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By D. J. Singleton and R. Blickensderfer

UNITED STATES DEPARTMENT OF THE INTERIOR

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UNIT OF MEASURE ABBREVIATIONS USED IN THIS REPORT

°C	degree Celsius	m	meter
cm	centimeter	mg	milligram
cm^2	square centimeter	mg/L	milligram per liter
cm^3	cubic centimeter	mL	milliliter
°F	degree Fahrenheit	mm	millimeter
g	gram	mpy	mil per year
g/cm^3	gram per cubic centimeter	min	minute
h	hour	m/s	meter per second
HB	Brinell hardness	pct	percent
in	inch	rpm	revolution per minute
in^2	square inch	s	second
kg	kilogram	V	volt
kV	kilovolt	V/h	volt per hour
kW	kilowatt	wt pct	weight percent
L	liter	y	year

WEAR AND CORROSION OF 12 ALLOYS DURING LABORATORY MILLING OF PHOSPHATE ROCK IN PHOSPHORIC ACID WASTE WATER

By D. J. Singleton[1] and R. Blickensderfer[2]

ABSTRACT

Erosion-corrosion of 12 alloys in phosphoric acid waste water was studied by the Bureau of Mines. Tests were conducted on oblate spheroids or cylindrical specimens in 12- and 60-cm-diam ball mills by grinding phosphate rock in gypsum pond water with a starting pH of 1.6. For comparison, tests were conducted while grinding phosphate rock in plain water. Static corrosion tests in gypsum pond water also were conducted. For all alloys, the wear by erosion-corrosion (milling with gypsum pond water) was greater than the sum of erosion (milling with water) plus static corrosion. Erosion-corrosion wear was about 1,500 to 3,000 mpy for the alloyed white cast irons, 1,000 to 1,400 mpy for commercial steel ball material and type 316 stainless steel, and 600 to 900 mpy for nickel-base alloys and a high-manganese, nitrided stainless steel. Alloy costs per unit of phosphate rock processed favor a low-alloy, high-carbon steel or a high-manganese, nitrided stainless steel.

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[1] Chemist.
[2] Metallurgist.
Albany Research Center, Bureau of Mines, Albany, OR.

INTRODUCTION

In the production of phosphoric acid from phosphate rock, the majority of U.S. plants impound and recirculate all water that has direct contact with any of the process gas or liquid streams. The impounded water contains fluosilicic and phosphoric acids and is known as gypsum pond water. Concentrations of 8,500 mg/L fluoride and over 5,000 mg/L phosphorus are common, as are pH levels down to 1.0 (1).[3] Although much of the gypsum pond water is consumed in wet-process phosphoric acid production, disposal of the pond water is a problem in regions of high rainfall and low evaporation (2). From a chemical process viewpoint, the gypsum pond water could be used instead of plain water in the ball mills that grind the phosphate rock. This would consume some of the gypsum pond water and reduce the amount of sulfuric acid required in the process. However, the low pH of the gypsum pond water could raise problems with the steel grinding balls and mill liners because both abrasive wear and corrosion would occur.

Abrasive wear and corrosion occurring simultaneously are generally called erosion-corrosion. This work was undertaken to evaluate the erosion-corrosion of a variety of alloys under conditions that simulate the grinding of phosphate rock in phosphoric acid waste water known as gypsum pond water.

Neither corrosion tests nor abrasive wear tests alone are adequate for predicting wear by erosion-corrosion. Erosion-corrosion results from the synergistic interaction between erosion and corrosion, each enforcing the other. Erosion-corrosion theory, mechanisms, and types of tests were reviewed by Vyas (3). Wieser (4), in a study of stainless steels in alumina slurries, showed that the combined effect of erosion-corrosion is greater than the sum of each occurring separately. Bond (5) reported that wear rates during grinding and crushing became extreme as the pH of the liquid dropped below 5.5. Ellis (6) did extensive tests on the effects of pH and atmosphere on steel balls with wet grinding sand. Norman and Loeb (7) extended the work to include the grinding of molybdenum ore in 3-m-diam mills.

