X

FIGURE 33(c). AS-GROUND (600 GRIT) SURFACE ON CEMENTED CARBIDE
(KENNOMETAL K703 GRADE)

carbides show very similar features on the eroded surfaces. This is consistent with the near identical wear rates noted in these tests. In each case the Co/Cr binder is preferentially removed leaving behind protruding WC particles. It is very likely that a dominant mechanism of material removal in these cemented carbides is through "liberation" of whole WC particles following an initial removal of the surrounding binder. Some evidence for this type of carbide grain loss is seen in Figure 33.

Figure 33(c) shows the structure of an as-ground (600 grit) surface of K703 grade cemented carbide. The surface is generally smooth with some evidence of grain pull-out along the deeper grooves. On the whole, the eroded and the ground surfaces are quite different in their appearance.

IV.3.3.2 B₄C (Norton Norbide). In contrast to the cemented carbides, the hot-pressed B₄C exhibits a smooth eroded surface as shown in Figure 34. No grain structure is apparent, thus indicating that the erosion rates are uniform both within the grains and in the grain boundary regions. Another characteristic feature of the eroded B₄C surface is the occurrence of "streaks" in the direction of the slurry jet flow (Figure 34(a)). Careful examination of the eroded surface in Figure 34(b) reveals that these "streaks" are regions of enhanced erosion on the downstream side of surface discontinuities such as pores. Within the streaks, the surface is again extremely smooth. The enhanced erosion forming the streaks is likely due to the higher impingement angle near the pores and also local turbulent flow of the slurry. The smoothness of the eroded surface suggests a ductile mechanism of wear. However, some of the surface discontinuities could have been due to brittle chipping by the larger slurry particles. Reduction of porosity should improve the wear resistance of this material by eliminating these localized sites of enhanced erosion.

IV.3.3.3 CVD SiC (Battelle). The eroded surface on the CVD SiC target tested under the reference conditions is shown in Figure 35. The erosion damage is nonuniform and appears to be localized along circular boundaries (Figure 35(a)). Comparison with Figure 6(a) suggests that these boundaries are the boundaries of the growth regions discussed previously

(a)

50X

(b)

250X

FIGURE 34. ERODED SURFACE IN SINTERED B_4C (NORTON NORBIDE)

(a)

35X

(b)

1500X

FIGURE 35. ERODED SURFACE ON CVD SiC (BATTELLE)

(Section IV.1.3). Since it has been established that these growth region boundaries are associated with the layered structure, the erosion wear of the CVD material must be influenced by this structure. It is suspected that one of the alternating bands is relatively more susceptible to erosion, and experience indicates that it must be the band with the microporosity. Optimization of the process parameters that lead to elimination of the layer structure should improve the wear resistance of the CVD SiC material. The higher magnification picture of the damage site (Figure 35(b)) indicates that there is erosion damage in the interior, but it is less severe as compared to the boundaries.

IV.3.3.4 α -SiC (Carborundum). Figure 36 shows the eroded surface on the α -SiC material. The low magnification picture of the test site (Figure 36(a)) shows "streaks" in the direction of the jet flow. This is similar to the observation on B_4C . Unlike B_4C , however, the grain boundary regions in the α -SiC show preferential erosion, creating the protruding grain surfaces as seen in Figure 36(b). The surfaces of the protruding SiC grains are very smooth suggesting a ductile mechanism of wear as in the case of B_4C . Some cracks are, however, noted in the grain boundary regions. The significance of these cracks and their role in the preferential erosive wear could not be ascertained. Segregated impurities, probably introduced as sintering agents, may have caused the degradation of the grain boundary wear resistance.

IV.3.3.5 Reaction-bonded SiC (Norton Noralide NC-430). The eroded surface on a reaction-bonded SiC target is shown in Figure 37. It is similar to the cemented tungsten carbides in the sense that the phase more susceptible to erosion, in this case the free Si, is preferentially removed. This results in a "mechanically etched" appearance. The large pre-existent SiC grains and the reaction-product SiC are more resistant to erosion and partially "protect" the free Si phase after the initial wear-in of the surface. This may account for the surprisingly strong performance of this material despite the large weight fraction of free Si (10.6 percent). The eroded surfaces of the large SiC grains are smooth (Figure 37(b)), with some streaks associated with surface chipping. These damage observations are similar to the findings of

(a)

75X

(b)

1500X

FIGURE 36. ERODED SURFACE OF α -SiC (CARBORUNDUM)

(a)

75X

(b)

1500X

FIGURE 37. ERODED SURFACE ON REACTION-BONDED SiC (NC430)

Routbort et al (10) who investigated the erosive wear of this material using angular Al_2O_3 particles.

The evaluation of the three forms of SiC, - CVD, sintered α and reaction-bonded, reveals that the intrinsic wear resistance of single crystal SiC is excellent. Deterioration of the wear resistance occurs due to microporosity effects (CVD SiC), grain boundary impurity effects (α -SiC), or a more susceptible phase (free Si in reaction-bonded SiC).

IV.3.3.6 Cemented TiB_2 (Oak Ridge National Laboratory - NT90G).

Cemented TiB_2 combines the erosion characteristics of B_4C and the reaction-bonded SiC; these include the erosion "streaks", the smooth eroded surfaces of TiB_2 grains, and the preferential removal of the Ni binder as seen in Figures 38(a) and 38(b). The intrinsic wear resistance of TiB_2 appears inferior to both B_4C and SiC. This accounts for the overall high erosive wear rates for these titanium borides. The apparent lack of a correlation between the wear rates and the Ni binder content in this material was surprising. It is known, however, that in cemented materials the residual porosity varies with the binder level, and this can complicate the erosion response of the target material.

Figure 38(c) shows the structure of the eroded surface within a "streak". The surface is generally smooth even at these high magnifications (5000X). Some surface protrusions elongated in the direction of the slurry flow (parallel to the streak) are noted within the streaks. Similar features have also been observed on B_4C , but their relation to the wear mechanism is not known.

IV.3.3.7 Hot-Pressed SiC (Norton HX341), Si_3N_4 (NC-132) and Sintered Al_2O_3 (GE Lucalox).

The eroded surfaces of hot-pressed grades of SiC and Si_3N_4 and the sintered alumina were characterized in the course of an earlier EPRI-funded program evaluating the application of advanced materials and fabrication technology to let-down valves⁽¹⁾. The three materials exhibited similar characteristics on their eroded surfaces. Whole grains were apparent, with very little damage noted on the individual grain faces. In the case of the sintered alumina, grain facets were visible. These

(a)

75X

(b)

300X

FIGURE 38. ERODED SURFACE OF CEMENTED TiB_2 (ORNL NT90G)

5000X

(c)

FIGURE 38. STRUCTURE WITHIN AN EROSION "STREAK" IN CEMENTED TiB₂

observations were consistent with the view that erosive wear in these materials occurred by the "plucking" out of whole grains of the material with very little intragrain damage. This accounts for the extremely high wear rates observed in these materials in relation to the other ceramics and the cemented carbides. This interpretation suggests that the wear rates of these materials could be significantly improved by increasing the grain boundary cohesion.

IV.3.4 Influence of Erosion Test Variables on Erosion Rates

A materials development approach, although essential, will not be sufficient by itself to solve the letdown wear problem. It is generally recognized that an integrated materials/design approach will have to be adopted. Valve design or modification will be influenced by material test data on the effects of testing variables such as slurry jet velocity and slurry jet impingement angle on the erosion rates. Investigations of the effects of slurry velocity and impingement angle are also useful to gain insight into the controlling mechanism(s) of erosion since these dependencies are characteristically different for different modes of erosion.

IV.3.4.1 Erosion Rate Dependence on Coal Slurry Jet Velocity. The dependence of the erosion rate on the slurry jet velocity was examined for the three grades of cemented WC and the hot-pressed B₄C. These investigations were conducted with the slurry derived from the Wilsonville SRC product (Illinois No. 6 coal) with a final solids content of 8 percent. The slurry velocities were varied by varying the back pressure in the slurry mixing chamber (Figure 1). The velocities were calculated from the volume displacement rates of the slurry through the jet orifice and the cross-sectional area of the orifice. This is a minimum velocity for the particles. Higher velocities are possible if the hydrogen gas dissolved in the slurry expands rapidly upon leaving the orifice and accelerates the particles. All tests were conducted for a fixed duration of one hour. A reproducible slurry condition was maintained by adopting the periodic slurry rejuvenation procedure.

