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EROSION OF MAGNESIUM POTASSIUM PHOSPHATE CERAMIC WASTE FORMS

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ABSTRACT

Phosphate-based chemically bonded ceramics were formed from magnesium potassium phosphate (MKP) binder and either industrial fly ash or steel slag. The resulting ceramics were subjected to solid-particle erosion by a stream of either angular Al_2O_3 particles or rounded SiO_2 sand. Particle impact angles were 30 or 90° and the impact velocity was 50 m/s. Steady-state erosion rates, measured as mass lost from a specimen per mass of impacting particle, were dependent on impact angle and on erodent particle size and shape. Material was lost by a combination of fracture mechanisms. Evolution of H_2O from the MKP phase appeared to contribute significantly to the material loss.

INTRODUCTION

Phosphate-based chemically bonded ceramics are being used to stabilize many types of industrial or nuclear wastes. Many of the industrial wastes consist of nonhazardous fly ash, which can be used in value-added products. For example, approximately one-third of the ash produced by utilities is recycled as an additive to cements [1]. Phosphate-based cements have advantages over Portland cements because they can incorporate substantially higher ash loadings and can form strong products from ash having wide ranges of chemical compositions [2-6].

We have developed a novel chemically bonded phosphate ceramic called Ceramicrete. Final ash-containing Ceramicrete products exhibit high strength and little open porosity. They are therefore suitable for many potential applications [2-6].

We have examined the resistance of Ceramicrete to solid-particle erosion because Ceramicrete products may find use in hostile environments and because of specific interest in grit erosion of cement and concrete. Decontamination of large buildings once used for reprocessing spent nuclear fuel at the Hanford site in Washington and the Savannah River Site in South Carolina will require removal of radioactive contaminants from structures before decommissioning and possible demolition [7,8]. Because of high radiation levels, decontamination will require use of remote or robotic technology, probably based on abrasive erosion provided by grit blasting. Such decontamination techniques must be well understood in order to predict the efficiency and costs of decontamination. Despite this technological interest in the solid-particle erosion of cement and concrete, relatively little effort has been devoted to its study [8]. Although a wealth of data is available on solid-particle erosion of engineering materials [9-11], and several models exhibit success in predicting response to erosive conditions [12-14], little is known about the response of Ceramicrete or other cement-based materials.

EXPERIMENTS

Specimen Fabrication

Ceramicrete synthesis is based on an acid-base reaction between MgO and a solution of alkali phosphate salts, such as sodium or potassium phosphate. Our specimens were formed by the reaction

This product is the binder (referred to as MKP) that constitutes the cement matrix [2-6]. Resultant composite products, which can incorporate ash, slag, low-level nuclear wastes, or other hazardous inorganic or organic materials, have been subjected to tests of stability in aqueous media [15,16] and found to be highly resistant to leaching [2-6].

For these studies, we fabricated 2-cm-diameter MKP-based test samples that incorporated 50 or 60 wt.% Class C or Class F fly ash, or 65 wt.% steel-mill slag. The samples were cured for ≈ 1 month, and then specimens for erosion testing were cut with a diamond-blade band saw. A few of the specimens were polished to a 1- μm finish so that the surfaces could be examined by X-ray diffraction (XRD) and scanning electron microscopy (SEM).

The ash-containing specimens exhibited average densities of $\approx 1.6\text{--}1.9\text{ g/cm}^3$ and porosities $<20\%$. The slag-containing specimens exhibited average densities of $\approx 2.6\text{ g/cm}^3$ and porosities $<20\%$.

Erosion Tests

The erosion tests were conducted at room temperature in a slinger-type apparatus that was evacuated to a pressure of $\approx 50\text{ Pa}$ [7,17,18]. The erodents were angular Al_2O_3 (Norton Alundum 38) with average particle size, D , of 42 or 390 μm ; or SiO_2 sand with an average diameter of $\approx 450\text{ }\mu\text{m}$. The erodent velocity, V , was 50 m/s, and the angles of impact, α , were 30 and 90°.

Specimens were weighed to the nearest 0.1 mg, subjected to erosion by one of the erodents, cleaned by brushing, and then reweighed. Steady-state erosion was determined as the mass lost from the target per mass of impacting particles. At least four test cycles were conducted to define the steady-state erosion rate, ΔM . Steady-state surfaces were then examined by SEM. In addition, polished specimens were impacted by only a few erodent particles so that individual impact sites could also be examined.