Corrosion tests of metals and ceramics in phosphoric acid were conducted by Yates (8), who found that austenitic stainless steel, copper, Duriron,[4] Illium G, and Monel were the more corrosion-resistant metals. The effects of erosion (grinding) on corrosion in phosphoric acid or mill pond water were not studied, and no such study is known. Hoey (9-10) and Lui (11) reported on the corrosion behavior of steels in grinding of hematite ore, a nickel-copper sulfide ore, and a zinc-lead-copper sulfide ore. The ability of inhibitors to reduce corrosion during wet milling was reported by Hoey (12-13), Lui (14-15), and Remark (16). The effect of chromate inhibitors in an aqueous slurry of sand was reported by Postlethwaite (17). Subramanyan (18) suggested de-aeration and corrosion inhibitors for reducing erosion-corrosion. Natarajan (19) showed that erosion was greater than corrosion during milling of taconite ore in water in small laboratory mills. Dodd (20) summarized the wear of balls in real ball mills and in laboratory ball mills during wet milling of ores and indicated that corrosion is much less significant in large- than in small-diameter mills. Sailors (21) reported that chromium additions of 12 to 27 pct in iron balls may be cost effective in reducing the wear in corrosive environments.

This investigation was undertaken to determine the potential of several commercial alloys for grinding phosphate rock in gypsum pond water. Twelve commercial alloys, representing a wide range of composition, were evaluated in two different sizes of laboratory ball mills.

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[3] Underlined numbers in parentheses refer to items in the list of references preceding the appendix.

[4] Reference to specific products is made for identification only and does not imply endorsement by the Bureau of Mines.

EXPERIMENTAL PROCEDURE

APPARATUS

The larger ball mill, 60 cm in diam by 20 cm long, was made of steel and lined with natural rubber 1 cm thick to prevent corrosion. One end of the mill could be unbolted to put materials inside. There were 12 lifters, 2 cm high, around the circumference of the mill. Two rollers driven by a 2.7-kW motor turned the mill at 42 rpm, or 78 pct of critical speed. Figure 1 illustrates the mill and drive assembly. A wooden cover fit over the equipment, and a constant temperature was maintained by an electrical heater controlled by a thermostat. Figures 2 and 3 show the mill and charge before and after a test.

The small ball mill, 12 cm in diam by 9 cm long, was a commercial porcelain mill with five silicone rubber lifters added inside. The porcelain mill and its charge components are shown in figure 4. A drive rotated the mill at 120 rpm.

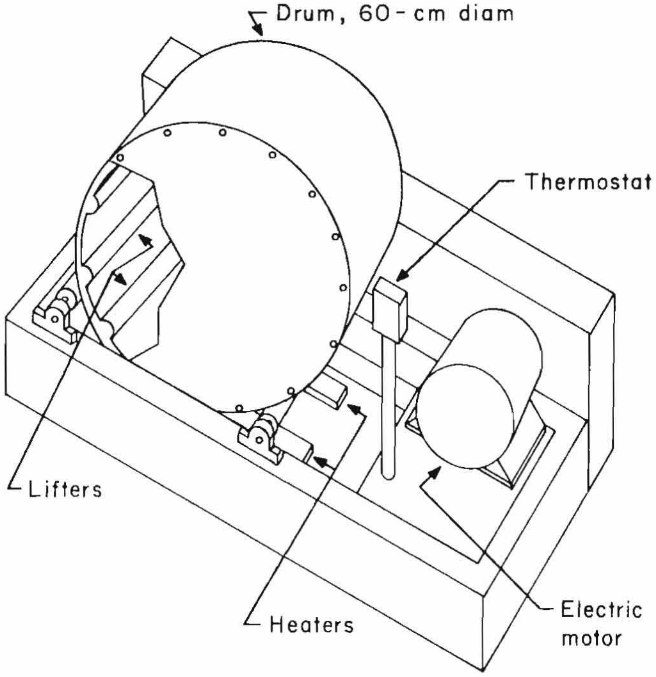

FIGURE 1. - Ball mill and drive assembly. Cover is not shown.

MATERIALS

The 12 alloys selected for evaluation as grinding media represent a range of corrosion and abrasion resistance as well as a range of cost. The alloys are listed in table 1 in the order of decreasing cost. This order also could be expected to be the order of decreasing corrosion resistance to acids in general. The relative cost of each alloy was based on the 1980 prices of the alloy additions; differences in fabricating or heat-treating costs could affect the rankings slightly. Specimens were tested in the shapes of cylinders or buttons because they were easier to obtain than spheres.

Two nickel-base alloys, Hastelloy C-276 and Incoloy 825, were selected to represent strongly corrosion-resistant materials. Two other corrosion-resistant materials evaluated were type 316 stainless steel and a Ni-Cu-Cr alloy, NiResist. Materials of strong abrasion resistance were represented by three white cast irons, NiHard 1, NiHard 4, and a high Cr-Mo white cast iron. The materials generally considered to have characteristics of both corrosion and abrasion resistance included three stainless steels, Cronifer 1713LCN, castable CA6NM, and Armco NP599, which contains appreciable manganese. Both Cronifer 1713LCN and Armco NP599[5] are nitrided for enhanced hardness. The cast superalloy, Illium P, was included because of its erosion-corrosion resistant qualities. Also included for evaluation was the grinding ball alloy currently being used in the phosphate industry, a high-carbon, low-alloy steel, heat-treated to a martensitic structure. This alloy was obtained from commercial 7.5-cm-diam balls.