Since all of the tests in this investigation were based on the same test period - 3.6×10^3 sec (1 hr), the tests at higher slurry velocities utilize larger volumes of slurry than the tests at lower slurry velocities. The measured erosion damage, i.e., the maximum depth of the crater, therefore, reflects both effects of the slurry velocity and the slurry volume. Generally wear rates due to solid particle impact damage are linear functions of the number of impacting particles in the steady state regimes(11). This suggests that wear depths in the present tests should be a linear function of the volume of the slurry. The volumes of the slurry used in the 1 hour tests are directly proportional to the velocity. Thus, the velocity dependence of the erosion rates in the present tests is exaggerated by an additional linear dependence due to slurry volume. This dependence should be accounted for in evaluating the true velocity dependence of erosion rates.

Figures 39 through 43 show log-log plots of the maximum depths of the erosion craters and the coal slurry jet velocities for the three grades of cemented carbides (K701, KZ701 and K703) and the hot-pressed B_4C , respectively. The tests were conducted at a 50 degree jet impingement angle. All the plots show linear relations between erosion depth, d , and the slurry jet velocity, v , on the log-log plots suggesting an empirical relation of the form:

$$d = \bar{A} \cdot v^{\bar{b}} \quad (1)$$

The apparent velocity exponents, b , determined by least-square fit of the data, are shown in each figure. As discussed before, Equation (1) includes an additional linear dependence of the erosion on volume of the slurry. We can rewrite Equation (1) as

$$d = A \cdot v^b (\text{avt}) \quad (2)$$

$$\text{or } d/\text{avt} = A \cdot v^b$$

where

- (avt) = volume of the slurry used in each test
- a = cross section of the orifice
- t = time of the test (1 hour)
- b = true velocity exponent = $\bar{b} - 1$
- A = erosion depth per unit slurry velocity and unit volume of the slurry = $(\bar{A}/at)$

FIGURE 39. MAXIMUM CRATER DEPTHS AS A FUNCTION OF THE COAL SLURRY JET VELOCITY FOR A CEMENTED WC (K701) AT A 50 DEGREE JET IMPINGEMENT ANGLE

The velocity exponent, b , is very nearly the same for the K701 and KZ701 grades of cemented carbide, $b = 2.5$. This is to be expected since they are identical in composition. The K703 grade exhibited a slightly higher value, $b = 3.1$. By contrast, the hot-pressed B_4C showed the smallest exponent, $b = 1.4$.

The erosion depth corresponding to the lowest test value of the slurry jet velocity (30 m/second) for the KZ701 grade cemented carbide showed significant deviation from the linear relationship suggested by the high velocity data. It was, therefore, not included in the evaluation of the slope of the line. Such deviations have been observed in other solid particle impact erosion studies⁽¹¹⁾, and they were attributed to the existence of a threshold velocity for initiation of damage. The other material tested at the lowest velocity, K703 grade cemented carbide (Figure 41), did not show a pronounced deviation from the velocity dependence shown at the higher velocities.

Figures 43 and 44 show the dependence of the maximum erosion depths on the slurry jet velocity for the KZ701 and the K703 grades of cemented WC. These tests were conducted at a 90 degree jet impingement angle, while all the other test conditions were identical to the 50 degree impingement angle tests. It is noted that the velocity exponents at 90 degree jet impingement angle are very nearly equal to the corresponding exponents at the 50 degree angle. This observation suggests that the velocity dependence and the impingement angle dependence of slurry erosion are essentially independent for these two materials. The empirical parameters of velocity dependence, b and A , for the four materials and the two impingement angles are listed in Table 4. The value of A is several orders of magnitude different for the different materials. This is a consequence of the extrapolation of the empirical equation (1) to low velocity (1 m/second), and as such it should not be used to compare material behavior and should only be used to calculate wear depths in the range of measurement.

The least-squares-fit straight lines of Figures 40 and 41 (velocity dependence at 50 degree impingement angle) are also included in the corresponding Figures 43 and 44 as broken lines. This comparison shows that the K703 grade material is relatively insensitive to the impingement angle in this high angle regime (angles >50 degrees) while the KZ701 grade shows more

FIGURE 40. MAXIMUM CRATER DEPTHS AS A FUNCTION OF THE COAL SLURRY JET VELOCITY FOR A CEMENTED WC (KZ701) AT A 50 DEGREE JET IMPINGEMENT ANGLE

FIGURE 41. MAXIMUM CRATER DEPTHS AS A FUNCTION OF THE COAL SLURRY JET VELOCITY FOR A CEMENTED WC (K703) AT A 50 DEGREE JET IMPINGEMENT ANGLE

FIGURE 42. MAXIMUM CRATER DEPTHS AS A FUNCTION OF THE COAL SLURRY JET VELOCITY FOR A BORON CARBIDE AT A 50 DEGREE JET IMPINGEMENT ANGLE

FIGURE 43. MAXIMUM CRATER DEPTHS AS A FUNCTION OF THE COAL SLURRY JET VELOCITY FOR A CEMENTED WC (KZ701) AT A 90 DEGREE JET IMPINGEMENT ANGLE. THE DASHED LINE IS FROM FIGURE 40

FIGURE 44. MAXIMUM CRATER DEPTHS AS A FUNCTION OF THE COAL SLURRY JET VELOCITY FOR A CEMENTED WC (K703) AT A 90 DEGREE JET IMPINGEMENT ANGLE. THE DASHED LINE IS FROM FIGURE 41.

TABLE 4. PARAMETERS CHARACTERIZING VELOCITY DEPENDENCE OF EROSION RATES

$$d = A' v^b$$

TARGET MATERIAL	PARAMETERS			
	Jet Angle = 50°		Jet Angle = 90°	
	b	A	b	A
K701	2.6	9.7×10^4		
KZ701	2.5	1.3×10^{-3}	2.5	2.8×10^{-3}
K703	3.1	1.3×10^{-4}	2.9	2.7×10^{-4}
B ₄ C	1.4	2.8×10^{-1}		

* Parameter b is dimensionless. A has the units: $\frac{(\mu\text{m})}{(\text{m/second})^b (\text{m})^3}$
 Erosion depth, d, is in μm .

sensitivity. This is consistent with the results obtained in the material screening studies and reported in Table 3. The wear rates for the K701 and KZ701 grades show more sensitivity to the impingement angle than the K703 grade in the high angle regime. More extensive data on the angle dependence of erosion rates are presented and discussed in the following section.

IV.3.4.2 Erosion Rate Dependence on Slurry Jet Impingement Angle (SRC-1 Slurry). The effects of the slurry jet impingement angle on the erosion rates were examined for the three grades of cemented WC (K701, KZ701 and K703) and the hot-pressed boron carbide (Norton Norbide). The tests were conducted at a fixed jet velocity of 100 m/second using the slurry derived from the Wilsonville SRC product at 8 percent solids concentration. All of the individual tests were again of 3.6×10^3 sec (1 hr) duration.

Figures 45 through 48 show the dependence of erosion depths on the jet impingement angle for the three grades of cemented carbide and the B₄C. In each figure, the points are the measured crater depths from individual test specimens. The broken line in each case is the visual best fitting curve.

FIGURE 45. THE EFFECT OF THE SLURRY JET IMPINGMENT ANGLE ON THE EROSION RATES IN A CEMENTED WC (KENNAMETAL K701)

FIGURE 46. THE EFFECT OF THE SLURRY JET IMPINGMENT ANGLE ON THE EROSION RATES IN A CEMENTED WC (KENNAMETAL KZ701)

FIGURE 47. THE EFFECT OF THE SLURRY JET IMPINGMENT ANGLE ON THE EROSION RATES IN A CEMENTED WC (KENNAMETAL K703)

FIGURE 48. THE EFFECT OF THE SLURRY JET IMPINGMENT ANGLE ON THE EROSION RATES IN SINTERED B_4C (NORTON NORBIDE)

There is no qualitative difference in the angular dependence of the erosion rates among the four materials. The erosion rate is a maximum at normal incidence $\theta = 90$ degrees, decreases slowly with decreasing impingement angle until θ is approximately 40 degrees, then drops rapidly with further decrease in the angle. There are some noticeable trend differences among the four materials. As discussed before, the K703 grade cemented carbide shows the minimum sensitivity to angle at high angles, while the B_4C is the most sensitive in this regime. The K701 and K703 grades of cemented carbides show intermediate behavior.