Property Characterization

It has been shown that impact by high-velocity solid particles can produce local melting in low-ductility metals [18] and ceramics [19]. We therefore examined the thermal stability of our MKP-based specimens. Differential thermal analysis (DTA) and thermogravimetric analysis (TGA) were used to determine the temperature range over which H_2O is lost from MKP and whether other phase transformations occur at elevated temperatures.

Specimens were also prepared for measurement of crushing strength. The compressive surfaces were ground to be flat and parallel. To examine the effects of heating, sets of four Ceramicrete specimens that contained 50 wt.% Class F fly ash were heated in air to temperatures of 225, 500, 750, and 1000°C. The heating schedule consisted of 10°C/h to 120°C, then 120°C/h to the maximum temperature, holding at that temperature for 2–30 h, and then cooling to room temperature at $\approx 120^\circ\text{C/h}$. Final densities were calculated from mass and dimension measurements. For the crushing-strength tests, specimens were placed between cardboard sheets and compressed at a rate of 0.2 mm/s.

RESULTS AND DISCUSSION

XRD indicated that all specimens consisted primarily of the crystalline MKP, unreacted MgO , and traces of the ash or slag additives. The residual MgO resulted because some cations from the fly ash or slag became incorporated in the MKP phase. The formulations were based on stoichiometric incorporation of Mg , and thus excess MgO remained. SEM revealed a complex microstructure that consisted of a very fine-grained matrix, porosity, and generally coarse silicate-based phases (Fig. 1). The silicate phases are the remnants of the ash or slag additives. This microstructure is different from those of most engineering materials, but is typical of a cement.

Fig. 1. SEM photomicrograph of 50 wt.% fly ash Ceramicrete specimen. This material is representative of all specimens. A relatively dense MKP matrix surrounds spherical silicate regions and small pores.

Typical raw data for mass loss per mass of erodent passing through the slinger are shown in Fig. 2. Although the data exhibit some scatter, they can be fitted reasonably well to a straight line. To calculate erosion rates, the data were corrected by a dose factor because only a fraction of the erodent that enters the test chamber actually strikes an individual specimen; the dose factor for 90° impact is twice that for 30° impact. ΔM is defined as the slope of a plot of specimen mass loss per mass of erodent striking the specimen surface.

ΔM data as a function of impact angle for the various Ceramicrete specimens eroded by $42\text{-}\mu\text{m}$ Al_2O_3 particles are shown in Fig. 3. Values were higher for $\alpha = 30^\circ$ impact than for $\alpha = 90^\circ$. The additive type and composition did not have a strong effect on erosion rate. The Class C fly ash samples were slightly more resistant to erosion than were the other materials. In general, because of higher Ca and lower C contents, Ceramicrete synthesized from Class C fly ash tends to be stronger than that synthesized from Class F fly ash or slag [20]. With impact by larger particles, the trend of ΔM versus α was reversed; maximum ΔM values were obtained at 90° .

Most metals, for which the dominant mechanism of material removal is some sort of ductile plowing, exhibit maximal erosion rates with impact at $\approx 20\text{--}30^\circ$ [21]. Most ceramics and brittle polymers, for which the dominant mechanism of material removal is formation of lateral cracks at elastic-plastic damage zones, exhibit maximal erosion rates with impact at 90° [8-14]. All of the Ceramicrete specimens were completely brittle, but when impacted by $42\text{-}\mu\text{m}$ Al_2O_3 particles, their response to erosion was characteristic of a material that exhibits some ductility. We can offer no credible explanation for the angular dependence of the erosion rate, but note that under some conditions, Portland cement also exhibits the same effect of ΔM versus angle [8].

As shown in Table I, the erosion rates for Ceramicrete are relatively high with respect to typical engineering materials, but are generally lower than those of Portland-based cement and concrete. Given the density and inherent strength of Ceramicrete, its erosion resistance is about as might be expected. For example, structural ceramics generally exhibit crushing strengths of $\approx 2\text{--}6$ GPa [24], whereas that of Ceramicrete is generally <100 MPa [20]. Ceramicrete is strong by the standards of cements, not by those of structural ceramics. However, given the large differences in erosion rates, one might assume that the erosion mechanisms are different for Ceramicrete than for other materials. SEM was used to examine this supposition more closely.