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[5] To be marketed in late 1984 as Nitronic 30.

TABLE 1. - Relative cost, composition, and hardness of alloys evaluated in 60-cm ball mill

Material	Relative cost[1]	Analyzed composition, wt pct								HB[2]
		C	Cr	Fe	Mn	Mo	Ni	Si	Other	
Ni alloy, Hastelloy C-276.	13	0.005	15.94	5.61	0.41	15.67	56.82	0.04	3.58 W, 1.82 Co, 0.11 V	183
Ni alloy, Incoloy 825.....	6.8	.03	23.2	27.70	.39	2.76	43.1	.11	1.69 Cu, 0.91 Ti	187
Stainless steel, Cronifer 1713LCN..................	4.2	.016	17.5	63.51	1.72	3.87	12.8	.03	0.42 Cu, 0.13 N	187
High Cr-Ni steel superalloy, Illium P..........	3.7	.20	26.90	57.63	.53	2.18	8.58	.76	3.22 Cu	269
Stainless steel, type 316.	3.6	.10	17.3	66.1	1.74	2.24	12.3	.26	NA	212
Ni-Cu-Cr steel alloy, NiResist.................	3.0	2.93	3.72	70.82	1.11	.018	14.5	1.75	5.15 Cu	167
Stainless steel, Armco NP599...................	2.5	.09	16.4	71.55	8.71	.21	2.16	.41	0.31 Cu, 0.16 N	217
Stainless steel, castable, CA6NM...................	2.2	.03	11.8	83.45	.03	.61	3.92	.16	NA	359
High Cr-Mo white cast iron	2.1	2.46	13.2	82.35	.51	1.4	.35	.19	NA	606
Ni-Cr white cast iron, NiHard 4.................	2.0	3.47	9.09	78.78	1.04	.2	5.66	1.76	NA	601
Ni white cast iron, NiHard	1.6	3.41	3.35	87.56	.74	.025	4.20	.72	NA	555
High-carbon steel commercial ball................	1.0	.75	.46	96.89	1.02	.13	.17	.40	0.18 Cu	450

NA Not available.

[1] Calculated values based on 1980 prices of alloy additions.

[2] HB Brinell hardness number.