The angular dependence of the erosion rates observed for the four materials suggested the possibility that only the vector component of the jet velocity resolved normal to the target surface might be important to the erosion process. If this were the case, the tests at different angles would then be essentially tests at different velocities given by the function

$$v_{\theta} = v_{90} \sin \theta \quad (4)$$

where v_{θ} = velocity component normal to the target surface in a test at an impingement angle θ (θ is measured with respect to the target surface)

v_{90} = velocity for the jet normal to the target surface, i.e., the constant velocity maintained in the tests (100 m/second).

Following the above argument, it then follows that the angular dependence of the erosion depth should follow the velocity dependence of the normal component:

$$d_{\theta} = d_{90} (\sin \theta)^b \quad (5)$$

where d_{θ} = calculated erosion depth at an impingement angle

d_{90} = erosion depth at normal impingement, i.e., $\theta = 90$ degrees.

Curves corresponding to Equation (5) were calculated and plotted in Figures 45 through 48 using the measured velocity exponents, b , listed in Table 4, and the experimentally-measured values of d_{90} . These curves are shown as full lines. As seen in the figures, Equation (5) is a reasonable fit to the data of B_4C . The equation significantly underestimates the erosion rates of the K703 grade material at intermediate angles. K701 and KZ701 grades of the cemented carbide represent an intermediate situation. It is interesting to note that the deviation of the experimental points from the predicted curves (Equation (5)) is in a direction such that a lower value of b would improve the agreement.

IV.3.4.3 Evaluation of Impingement Angle Dependence of Erosion Rates Using Slurries Prepared from H-Coal Products. A limited number of tests were also conducted to investigate the impingement angle dependency of erosion rates using slurries prepared from the H-Coal products derived from Wyodak and Illinois No. 6 coals. Figure 49 shows the erosion rates for the cemented WC (KZ701) at three impingement angles using a Wyodak slurry at 13.3 percent concentration of suspended solids. Freshly prepared slurry was used in the tests at 20 and 90 degrees while the slurry used in the 50 degree test was the used slurry from the 90 degree test. As in the case of the slurry prepared from the Wilsonville SRC product (Figure 46), erosion depth decreases monotonically with decreasing impingement angle. The drop in the erosion rate with impingement angle appears at first glance to be more linear for the Wyodak slurry. But if the erosion rate at 50 degrees is normalized to a fresh state of the slurry using the data of Figure 27, the trend in the angle dependence of erosion rates is very similar for both the slurries. The absolute wear rates with the Wyodak slurry (Figure 49) are, however, significantly higher than the wear rates with the SRC-Illinois No. 6 slurry (Figure 46). This is due to both the higher concentration of the suspended solids in the Wyodak slurry (13.3 percent versus 8 percent for Wilsonville slurry) as well as the fresh condition of the slurry in the Wyodak series.

Figure 50 shows erosion wear depths as a function of the jet impingement angle for the KZ701 grade cemented carbide with a slurry prepared from the Illinois No. 6 coal product from H-Coal at 8.5 percent solids

FIGURE 49. THE EFFECT OF THE SLURRY JET IMPINGMENT ANGLE ON THE EROSION RATES IN A CEMENTED WC (KZ701) USING THE SLURRY PREPARED FROM WYODAK COAL (H-COAL PRODUCT)

FIGURE 50. THE EFFECT OF THE SLURRY JET IMPINGMENT ANGLE ON THE EROSION RATES OF A CEMENTED WC (KZ701) USING THE SLURRY PREPARED FROM ILLINOIS NO. 6 COAL (H-COAL PRODUCT)

concentration. The tests at 20, 50, and 90 degrees were run consecutively starting with a fresh slurry. An attempt was again made to normalize the wear rates with the used slurry to the values that would be representative of a fresh slurry using the slurry aging data of Figure 28. The qualitative trend in the variation of erosion depth with impingement angle for this slurry is similar to the trends observed with the Wilsonville and Wyodak slurries.

IV.4 Simulated Slurry Development

A need exists to establish a standardized slurry test method which will permit a direct comparison of results between laboratories, and provide a reference point for comparison of the erosivity of different slurries. An important aspect of the slurry erosion tests is that of the type of erodent used. Although a coal-derived, reconstituted slurry of the type used in this and previous programs provides very meaningful data, results may differ if the coal source or pilot plant source, or operating conditions are changed. A synthesized slurry using an accurately characterizable erodent and carrier fluid, which preferably involves reduced levels of health risks and handling problems than the coal-derived slurries, would be an important step towards the standardization of a test. The intent of this task was to examine the potential of synthesizing a slurry which has erosion properties similar to the coal-derived slurries.

IV.4.1 Selection and Synthesis of a Simulated Slurry

The ideal constituents of a synthesized slurry should be readily available and should present a minimum of handling and operating problems. One of the chief objections to the reconstituted coal-derived slurries currently used is the hazardous nature of the anthracene oil carrier fluid. Further, the source of the erosive solids is solidified, unfiltered product from the pilot plants, which is difficult and hazardous to handle. A search for readily available and more easily handled liquids for use as a replacement carrier suggested that, in fact, water might provide a simple choice. Water exhibits, at room temperature, the same viscosity as that measured for the

pilot plant slurry at the plant stream temperature of 343 C (650 F) (Table 5), so that with water it might be possible to run the erosion tests at room temperature.

The search for a suitable replacement erodent was initially directed towards materials having compositions which reflected the major constituents of the insoluble particles in the coal-derived slurries, that is Si, Al, Ca, or Fe oxides or sulfates/sulfides. Samples of silica flour, fused silica, glass spheres, alumina, dolomite, calcium sulfate, and flyash were examined by scanning electron microscopy and by Coulter Counter analysis. Unfortunately, of the samples examined, only the dolomite contained particles of the desired shape or size distribution. Attempts to crush the silica and calcium sulfate samples to produce particles of a more desirable shape and size were only partially successful, in that a prohibitive amount of sieving and blending were required to provide sufficient sample of the desired size range. The dolomite sample, however, exhibited an acceptable particle size distribution and shape as shown in Figures 51 and 52. Compared to the size distribution of the reconstituted SRC-1 slurry, the dolomite particles size ranges over a slightly smaller range (maximum size of 38 μm versus 62 μm), and has fewer particles in the sizes greater than 12 μm . Even though the composition of dolomite $[\text{CaMg}(\text{CO}_3)_2]$ is not a good representation of the insoluble solids from the coal-derived slurries, and therefore, the different physical characteristics of the particles (such as hardness) will probably result in a different degree of erosivity, it was decided to prepare a slurry based on this material for evaluation.