SEM examinations of steady-state fracture surfaces suggested that the material-removal mechanisms were common to all specimens. Surfaces were rough and covered by debris (Fig. 4). The scale of the fractures correlated well with that of the microstructure shown in Fig. 1.

Fig. 2. Representative data for mass loss from 65 wt.% steel slag specimens per dose of 42- μ m Al_2O_3 erodent.

Fig. 3. Erosion rate vs. α for 42- μ m Al_2O_3 erodents impacting Ceramicrete specimens at 50 m/s.

Individual impact sites generally contained many small fractures, most of which appeared to be intergranular. In general, the material removed per impact was substantial, and little embedding of erodent was observed. There was little difference in appearance between damage from impact at 30° and at 90° (Fig. 5). Given the extent of penetration of each erodent particle, it appears that nearly complete transfer of kinetic energy to the target occurred at both angles of impact.

Material removal was a consequence of propagation of large and small fractures. In more-conventional brittle material, impact creates an elastic-plastic zone beneath the impact site. A few radial and lateral cracks emanate from this zone. Furthermore, some of the kinetic energy of

Table I. Erosion rates for various engineering materials impacted by 42- μ m angular Al_2O_3 particles at $V = 50$ m/s.

Material	$\Delta M, \alpha \approx 30^\circ$ (mg/g)	$\Delta M, \alpha = 90^\circ$ (mg/g)	Reference
MKP ceramics	2.3–7.0	1.1–3.4	This work
Portland cement	19	5	[8]
Portland concrete	5	2.5	[8]
Nuclear-waste glass	0.36	0.67	[8]
Amorphous NiP	—	0.3	[18]
Bismaleimide	—	0.1	[22]
2014 Al, T6	0.06	0.04	[23]
2014 Al + 20% SiC	0.08	0.06	[23]
SiC	—	0.045	[23]

Fig. 4. SEM photomicrographs of eroded Ceramicrete specimens containing 50 wt.% Class F fly ash: (a) $\alpha = 30^\circ$ and (b) $\alpha = 90^\circ$; $V = 50$ m/s, erodent = $42\ \mu\text{m}\ \text{Al}_2\text{O}_3$.

Fig. 5. SEM photomicrographs of individual impact sites of 65 wt.% steel slag Ceramicrete samples eroded by $42\text{-}\mu\text{m}\ \text{Al}_2\text{O}_3$: (a) $\alpha = 30^\circ$ and (b) $\alpha = 90^\circ$.

an impact is spent as the erodent particle rebounds. Ceramicrete has a relatively low elastic modulus [20] and there was little evidence of lateral cracks propagating from an elastic-plastic zone or of erodent rebound.

In Portland cement and concrete, many small fractures have also been observed at impact sites [8]. These fractures were attributed to a creep phenomenon caused by loss of H_2O , and

hence destruction of the basic crystal structure of the matrix, because of heating induced by particle impact. As shown in Fig. 6, Ceramicrete loses H_2O from the hydrated MKP crystals at $\approx 100^\circ\text{C}$. Crushing strength and density decrease substantially with this loss (Fig. 7). Except for this H_2O loss, the phosphate-based binder phase exhibits no other phase transformations to 1400°C [20].

If H_2O loss is indeed integral to erosion of Ceramicrete, we might expect that erosion rates would be higher from impact by angular Al_2O_3 particles than by rounded SiO_2 sand. The kinetic energy from the sand should be absorbed over a much large area because of its shape, and the maximum temperature at an impact site should therefore be lower. As shown in Fig. 8, ΔM values were in fact significantly lower when the rounded erodent was used, especially with impacts at 90° .

With respect to applications, it has also been shown that after exposure to elevated temperatures, Ceramicrete remains highly resistant to chemical leaching [20,25]. Thus, although its strength is reduced by elevated temperatures, Ceramicrete retains its ability to stabilize wastes.

Both Ceramicrete and Portland-based cements [8] erode rather quickly. From the standpoint of nuclear-facility decontamination procedures, this property is probably advantageous. For maximum efficiency of material removal, our studies suggest that angular erodents should be used. The erosion studies to date leave, however, many questions unanswered [8]. More work is required before cement erosion can be modeled effectively. In particular, the range of experimental conditions should be broadened to include a wider range of particle size and impact velocity.