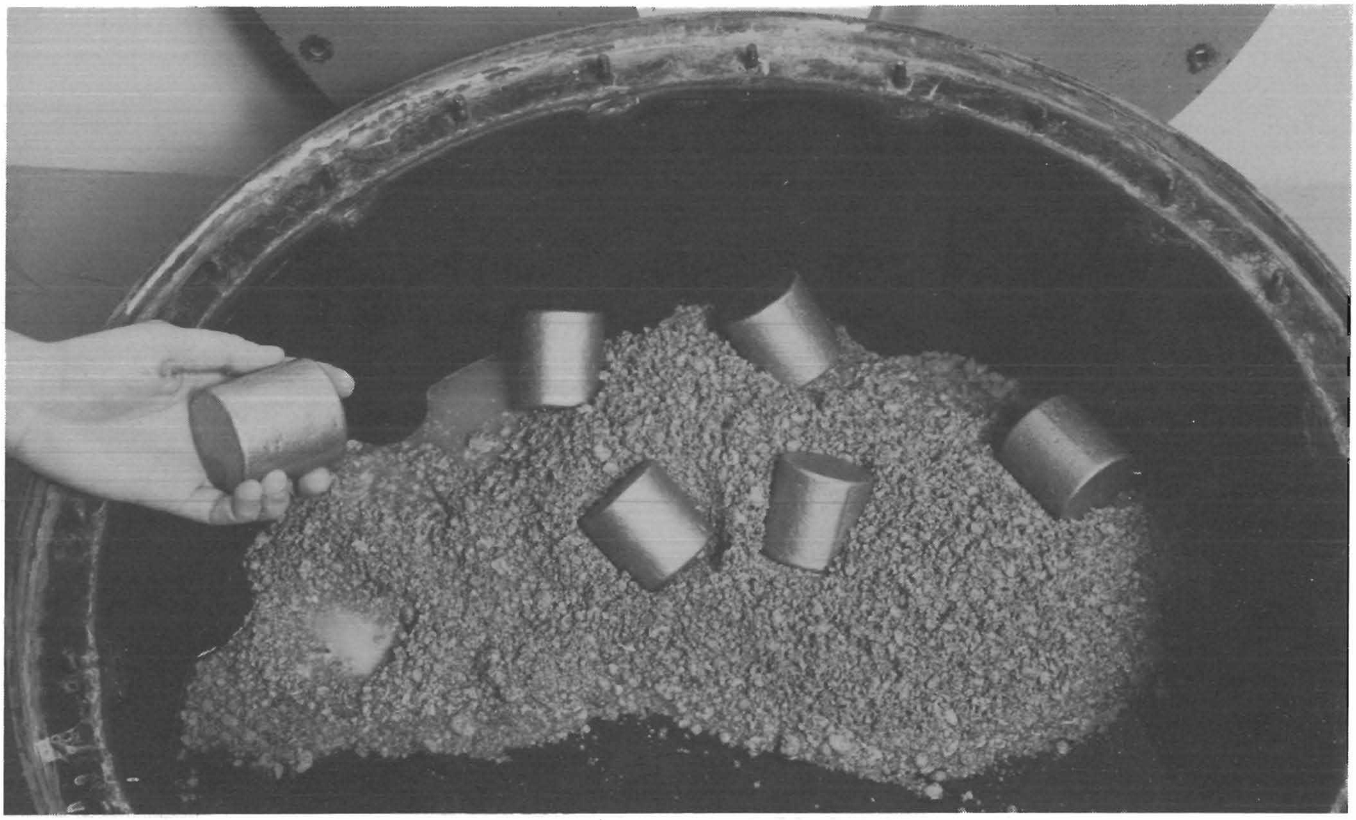

FIGURE 2. - Charge components in 60-cm ball mill.

FIGURE 3. - Interior of 60-cm ball mill after 1-h run.