IV.4.2 Erosion Tests with the Simulated Slurry

Two erosion tests were conducted with the simulated slurry at a dolomite concentration of 11 weight percent in water. Tests were run on the KZ701 grade cemented carbide material at 90 degrees jet impingement angle for durations of one hour each. The slurry velocity in these tests was 199 m/second. The higher velocity in these tests was apparently the result of the lower viscosity of the simulated slurry, as compared to the coal slurry, causing a higher volume flow for the same pressure drop across the orifice

TABLE 5. PROPERTIES OF SEVERAL LIQUIDS

Liquid	Density (Mg/m ³) at 60F	Viscosity (cp) at Temperature, °F							REF
		32	61	68	104	158	212	650	
Anthracene oil	1.04-1.10			12				1.0*	A, B
Light machine oil	-		114		34		5		B
Olive oil	0.92			84	36	12			B
Kerosene	0.82			2.4					B, C
Hexane	-	0.40	0.37	0.33	0.27				B, C
N-octane	-	0.71	0.57	0.54	0.43				B, C
Ethanol	0.79	1.8	-	1.2	0.8	0.5	-	-	B, C
Water	1.0	1.8	1.1	1.0	0.65	0.40	0.28	-	D

*Viscosity of actual slurry, which contains 12 percent solids

A Personal communication, SRC-1 plant personnel 1980

B CRC Handbook of Chemistry and Physics (1972)

C J. H. Perry, Chemical Engineer' Handbook, McGraw-Hill (1950)

D National Bureau of Standards

**FIGURE 51. TYPICAL VIEW OF DOLOMITE PARTICLES
(AVERAGE PARTICLE SIZE 10 μm)**

FIGURE 52. CHANGE IN PARTICLE SIZE DISTRIBUTION OF DOLOMITE-WATER SLURRY WITH TIME OF USE (COULTER-COUNTER ANALYSIS, SCHIFF DOLOMITE)

length as that used with the coal-derived slurries. It should be noted that when the rig is operated with the anthracene oil-coal solids slurries, the main body of the slurry is heated in the immediate vicinity of the orifice in the chamber head, and so only attains the lower viscosity value in this location.

A wear depth of 5 μm was obtained in the first test which used the freshly-prepared slurry. The second test, which used the same slurry as the first one, yielded a wear depth of 2.8 μm . Both the values are considerably less than the typical wear rates obtained with the coal slurries under similar test conditions (50-60 μm). Examination of the particle size distribution shows very little change with time (Figure 52), suggesting, in fact, very acceptable behavior.

The reasons for the lower erosion rates, compared to the coal-derived slurry, are probably less important at this stage than the causes of the lack of reproducibility of the tests. The most likely source of error appears to be a lack of uniformity of the particle loading in the slurry reaching the specimen. Examination of the interior passages of the erosion rig after test indicated that a significant amount of dolomite had settled out, which suggests that there was insufficient agitation of the water to maintain the solids in suspension. With the anthracene-based slurry, this problem was apparently alleviated by the higher viscosity of the cold fluid.

Preliminary trials were made with several available light oils, at room temperature, with a view to taking advantage of the large effect of temperature on the viscosity of these materials, as suggested in Table 5. Heating of these oils to 98-120 C (200-250 F) to reduce the viscosity would not present any practical problem, provided the oils did not degrade. This screening was carried out by suspending dolomite particles in the oils by stirring, and observing the rate of settling out. A silicone oil (Dow Corning No. 705) showed good characteristics, but proved to be too expensive for further consideration.

Alternate solutions to the loss of suspension problem with the water-based slurries could probably be achieved by modification of the erosion rig to provide stirring of the liquid in the pressure vessel and specimen chamber, and higher flow velocities in the return lines.

IV.5 Service Trials

IV.5.1 Selection of Materials

Reaction-bonded SiC (Norton Noralide, NC-430) and hot-pressed B₄C (Norton Norbide) were the two commercial ceramic materials selected for service trials in the H-Coal process development unit (PDU) in Lawrenceville, New Jersey. These materials were selected because of their good performance in the laboratory erosion tests (Table 3) and their availability in the required size for fabricating the valve components. Both materials were obtained as flat plates approximately 15.2 x 2.5 x 1 cm (6 x 1 x 0.4 inches). The SiC material was somewhat nonuniform through the thickness of the sheet, having a lower Si content and a somewhat larger grain size in the center thickness region. No variation in the microstructure of B₄C was observed.

Valve stems for the service trials were machined from each material, the SiC and B₄C. Round blanks, nominal 5.5 cm (2.25 inches) long by 0.65 cm (0.255 inch) diameter were sent to H-Coal. H-Coal then final-machined these blanks into the required configuration for their valve stems.

IV.5.2 Service Conditions and Results

Due to the unexpected difficulties encountered in the final machining of the stems and in assembling the valves, only one ceramic stem, made of the reaction-bonded SiC, was actually tested in the service trial at the H-Coal PDU. This stem was inserted into a valve in the first stage system that lets-down the process stream from 18.6 to 8.6 MPa (2700 to 1250 psig) at about 371 C (700 F). The process stream was derived from the Wyodak coal with 28-30 weight percent undissolved solids and a nominal ash content of 13 weight percent. The test ran for 6.39×10^5 sec (178 hr) and was terminated because level and pressure control in the hot separator became erratic. The life of a valve with a standard cemented WC trim under similar test conditions was about 2.59×10^6 sec (720 hr). On disassembling the valve it was discovered that the SiC stem had fractured at two locations; one of the fractures occurred at approximately the midlength of the stem and stainless steel head. Figure 53

FIGURE 53. LET-DOWN VALVE STEM SERVICE TESTED IN THE H-COAL PDU. ARROWS INDICATE THE LOCATIONS OF THE FRACTURES ON THE SIC STEM.

FIGURE 54. CEMENTED CARBIDE VALVE SEAT USED IN THE SERVICE TRIAL IN THE H-COAL PDU. NOTE THE WEAR PATTERN ON THE INSIDE SURFACE OF THE BORE HOLE.

shows the three pieces of the stem unit reassembled to approximately their original configuration. The arrows indicate the locations of the two fractures. These fractures, however, were not directly responsible for the failure of the valve. If the fractures had occurred during the trial, the fragments of the stem would have been lost in the downstream material. The fact that they were found in the valve unit following disassembly indicates that the breakage must have occurred during disassembly.

Figure 54 shows the cemented WC valve seat after the service trial. Although the length of the trial was short and the seat was new prior to the test run, it shows a significant wear pattern on the inside surface of the bore hole.

IV.5.3. Analysis of Material After Service

A post-mortem failure analysis was conducted on both the SiC stem and the cemented carbide valve seat. This included characterization of the wear surface by scanning electron microscopy and measurements of the wear depth using either a Talysurf surface profilometer or a Leitz-Strassman Optical Measuring Unit.

IV.5.3.1 SiC Stem. Examination of the flat tapered surface on the SiC stem in a scanning electron microscope at low magnification revealed that maximum wear had occurred at the base of the taper where the flat surface meets the cylindrical surface. Figure 55 shows this region of maximum wear. The eroded surface shows grooves in the direction of the slurry flow (parallel to the stem axis). Not surprisingly, one of the fractures occurred in this region presumably because of the stress concentration effect of the surface discontinuities. To obtain a quantitative measure of the wear experienced by the SiC stem, a Talysurf surface trace was made in a transverse direction (perpendicular to the stem axis) along a surface line close to the fracture surface as indicated by the arrows in Figure 55(a). This trace is shown in Figure 56. The difference in the scales used for the horizontal and the vertical dimensions tends to exaggerate the wear profile. The surface peaks at the two extremes, indicated by arrows, are the edges where the flat surface

(a)

12X

(b)

25X

FIGURE 55. ERODED SURFACE ON SiC STEM SERVICE TESTED IN THE H-COAL PDU (ARROW IN FIGURE (a) INDICATES THE LINE ALONG WHICH SURFACE PROFILE WAS TRACED)

FIGURE 56. TALYSURF TRACE ON THE ERODED SURFACE OF THE SiC VALVE STEM.
THE TRACE DIRECTION IS NORMAL TO THE STEM AXIS (FIGURE 34a)

meets the cylindrical surface. If these are taken as reference points, the maximum wear depth in Figure 56 is 160 μm . The average wear rate for the service trial run is, therefore, less than 2.8×10^{-4} $\mu\text{m}/\text{sec}$ (1 $\mu\text{m}/\text{hour}$). This value is very much smaller than the wear rates observed in the laboratory tests for the same material (see Table 3). This may either be due to less severe erosion conditions (slurry velocity and angle of impingement) in the let-down valve in the H-Coal PDU or due to a lower concentration of suspended solids in the process stream. It is known that the usual solids content in the PDU slurry is significantly higher than the content used in the laboratory tests, i.e., 28 to 30 percent versus 13 percent. This factor would tend to cause higher erosion rates. However, information on the critical geometric and velocity variables characterizing the erosion conditions in the H-coal let-down valve is currently lacking, and no definitive conclusions can be made at this stage.