CONCLUSIONS

Ceramicrete that contained 50 or 60 wt.% industrial Class C or F fly ash, or 65 wt.% steel slag, was subjected to solid-particle erosion by a stream of angular Al_2O_3 particles or rounded SiO_2 sand. The impact velocity was 50 m/s and the impact angle was 30 or 90° . The material-loss mechanism was dominated by formation of large and small fractures at each impact site. Fracturing appeared to have been caused by a combination of direct impact damage and creep from local loss of H_2O , with concomitant reduction in strength, induced by local heating.

Fig. 6. Ceramicrete specimens containing 50 wt.% Class F fly ash heated in air at $300^\circ\text{C}/\text{h}$: (a) DTA and (b) TGA plots.

Fig. 7. Crushing strength and density of Ceramicrete containing 50 wt.% Class F fly ash vs. exposure at temperature for 2 h.

Fig. 8. ΔM values for Ceramicrete containing 60 wt.% Class F fly ash; $V = 50$ m/s, erodents as shown.

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REFERENCES

1. L. Lamarre, *Elect. Pow. Res. Inst. J.*, 1994, April/May, 22.
2. D. Singh, A. S. Wagh, J. C. Cunnane, and J. L. Mayberry, *J. Environ. Sci. Health A32*, 527 (1997).
3. D. Singh and A. S. Wagh, *Mater. Technol.* **12**, 149 (1997).
4. A. S. Wagh, S. Y. Jeong, and D. Singh, *Ceram. Trans.* **87**, 63 (1998).
5. D. Singh, V. Mandalika, A. S. Wagh, R. V. Strain, and M. Tlustochowicz, *Ceram. Trans.* **87**, 653 (1998).
6. A. S. Wagh and D. Singh, *Radwaste Mag.*, 1998, January, 46.
7. *Closing the Circle on the Splitting of the Atom*, U.S. Department of Energy, Office of Environmental Management, Washington, DC, 1995.
8. K. C. Goretta, M. L. Burdt, M. M. Cuber, L. A. Perry, D. Singh, A. S. Wagh, J. L. Routbort, and W. J. Weber, *Wear*, in press (1999).
9. J. L. Routbort and R. O. Scattergood, *Key Eng. Mater.* **71**, 23 (1992).
10. G. P. Tilly and W. Sage, *Wear* **16**, 447 (1970).
11. A. G. Evans, M. E. Gulden, and M. Rosenblatt, *Proc. R. Soc. London Ser. A* **361**, 343 (1978).
12. A. W. Ruff and S. M. Wiederhorn, in *Treatise on Materials Science and Technology*, Vol. 16, edited by C. M. Preece (Academic Press, New York, 1979), p. 69.
13. G. Sundararajan, *Wear* **84**, 217 (1983).

14. C. M. Preece and N. H. MacMillan, *Ann. Rev. Mater. Sci.* 7, 95 (1977).
15. U.S. Environmental Protection Agency, Method 1311, Toxicity Characteristic Leaching Procedure (TCLP), Rev. II (1992), p. 138.
16. Method ANSI/ANS 16.1, American Nuclear Society, La Grange Park, IL (1986).
17. J. L. Routbort and R. O. Scattergood, *J. Am. Ceram. Soc.* 63, 595 (1980).
18. K. C. Goretta, J. L. Routbort, A. Mayer, and R. B. Schwarz, *J. Mater. Res.* 2, 818 (1987).
19. C. S. Yust and R. S. Crouse, *Wear* 51, 193 (1978).
20. S. Y. Jeong, Ph.D. thesis, Illinois Institute of Technology, 1997.
21. A. V. Levy, Z. R. Shui, and B. Q. Wang, *Wear* 127, 193 (1988).
22. A. Brandstädter, K. C. Goretta, J. L. Routbort, D. P. Groppi, and K. R. Karasek, *Wear* 147, 155 (1991).
23. W. Wu, K. C. Goretta, and J. L. Routbort, *Mater. Sci. Eng.* A151, 85 (1992).
24. See, for example, "Ceramic Source, Vol. 6," *Am. Ceram. Soc.*, Westerville, OH (1991).
25. M. Tlustochowicz, M.S. thesis, Northwestern University, 1998.