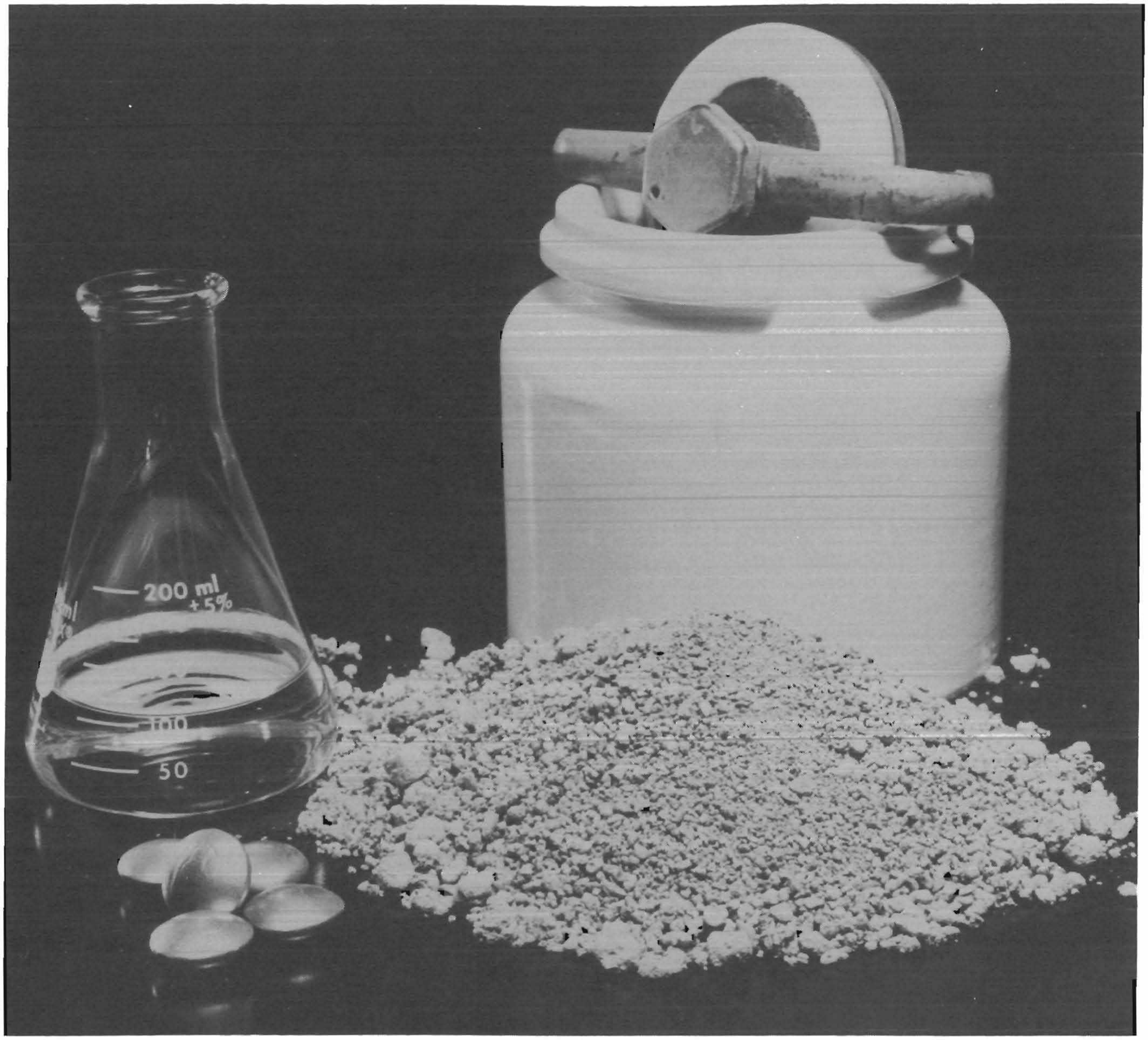

FIGURE 4. - Small ball mill and charge components.

Test specimens for the large mill were in the form of cylinders 5 cm in diam by 5 cm long. Available materials were obtained from commercial sources as 5-cm-diam bars that were cut into 5-cm lengths. Cast iron and castable stainless steel specimens were cast in sand molds. They were heattreated, sandblasted, and rough ground. The commercial 7.5-cm-diam balls mentioned above were forged into cylinders, cut, and heattreated. The sharp edges of all test specimens were rounded by grinding. Table 1 lists the analyzed composition and hardness of the cylindrical test specimens.

The test specimens used in the small ball mill were buttons in the shape of oblate spheroids approximately 2 cm in diam by 1 cm thick. The buttons were prepared by melting 25 g of material from the same stock as that of the cylinders. Melting was done under inert atmosphere on a water-cooled copper hearth plate using a tungsten electrode. The composition and hardness of the button specimens were approximately the same as for the cylindrical specimens and are given in the appendix.

The gypsum pond water was obtained from a commercial phosphate plant in Florida. An analysis of the liquid used in ball mill tests is shown in table 2. The liquid as received had a pH of 1.6. At the end of each 1 h experimental run, the slurry was pressure filtered to remove solids, and the pH of the liquid was determined. It was then consistently around pH 3.

TABLE 2. - Analysis of gypsum pond water (phosphoric acid waste water), grams per liter

	As received, pH 1.6	After 1 h ball milling, filtered pH 3.0
P_2O_5....	17.5	16.2
Al......	.082	.009
Ca......	.95	1.78
Cl......	.11	.095
F.......	8.29	.56
Fe......	.23	.03
K.......	.24	.14
Mg......	.27	1.31
Na......	1.87	1.65
Si......	2.45	.51
SO_4^{-2}...	5.10	3.15

For the static corrosion tests, two different liquors were used. One was the as-received gypsum pond water, pH 1.6. The other was prepared with a pH of 3.0 from several liters of gypsum pond water and phosphate rock mixed in the large ball mill until the pH of the filtrate was over 3. The filtrate was then adjusted to a pH of 3.0 with the addition of gypsum pond water. The resulting liquor simulated the liquid portion of the mill charge at the end of an hourly test.

The phosphate rock consisted of small pebbles, very coarse to very fine sands, and clay. A screen analysis of the phosphate rock before milling is given in table 3. The size after a 1-h milling test in the 60-cm mill also is included. It is believed that the particle size distribution after all milling runs was the same because all geometrical and operating parameters were the same.

TABLE 3. - Size distribution of phosphate rock

U.S. Standard screen size	Particle size, mm	wt pct Before milling	wt pct After milling[1]
Plus 3/8..........	19.1	2.1	0.7
Minus 3/8 plus 3..	9.42	4.5	1.0
Minus 3 plus 6....	6.68	20.7	4.0
Minus 6 plus 12...	3.35	35.2	18.1
Minus 12 plus 20..	1.70	25.5	26.0
Minus 20 plus 30..	.850	3.8	7.8
Minus 30 plus 40..	.600	2.1	6.3
Minus 40 plus 50..	.425	1.8	5.5
Minus 50 plus 70..	.300	1.6	5.0
Minus 70 plus 100.	.212	1.4	4.5
Minus 100 plus 200	.147	.8	6.3
Minus 200.........	.075	.5	14.8

[1] 2-ft-diam ball mill, 1-h milling time, mill pond water.