Figure 57 shows the structure of the eroded surface of the SiC trim. The microstructural features are very similar to those found in the laboratory material screening studies (Figure 37). Free Si is preferentially eroded, leaving behind protruding grains of SiC. Some of the large pre-existent grains of SiC do show some brittle cracking (Figure 57(b)) in addition to the commonly observed smooth eroded surface. This feature was not evident in the laboratory study. This may be due to the large overall cumulative wear in the trim specimen. Grains that are worn down sufficiently by the ductile process (which produces the smooth surface) may be vulnerable to cracking when they become very thin.

IV.5.3.2 Cemented Carbide Valve Seat. Characterization of the erosion damage on the valve seat was more difficult because of the location of the damage site on an internal diameter. The Talysurf profilometer could not be employed to make a quantitative measure of the erosion depth. A Leitz-Strassman Optical Measuring machine was used to optically measure the wear depth. The wear pattern, as seen along the axis of the bore hole, is shown in Figure 58(a). It is reasonable to assume that this groove in the seat corresponds to the location of the tapered surface on the valve stem. The accompanying schematic sketch, Figure 58(b), illustrates the measure of wear as determined by the Leitz-Strassman unit. The maximum increment in the

(a)

100X

(b)

500X

FIGURE 57. STRUCTURE OF THE ERODED SURFACE ON THE SiC STEM FOLLOWING THE SERVICE TRIAL IN THE H-COAL PDU.

(a)

(b)

FIGURE 58. (a) ERODED CEMENTED WC VALVE SEAT USED WITH THE SiC VALVE STEM AFTER SERVICE IN THE H COAL PDU; THE VALVE SEAT AS SEEN ALONG THE AXIS OF THE BORE HOLE

(b) A SCHEMATIC SKETCH ILLUSTRATING THE WEAR DEPTH

internal diameter of the bore hole, measured by this technique, was 364 μm . This corresponds to an average wear rate of roughly $5.6 \times 10^{-4} \mu\text{m}/\text{sec}$ ($2 \mu\text{m}/\text{hr}$) during the service trial. This value is also considerably smaller than the wear rates observed in the laboratory evaluations of the cemented carbide (Table 3). It is significant, though, that under nearly identical conditions, the SiC trim wore at approximately half the rate of the WC valve seat.

Figure 59 shows the site (Figure 59(a)) and the structure of the eroded surface (Figure 59(b)) on the cemented carbide valve seat. This structure is very typical of the cemented carbides; WC grains appear in relief due to the preferential loss of the binder.

IV.5.3.3 Preliminary Conclusions From Failure Analysis. No definitive conclusions can be given as to the cause(s) for the short life of the let-down valve employing the SiC stem. The wear on the tapered flat surface was not as great as one normally encounters in a conventional stem. Figure 60, for example, compares typical wear on a cemented WC stem (Figure 60(b)). Both the stems were tested in similar let-down valve conditions at the H-Coal PDU. Although the length of service for the cemented carbide was roughly twice that for the ceramic, the total wear on the carbide is orders of magnitude greater. Thus, the cemented carbide lasted longer even though it had experienced much greater wear. The reason for this becomes apparent when we compare the wear patterns on the tapered surfaces for the two materials. In the case of the cemented carbide stem, the area of the tapered flat was less, and the wear pattern initiated almost at the end of the stem. This suggests that the control position of the stem in the valve seat gradually changed with wear moving up toward the stem head. The SiC stem, on the other hand, shows distinctly different features. The flat area on the stem is much larger, suggesting that there was too much taper. As a result, wear initiated almost at the end of the taper (toward the stem head). There was no margin for further control as wear progressed. In addition, the wear on the valve seat produced a groove which could not be closed by lowering the valve stem, and probably contributed to the loss of process control. It is not known whether the wear in this valve seat is excessive for the length of

(a)

10X

(b)

1500X

FIGURE 59. (a) ERODED SURFACE ON THE CEMENTED WC VALVE SEAT;
VIEW OF THE ERODED PATH IN THE VALVE SEAT

(b) STRUCTURE OF THE ERODED SURFACE ON THE CEMENTED
CARBIDE VALVE SEAT AS INDICATED BY ARROW IN (a)

3X

(a)

3X

(b)

FIGURE 60. COMPARISON OF A CEMENTED WC VALVE STEM AND THE SiC VALVE STEM AFTER SERVICE EXPOSURES

- (a) CEMENTED WC STEM SHOWING TYPICAL WEAR FROM NOMINAL 14 DAYS OF OPERATION
- (b) REACTION-BONDED SiC STEM SHOWING WEAR FROM NOMINAL 7.4 DAYS OF OPERATION

service (6.39×10^5 sec or 178 hr) compared to other cemented carbide seats matched with cemented carbide stems. The seat may have been of poor quality or the harder SiC stems may have caused a greater than usual deflection of slurry onto the valve seat.

On balance, the results were very encouraging. The failure of the ceramic stem can be tentatively attributed to the orientation and position of the ground, flat control surface, and possibly also to unusually heavy wear on the valve seat relative to the stem.

V. GENERAL DISCUSSION

V.1 Slurries

V.1.1 Coal-derived Slurries

There has been considerable interest during this and previous programs⁽¹⁻³⁾ in the erosive nature of the reconstituted coal-derived slurries. It was found in earlier work⁽²⁾ that, in the typical duration of the laboratory erosion runs, up to five hours, no observable corrosion attack occurred of materials such as the cemented tungsten carbides. Nor did any measurable erosion of these materials result from the use of particle-free anthracene oil in a typical test run. Clearly, the degradation observed, at least in the laboratory tests, is produced by the suspended, insoluble particles in the process product.

The attempts in this program to categorize the erodents have been fraught with difficulties, not the least of which was concerned with the separation of clean particles suitable for analysis from the complex mixture of hydrocarbons in the carrier fluid. Essentially, the insoluble particles comprised, in descending order of size: pieces of undissolved carbon which could be angular with sharp edges; particles rich in Si and Al, related to the ash content of the coal; fossilized plant forms which appeared to be friable; and small, sharp-edged particles rich in heavy metals such as Fe and Cu, and probably related to the pyrites content of the coal. Differences in relative distribution of these particle types undoubtedly exist between different coals

and processing routes, but a definitive classification was beyond the means and scope of this program. The sharp edges on the irregularly-shaped larger particles, and the abundance of small particles, however, indicate that these solids are certainly capable of causing the damage observed.

The difficulties in separating suitably clean solids from these slurries also caused difficulties in obtaining proper size analyses using conventional techniques. The method which proved to provide results acceptably consistent with the laborious optical techniques involved a laser particle size analysis, using the solidified liquid product dissolved directly in pyridine. While this technique would not differentiate between agglomerates, such as interlocked small particles or small particles embedded in larger ones, and large single particles, the resulting size distributions were close to those obtained by the optical line intercept methods, and were far more convenient to make. We considered this method to be the best obtainable under the conditions and to be adequate for our purposes.

Comparisons of the size distributions of the insoluble particles from two coals processed by SRC-1 and three from H-Coal showed them to be remarkably similar. The average particle size from all five sources ranged from 5.4 to 8.0 μm , and the maximum particle size was around 170 μm for all cases, except that for the Wyodak coal from H-Coal, which was noticeably smaller, at 53 μm . Comparison of the samples of Illinois No. 6 coal processed in each pilot plant showed some differences, although of a fairly minor nature. Essentially, the particle size distribution of the SRC-1 product was skewed slightly towards the finer ($<4.7 \mu\text{m}$) sizes. However, neither this difference nor the small difference in particle content in the slurries used for erosion testing, provide a fully satisfactory explanation of the factor of four difference in erosion rates observed for the Z701 target material eroded in the Illinois No. 6-derived slurries. (Figures 26 and 28).