The chemical analysis of the feed rock, in weight percent, was 28.5 P_2O_5, 7.48 acid insoluble, and 5.30 total SiO_2.

PROCEDURES

The procedures used for experimental runs in both of the ball mills were essentially the same. Test specimens comprising one alloy composition were used to grind rock in the ball mill in a series of 1-h runs. Fresh rock and liquid were used for each 1-h run. Tests were continued until the weight loss of the specimens was nearly constant for each run. The starting materials, namely the rock, liquid, and specimens, and the ball mill were prewarmed to 37° C to represent Florida and Louisiana milling temperatures.

Before the experimental runs in phosphate rock, the surfaces of the specimens were conditioned. This was done by milling river rock in water for several runs until the weight loss per 1-h run became constant.

The experimental conditions for the 60- and 12-cm ball mills are summarized in table 4. The proportion of phosphate rock to liquid was kept the same in both mills. The temperature in the ball mill was measured at the beginning and end of each run. The pH of the gypsum pond water was measured just before the run, and the pH of the slurry filtrate was measured at the end of the hour run. The mean temperature and pH for all runs are included in table 4.

TABLE 4. - Comparison of experimental conditions for tests using large and small ball mills

	60-cm mill	12-cm mill
Specimens:		
Quantity..................	6	5
Area (per specimen)..cm^2..	120	8
Charge:		
Rock.................kg..	5.75	0.65
Liquid................L..	1.15	0.130
Test time................h..	1	1
Mean temperature........°C..	37	30
Mean pH....................	2.56	2.44

All weight loss was converted to units of mils per year, mpy, by the following formula:

$$\text{Rate, mpy} = \frac{534 \times \text{weight loss (mg)}}{\text{density (g/cm}^3) \times \text{surface area (in}^2) \times \text{time (h)}}.$$

The density was determined by the water immersion method, and the units for the constant are

$$\frac{\text{g in}^2\text{ h mil}}{\text{mg cm}^3\text{ y}}.$$

When determining weight losses, specimens were cleaned in water with a nylon bristle brush, oven dried, and weighed with a precision of ±0.1 mg.

To determine the static corrosiveness of the gypsum pond water and ball mill slurry on the test materials, potentiodynamic corrosion tests were conducted. After the milling tests were completed, specimens were cut from the cylinders and machined to about 1.6-cm diam by 0.3 cm thick. These were polished on 60- and 120-grit paper.

Potentiodynamic polarization measurements were made using a rapid-scan potentiodynamic technique developed by Monris and Scarberry (22) with the electrochemical corrosion rates determined from the third cathodic scan by Tafel extrapolation (23). Corrosion potentials were measured at a scan rate of 60 V/h in stirred phosphoric acid waste liquor at 37° C after an equilibrium period of 30 min. The solution was open to the atmosphere through a water-cooled condenser, and fresh solution was used for each run. For each test material, the corrosion potentials were measured both in the original gypsum pond water of pH 1.6 and in the solution of pH 3.0 that approximated the liquor after a 1-h ball mill run.

RESULTS

Results of the milling tests in the larger ball mill are shown in figure 5. Erosion-corrosion rates are shown for each successive 1-h test in units of mils per year (0.025 mm per year). The white cast irons, which are very abrasion resistant in ordinary milling, suffered the highest erosion-corrosion rates of all materials, ranging from about 2,000 to 2,400 mpy. The rate for high-carbon steel commercial ball material, typical of that now being used by the phosphate industry, was only about two-thirds of the rate for the alloyed white cast irons, or 1,400 mpy. Erosion-corrosion rates decreased generally with increasing alloy content for the stainless steels and nickel-base alloys with the exception of the excellent behavior of ARMCO NP599 stainless steel. It performed nearly as well as Hastelloy C-276, which had the lowest rate, 550 mpy.