The investigation of the change in slurry particle size with time of operation of the laboratory test loop showed that, for two different slurries, there was an initial trend to a slight reduction in particle size, with some continuing comminution throughout the duration of the tests. The extent of the size reduction can be judged from the fact that the maximum observed change in the average particle size for the SRC-1 Illinois No. 6-derived

slurry (by Coulter counter analysis) was from 11 to 7.8 μm over 9.6×10^3 sec (2.67 hr); even less change was observed for the H-coal/Wyodak-derived slurry. Any change to a smaller average particle size means an increase in the particle loading, or number of impacts per unit area in unit time. These, in turn, imply a possible change in the erosion rate, depending on the efficiency of material removal of the different particle sizes. Perhaps more important in explaining the high initial erosion rates for fresh slurry are the observations that some particle types, especially the fossilized cellular ones, were quickly broken into smaller pieces during the first hour of use. The exposed sharp fracture surfaces might be expected to contribute to the erosive nature of the slurry until they became rounded or removed. The general asymptotic decrease in erosivity of the slurries with time is an expected trend as the sharp corners and edges are exhausted.

V.1.2 Synthetic Slurry

The limited results obtained with a synthetic slurry provided encouragement that this concept could be made to work. Although the erodent medium of dolomite was not ideal, since it neither properly represented any of the constituents of the coal-derived slurries, nor comprised very easily-characterized particles, it is a readily available, consistent product with a desirable particle size range, and acceptable aging characteristics in the erosion test. The erosion rates using dolomite were less than with a coal-derived slurry, which was not unexpected. Such discrepancies in absolute erosion rates are unlikely to be important as long as the erosion mechanisms are similar and correlations between the erosion behavior of candidate materials in the laboratory using the synthetic slurry and that observed in service can be made. This is the primary objective of laboratory testing of candidate materials.

For some phases of materials development, an understanding of the mode in which a material is destroyed by erosion is necessary. A synthetic slurry would be ideal for these purposes, since larger particles than found in coal-derived slurries could be used initially to allow the damage by individual impacts to be analyzed.

V.2.1 Erosive Wear Mechanisms in Cemented Carbides and Ceramics

Examination of the eroded surfaces of the candidate valve materials in the scanning electron microscope and comparison of their features with the material microstructures provided valuable insight into the underlying material removal processes in coal slurry erosion. Three distinct modes of erosive wear could be identified among the target materials.

- (1) Preferential removal of one phase in a multiphase microstructure.
- (2) Uniform wear of the microstructure.
- (3) Erosive wear through intergranular decohesion.

The cemented WC (K701, KZ701, and K703), the cemented TiB_2 , and the reaction-bonded SiC (NC-430) clearly exhibit the first type of wear. The metal binders, Co-Cr for WC and Ni for TiB_2 , and the excess free Si in the reaction-bonded SiC are the softer phases preferentially eroded by the coal slurry. The mechanism of wear is uncertain, but in the case of the metal binders, it is likely to involve ductile cutting. In the cemented WC, the removal of the binder and the undercutting of the carbide phase results in liberation of the whole carbide grains and thus directly controls the wear rates. This process is aided by the small size of the WC grains. By comparison, in the reaction-bonded SiC, after an initial loss of the free Si, the material becomes more erosion resistant because the large SiC grains "protect" the free Si. The wear rate is increasingly controlled by the wear of the SiC grains which are intrinsically more wear resistant. Also, there appears to be better intercarbide bonding in the SiC system than in the cemented WC. This coupled with the larger grain size prevents the loss of whole SiC grains. These effects account for the overall good performance of the reaction-bonded product even though it has about 11 weight percent free Si. The smooth surface of the large prereaction SiC grains (Figure 37) suggests a ductile mechanism of wear for the matrix. The cemented TiB_2 is qualitatively similar to the reaction-bonded SiC in that after the initial loss of the Ni binder, the wear rate of the material is increasingly controlled by the wear rate of the TiB_2 phase. However, the higher wear rate indicates that the intrinsic wear rate of the TiB_2 is higher than that of the SiC. The residual porosity in the cemented TiB_2 also contributes to enhanced

localized erosion as evidenced by the streaks on the eroded surface. These characteristics deteriorate the overall performance of the TiB_2 system.

The erosive wear of the CVD SiC can be approximately classified in the first category, even though it is chemically homogeneous. In processing the material, the cyclic variation in the deposition conditions leads to alternating layers that differ in physical structure, size of the microcrystallites and distribution of microporosity (Figure 6d). It is suspected that the localized microporosity causes the deterioration of the local wear resistance which in turn increases the overall wear rates. There is potential for significant improvement in the erosive wear resistance of the CVD SiC by careful control of the deposition conditions and the resulting structure of the deposited material.

Hot-pressed B_4C (Norton Norbide) is typical of the materials that exhibit the second type of wear. The grain faces and the grain boundaries erode at approximately the same rate. As a result the eroded surface is smooth even at high magnifications. This suggests that the dominant erosion mechanism is ductile in nature. This erosion mechanism would be unexpected, for B_4C , because it is extremely hard and brittle (low fracture toughness) and chips easily while polishing. The influence of the pores in increasing local erosion rates due to increased angle of impingement and turbulence effects of the jet is clearly evident in B_4C (Figure 34b) in the form of streaks. Similar features were noted in TiB_2 and ZrB_2 .⁽¹⁾ The wear rates in all of these materials should decrease with decreasing residual porosity.

The hot-pressed grades of SiC (Norton HX 341) and Si_3N_4 (Norton NC 132) and the sintered alumina (GE Lucalox) erode by intergranular cracking and loss of whole grains. This accounts for the high erosive wear rates observed in these materials. The grain boundary failure in the hot-pressed Si_3N_4 may be related to the glassy magnesium silicate-based intergranular phase. The presence of this amorphous phase at grain boundaries in MgO-fluxed hot-pressed Si_3N_4 has been confirmed by high-resolution transmission electron microscopy⁽¹²⁾. Al_2O_3 is a common additive in commercial hot-pressed grades of SiC and is retained as a grain boundary phase.⁽¹³⁾ In

both hot-pressed Si_3N_4 and SiC the grain-boundary phases degrade and control the high-temperature strength, creep, and slow crack growth properties. They may also be responsible for the deterioration of the ambient erosion properties of these materials. In sintered Al_2O_3 (GE Lucalox), MgO is added as a sintering aid. The segregation of MgO to the grain boundaries in Al_2O_3 is a subject of much controversy⁽¹⁴⁾; but commercial aluminas with MgO dopant levels >0.1 weight percent (as in Lucalox) do contain a rather large area fraction of spinel (MgAl_2O_4) precipitate particles at the grain boundaries^(14,15). These precipitate particles may provide subsurface crack nuclei at the grain boundaries that grow during impact erosion and give the appearance of intergranular cracking.

The sintered α - SiC exhibits erosive wear characteristics of both modes (1) and (2). The eroded surface is not uniform as in B_4C because the grain boundary regions erode at a slightly higher rate than the grains. But there is no distinct second phase as in reaction-bonded SiC . The residual porosity also tends to make the eroded surface nonuniform due to local enhancements of erosion rates.

V.2.2. Comparison of Coal Slurry Erosion Characteristics With Particle Impact Damage Erosion Models

Several key experiments conducted at Battelle's Columbus Laboratories in earlier programs⁽¹⁾ have demonstrated that the coal slurry erosive damage obtained on the target materials is unambiguously associated with the suspended particles in the slurry stream. These observations require that the characteristics of coal slurry erosion be examined in the light of the erosion models based on particle impact. By necessity, this comparison will be qualitative firstly because the analytical models assume idealized conditions such as targets with uniform physical and mechanical properties unaffected by local microstructural variations, and also uniform size, shape, velocity and physical properties of the impacting particles. By contrast, experiments conducted in the coal slurry erosion studies involved target materials with complex multiphase microstructures and suspended slurry particles of variable sizes, shapes, and physical and mechanical properties. Secondly, erosion

models are based on isolated single particle events without considering material damage effects, while experiments on real materials measure cumulative damage from numerous particle/material impacts. In spite of these difficulties, particle impact damage models have been successful in explaining the dependence of erosion rates on target material properties such as hardness (H) and fracture toughness (K_{IC}), and critical particle impingement variables such as angle and velocity of impingement. These predictions are briefly reviewed in the following section and compared with the results obtained in the coal slurry erosion tests.