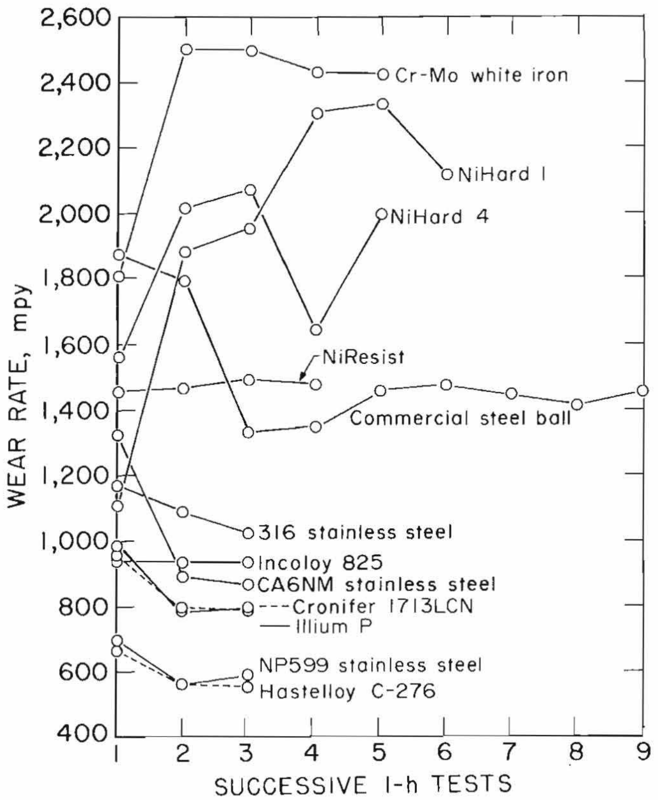

FIGURE 5. - Erosion-corrosion rates in 60-cm ball mill.

The results of the milling tests in the smaller ball mill are shown in figure 6. The ranking of the materials is approximately the same as the ranking from the larger ball mill, but the small-scale tests produced a greater range of results. Two of the white cast irons had rates greater than in the large ball mill, but the other white cast iron, NiHard 1, had a much lower rate. The high-carbon steel commercial ball material had a wear rate of 2,300 mpy, or 64 pct greater than in the larger mill. On the other hand, the stainless steels and the nickel alloys had a much lower wear rate in the smaller scale tests.

Static corrosion measurements showed that the materials could be categorized as those with good corrosion resistance and those with poor corrosion resistance.

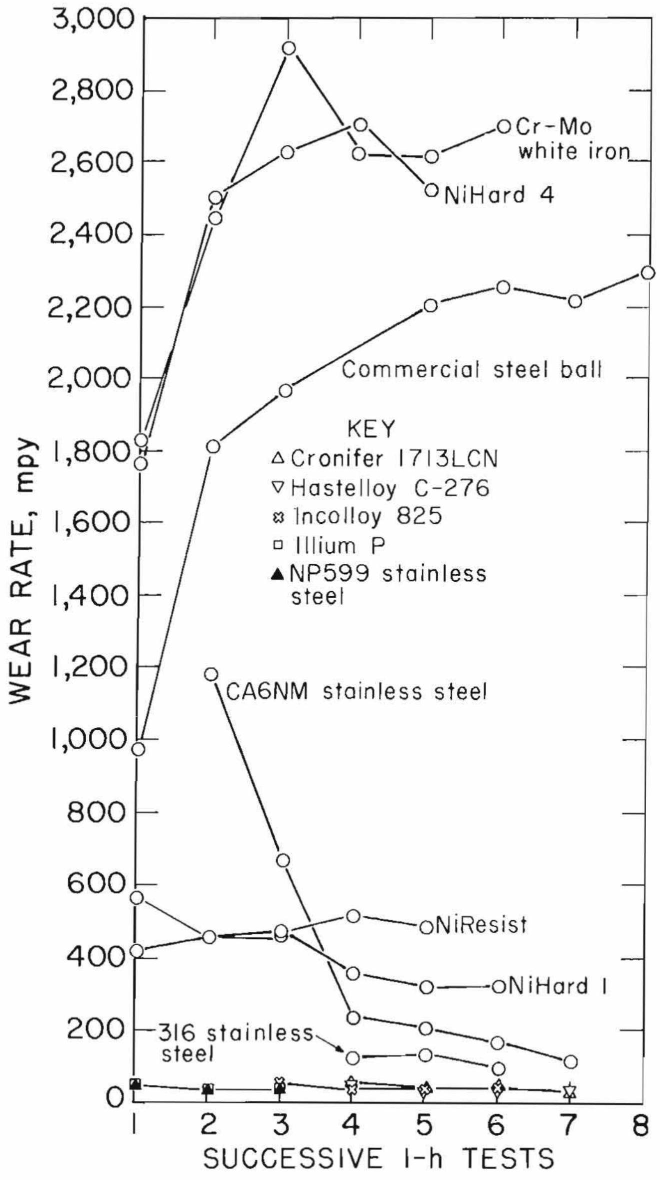

FIGURE 6. - Erosion-corrosion rates in 12-cm ball mill.