V.2.2.1 Particle Impact Damage Erosion Models. Erosion models based on particle impact damage concepts can be classified into three categories:

- (a) Ductile (deformation) cutting models
- (b) Brittle chipping models
- (c) Elastic-plastic indentation fracture models.

A variety of models have been developed in each category using similar concepts. Table 6 lists the predictions of three representative erosion models, one from each category. These predictions are expressed as the dependence of the erosion rate (i.e., the volume of the target material removed per impacting particle), on the velocity, impingement angle and size of the particle, and the mechanical properties of the target materials.

Finney⁽¹⁶⁾ proposed a ductile cutting model of erosion in which the volume of the material eroded was equated to the volume covered by the particle trajectory in and out of a plastically-responding target (Model I in Table 6). The model predicts a velocity exponent of 2, a complex angular dependence that predicts a maximum erosion rate at an intermediate angle ($\theta = 20$ degrees) and an inverse dependence on the dynamic flow stress of the target which was equated to the hardness. The model was very successful in predicting the maximum erosion rates observed in metals at small angles and an inverse hardness dependence of the erosion rates⁽¹¹⁾. Velocity exponents greater than 2 have been observed for ductile materials, however, and these have been explained by recent refinements of the model⁽¹⁷⁾.

Sheldon and Finney⁽¹⁸⁾ demonstrated that at high impact loads (i.e., high particle velocities, large particle mass) a ductile-brittle

TABLE 6. PREDICTIONS OF EROSION MODELS.

Dependence of the Volume of target material Removed per Impacting particle (V) on Particle Velocity (v), Particle Impact Angle (θ), Particle Size (r_p), and the target/particle physical properties, Hardness (H), Fracture Toughness (K_c), Density (ρ_p), Modulus (E), etc.

Erosion Model	Velocity Dependence $V \propto (v)^b$	Impingement Angle Dependence $V \propto f(\theta)$	Particle Size Dependence $V \propto (r_p)^a$	Physical Properties $V \propto F(H, K_c, \rho_p, E)$	Equation
I. Ductile Cutting Finney (1958) Reference (16)	$b = 2$	$f(\theta) = \sin 2\theta - 3 \sin^2 \theta$ for $\tan \theta < 1/3$ $f(\theta) = \frac{\cos^2 \theta}{3}$ for $\tan \theta \geq 1/3$	$a = 3$	$V \propto \frac{\rho_p}{H}$	$V = k_1 \frac{\rho_p M v^2}{H} f(\theta)$ M: mass of the particle k_1 : constant depending upon contact parameters
II. Brittle Cutting Sheldon-Finney (1966) Reference (19)	$b = \frac{2.4m}{m-2}$ m: Weibull Modulus $b = 2.4$ for large m	Only normal incidence considered $V \propto (\sin \theta)^b$	$a = \frac{3.6m}{m-2}$ $a = 3.6$ for large m	$V \propto \frac{E^{0.8} \rho_p^{1.2}}{K_c^2}$ for large m	$V = \frac{k_2 (v)^{2.4} (r_p)^{3.6} E^{0.8} \rho_p^{1.2}}{K_c^2}$ $k_2 = \text{constant}$
III. Elastic-Plastic Indentation Evans-Gulden-Rosenblatt (1978) Reference (20)	$b = \frac{19}{6}$	Only normal incidence considered $V \propto (\sin \theta)^b$	$a = \frac{11}{3}$	$V \propto \frac{\rho_p^{1/4}}{K_c^{4/3} H^{1/4}}$	$V = \frac{k_3 (v)^{19/6} (r_p)^{11/3} (\rho_p)^{1/4}}{K_c^{4/3} H^{1/4}}$ $k_3 = \text{constant}$

transition occurs for nominally brittle materials. They developed a brittle cutting model using Hertzian contact stress theory and Wiebull's statistical theory of fracture strengths⁽¹⁹⁾ (Model II in Table 6). The model predicts a velocity exponent $b = 2.4$ for large values of the Weibull modulus (a measure of the dispersion of fracture strengths of a material). Only normal incidence was considered in the model and so the angle dependence should correspond to Equation (5). Since only elastic contact was assumed, the only target material properties influencing erosion according to this model are Young's modulus, E , and fracture toughness, K_{Ic} .

In recent years it has been recognized that purely elastic Hertzian contact fracture is more of an exception than the rule in particle impact (confined to blunt particles) even for extremely brittle targets. Impacts with particles having sharp edges involve localized plastic indentation as well as cracking. Recently, Evans, Gulden, and Rosenblatt⁽²⁰⁾ have developed an erosion model using concepts of elastic-plastic indentation fracture mechanics (Model III in Table 6). The volume of the target material removed per particle is the volume enclosed by the radial and lateral cracks generated in the impact event. The lateral crack depth is a function of the target hardness while the length of the radial crack is controlled by the fracture toughness. Thus the erosion rates depend on both of these material properties (see Table 6). The predicted velocity exponent is close to 3 and the angular dependence of Equation (5) is expected for this model. Wiederhorn and Lawn⁽¹¹⁾ have also derived an erosion model based on similar elastic-plastic indentation concepts.

V.2.2.2 Coal Slurry Erosion Test Results and Particle Impact Erosion Model Predictions. The eroded surfaces of all of the candidate valve materials, except the hot-pressed grades of SiC and Si_3N_4 and the sintered alumina, exhibited characteristics of ductile erosion processes. This was especially apparent in B_4C and TiB_2 . The approximate inverse correlation of the erosion rate with the Vickers hardness observed in Figure 30 is also consistent with a ductile cutting mode of erosion (Table 6). However, the angular dependence of erosion rates observed in the cemented carbides and B_4C show a maximum at normal incidence rather than at an intermediate angle as required by the ductile cutting process in Finnie's model.

One explanation that can resolve the apparent discrepancy is as follows. The suspended solids in the coal slurry stream cover a range of size distributions. The larger particles in the stream might produce erosion by chipping, possibly by an elastic-plastic indentation fracture mechanism, while the smaller size particles erode by a ductile cutting mode. This would result in a mixed mode of erosion. This can also explain the deviation of the experimental points from the predicted lines of Equation (5) in the angular dependence plots of Figures 45 through 48. The observed angular dependence is, in this case, a combination of the angular dependence of a ductile cutting mechanism from small particles and a brittle chipping mechanism from the larger particles as illustrated schematically in Figure 61. It is shown in Figure 61 that the maximum erosion rate in the brittle mode is much greater than the maximum erosion rate in the ductile mode. This indeed is the case for brittle materials as demonstrated, for example, in plate glass by Sheldon and Finnie.⁽¹⁸⁾ Thus, the large particles, in the coal slurry can have a strong influence on the erosion rate even though this size fraction is small. The smaller particles, on the other hand, smooth out the rough surface produced by the large particles giving the surface an appearance of smooth ductile erosion.

Direct evidence for brittle chipping in coal slurry erosion testing was obtained in a sapphire crystal target. Because of its fairly high hardness ($H \approx 20 \text{ GPa/m}^2$) and low fracture toughness ($K_{IC} \approx 1\text{--}2 \text{ MPa m}^{1/2}$) the brittle chipping mechanisms are favored over the ductile cutting mechanisms. Figure 62 shows the eroded surface of the sapphire crystal following a short duration slurry erosion test (4 minutes). The material removal is through lateral cracking as suggested by the elastic-plastic indentation fracture theories of erosion.

The above discussion suggests that coal slurry erosion rates should be influenced by both the hardness and the fracture toughness of the target materials. To evaluate the combined role of these material parameters, erosion rates were plotted versus $K_C^{4/3} H^{1/4}$, the combination suggested by the elastic-plastic indentation models of erosion⁽²⁰⁾ (Model III in Table 6). Figure 63 shows this plot for a variety of target materials. An

FIGURE 61. SCHEMATIC REPRESENTATION OF THE EROSION RATE DEPENDENCE ON PARTICLE IMPINGEMENT ANGLE FOR DUCTILE, BRITTLE AND COMBINED MODES OF EROSION

400X

(a)

2000X

(b)

FIGURE 62. SURFACE OF A POLISHED ALUMINA SINGLE CRYSTAL (SAPPHIRE) AFTER 4 MINUTES OF COAL SLURRY IMPINGEMENT AT TWO MAGNIFICATIONS. MATERIAL REMOVAL IS BY SUBSURFACE LATERAL CRACKING.

FIGURE 63. LOG-LOG PLOT OF THE EROSION RATE, EXPRESSED IN TERMS OF VOLUME ERODED PER HOUR OF TEST DURATION, AND A COMBINED FRACTURE TOUGHNESS-HARDNESS PARAMETER; THE BROKEN LINE IS THE PREDICTED INVERSE CORRELATION; HP = HOT PRESSED, RS = REACTION SINTERED, a: FRACTURE TOUGHNESS FROM THE LITERATURE, b: FRACTURE TOUGHNESS MEASURED AT BCL

approximate inverse relation is noted in the plot, but the deviations of the individual data points from the correlation line are large, possibly because of the complexities of the microstructures and the uncertainties of the fracture toughness values.

It is difficult to conclude at the present time whether the coal slurry erosion process is dominated by a ductile mechanism (hardness controlled, Figure 30) or an elastic-plastic fracture mechanism (both hardness and fracture toughness controlled, Figure 63). The relevance of fracture toughness to material erosion resistance is, indeed, suggested in other ways. In the cemented WC system, for example, erosion rates decrease with decreasing binder level. This can be interpreted as an effect of increasing hardness. But beyond an optimum low binder level the fracture toughness is so low that the erosion rates begin to increase again. Thus, the maximum erosion resistance is obtained at a maximum value of some combination of the hardness and the fracture toughness.

The intergranular decohesion observed in the hot-pressed SiC and Si_3N_4 and the sintered Al_2O_3 can be considered to be a modified elastic-plastic fracture mechanism of erosion. In these cases, the lateral cracking occurs preferentially at subsurface grain boundaries, thereby causing whole grains to break loose⁽¹⁾.

The velocity exponents obtained in the present study for the cemented carbides are consistent with the concept of a combined erosion mode. An exponent of 2 or slightly higher is expected for ductile cutting, while the indentation fracture mechanisms predict exponents of 3 or slightly higher. Experimentally measured exponents are in the range 2.5 to 3.0, but the hot pressed B_4C is a notable exception. The experimentally observed exponent of 1.4 is lower than the predictions of any of the theoretical erosion models or those reported in experimental studies⁽¹¹⁾. Additional experiments will be needed to verify if the exponent is indeed so low.

V.3 Approaches to Materials Improvements

From the discussion of the erosive wear mechanisms of the candidate valve materials in coal slurries and their relation to impact damage models,

it is clear that wear resistance should improve with some combination of increased hardness and fracture toughness. These two material properties, however, usually vary in opposite directions with controlled changes in microstructure. As discussed before, a notable example is the WC-metal binder systems.

In ceramics there are several routes to improved coal slurry erosion resistance. These include minimizing residual porosity and reducing additive agents that segregate to or form second phases at grain boundaries. Here again, these requirements are often in conflict. Additives in hot-pressing or sintering are added to aid densification. Thus, in many ceramics processed by these conventional methods, reduction of porosity may not be possible without additive agents. New processes such as hot isostatic processing can densify ceramics by application of isostatic pressure and temperature and possibly minimize or remove the need for harmful additives. Also, chemical vapor deposition, though expensive, may be an attractive route to fabrication of pure ceramic compounds at near theoretical density. Another possible route to improving ceramic erosion performance is through the application of fiber composites. Fibers of high erosive wear resistance such as SiC in an Si matrix, with the fibers aligned normal to the impingement plane, should exhibit excellent erosive wear resistance. Alternatively, fibers aligned parallel to the impingement plane but normal to the impingement direction of the slurry, could offer significant protection to the matrix phase by a shadowing effect, particularly at low impingement angles.

VI. CONCLUSIONS

A summary of the conclusions which can be drawn from this program are listed below.

- Although the three grades of cemented WC investigated had comparable erosion rates at low impingement angles, at higher impingement angles, the low binder grade, K703, had a higher erosion resistance. This is a result of the erosion mechanism, undercutting the carbide particles through erosion of the binder phase.
- B₄C and reaction-bonded SiC had erosion rates comparable to the cemented carbides. The erosion resistance of these materials

could be improved by optimizing the microstructures; initially by decreasing the residual porosity in B_4C and the amount of free Si in the RB SiC.

- CVD SiC and α -SiC had significantly lower erosion rates than the other materials. At low impingement angles, the erosion rate for the CVD SiC was nearly an order of magnitude lower than that of the cemented carbides.
- Cemented TiB_2 -Ni had significantly higher erosion rates than the other materials. No correlation of erosion rates with Ni binder content was observed, probably due to the effects of variations in the residual porosity.
- The notable erosion resistance of the large grains of SiC indicates that single crystal SiC would have excellent erosion resistance. Advantage of this property must be taken by minimizing the degradation of the erosion properties by other aspects of the microstructure, e.g., microporosity effects (CVD SiC), grain boundary impurity effects (α -SiC) and more susceptible phases (free Si in reaction-bonded SiC).
- The particle size distributions in the five coal slurries from coals processed by H-Coal and SRC-1 were very similar, the average particle size ranging from 5.4 to 8.0 μm . The largest particle size was around 170 μm in each coal except for the Wyodak coal from H-Coal which was only 53 μm .
- A commercially-available dolomite product might provide a suitable synthetic slurry when mixed with a suitable carrier liquid. A good synthetic slurry would provide more controllable, reproducible laboratory characterization of candidate materials for correlation with service experience. It would also allow more flexibility in adjusting size and shape distributions in a controlled manner to simulate those found in the various coals.
- The service trial of a reaction-bonded SiC valve stem in the H-Coal PDU was very encouraging. The SiC stem showed less relative wear than the cemented WC valve seat. Premature failure of the stem appeared to be related to the shape to which it was machined.

VII. RECOMMENDATIONS

A number of recommendations for further work were identified during the course of this program, and through discussions with manufacturers and users of let-down valves and manufacturers of candidate materials.

- The materials having high wear resistance already identified in this program, CVD SiC, reaction-bonded SiC, α -SiC and B₄C, should be exposed to service plant trials as quickly as possible to provide service experience on erosion rates, mechanisms and microstructure/property effects, correlations with the laboratory tests, and feedback on adjustments in valve design required to use these materials.
- The processing and composition of the promising candidate materials should be modified to reduce the detrimental degrading microstructural features identified in this and future programs to optimize erosion resistance. Significant increases in erosion resistance may be possible in materials such as B₄C, the SiC materials, and the hot-pressed ceramics.
- This candidate material evaluation program under simulated specific service conditions should be continued and expanded to take advantage of the valuable comparative reference data which have already been accumulated in the Battelle erosion rig using actual coal-derived slurries. This effort should have the objective of evaluating advanced, commercially-available and developmental materials supplied by industry or others on a demand basis, and to qualify materials for pilot plant evaluation by laboratory tests simulating actual slurry let-down conditions.
- To implement new findings and candidate materials in pilot plant service as quickly as possible, a mechanism for frequent communication should be implemented between the materials evaluation groups, pilot plant engineering staffs, valve manufacturers, and commercial sources of advanced materials.

- To rapidly identify and develop promising candidate materials, and avoid endless empirical testing and optimization effort, is necessary to identify the erosion controlling mechanisms for the different classes of materials. This effort includes analysis and identification of microstructural features degrading the erosion properties, and recommendations for optimizing the properties of specific materials. This program was able to do the latter for each of the materials tested.
- The specific recommendations for directions to improve the wear properties of the materials investigated in this program are:
 - Hot, isostatic processing of high-purity B_4C , sintered α -SiC and cemented TiB_2 -Ni to reduce residual porosity.
 - Modify the deposition conditions for CVD SiC to increase the amount of the erosion-resistant bands in the material.
 - Homogenize the surface layers in the cemented WC to develop a refined distribution of matrix and carbide.
 - Utilize and develop directionality of the hard and soft phases in the microstructure to advantage in orienting the material to have the greatest erosion resistance in the direction of slurry impingement.

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