Results are presented in table 5. The nickel-base alloys and stainless steels proved to be quite corrosion resistant. All corrosion rates for these were below 1 mpy at pH 3 and below 2 mpy at pH 1.6, except for castable stainless steel CA6NM, which exhibited severe corrosion at pH 1.6. The remaining five materials were severely attacked at both pH values.

TABLE 5. - Static corrosion rates in gypsum pond water (phosphoric acid waste water), mils per year

Material	pH 1.6 (fresh waste liquor)	pH 3.0 (liquor filtered from mill slurry)
Hastelloy C-276......	<1	<1
Incoloy 825..........	<1	<1
Cronifer 1713LCN.....	2.0	<1
Illium P.............	1.8	<1
316 stainless steel..	1.0	<1
NiResist.............	290	77
NP599 stainless steel	2.0	<1
CA6NM stainless steel	47	<1
Cr-Mo white iron.....	840	580
NiHard 4 white iron..	820	360
NiHard 1 white iron..	770	440
Commercial steel ball	880	670

The static corrosion results can be compared with the results of other investigators on corrosion by H_3PO_4 and phosphoric acid fertilizers; no corrosion data by mill pond water are known. Riggs and Banks (24) showed that the maximum corrosion rate of 1020 carbon steel in an aqueous solution of H_3PO_4 occurred at 85 wt pct acid. Their maximum rate of 21 mpy is far below our mean value of 775 mpy for high-carbon steel commercial ball material. In studies of the corrosion of mild steel by ortho- and super-phosphoric acid fertilizers, Crow and Silverbert (25) found little corrosion except at the liquid-air interface, where rates reached 100 mpy. Hatfield (26) found corrosion rates of mild steel on the order of 1 mpy in a variety of fertilizers with a pH of 5.8 to 7.0. In evaluations of materials for processing phosphoric acid, Scott (27-28) found corrosion rates below 1 mpy at 200° F (93° C) for several types of stainless steel, Carpenter 20Cb-3, Monel, Illium G, Hastelloy B, and Hastelloy C, but measured a rate of 23 mpy for mild steel.

DISCUSSION

COMPARISON OF TESTS

The results of the erosion-corrosion tests in the larger and smaller ball mills can be compared with each other and with a few results of Oden (29) and Patterson (30) in table 6. The tests by Oden were conducted by rotating a disk specimen at a peripheral speed of 1.4 m/s in H_3PO_4-phosphate rock slurry at 170° C. The test specimens of Patterson were located in a phosphoric acid reactor at the foam-slurry interface at 105° to 125° C.

Comparison of the present results shows that the erosion-corrosion rates for two white irons and the commercial steel ball material were roughly the same for the two sizes of ball mills. However, the rate of the more corrosion-resistant alloys was only 5 to 10 pct as much in the smaller mill as in the larger mill. The larger mill, capable of producing much greater impacts between specimens, undoubtedly damaged the passivated surface, and this resulted in much greater erosion-corrosion rates. In the small mill, however, the impacts were not sufficiently intense to remove the passivated surface of the more corrosion-resistant alloys. Therefore, the erosion-corrosion rates of the more corrosion-resistant alloys were much lower in the small mill. The widely different results between the large and small ball mills illustrate the limitations of erosion-corrosion data from small laboratory ball mills.

The slurry pot tests of Oden gave wear rates that were very similar to those of the larger ball mill for 316 stainless steel and about half for Incoloy 825. For Hastelloy C-276 the rate in the small ball mill was about 5 times greater than the rate by Oden, and the rate in the larger ball mill was over 50 times greater than Oden's. These results again agree with the idea that a passivated surface can be damaged by impact. Actually, the conditions in ball mills are more harsh at comparable temperatures than the above factors indicate because the temperature of the slurry pot was over 100° C higher than that of the ball mills.

TABLE 6. - Comparison of erosion-corrosion data, mils per year

Material	60-cm mill	12-cm mill	Oden[1]	Patterson[2]
Hastelloy C-276	560	47	10	ND
Incoloy 825....	935	43	411	68
Cronifer 1713LCN.......	795	50	ND	ND
Illium P.......	790	43	ND	ND
316 stainless steel.........	1095	120	1050	260
NiResist.......	1470	500	ND	ND
NP599 stainless steel.........	575	40	ND	ND
CA6NM stainless steel.........	880	170	ND	ND
Cr-Mo white iron..........	2465	2700	ND	ND
NiHard 4 white iron..........	1935	2600	ND	ND
NiHard 1 white iron..........	2180	320	ND	ND
Commercial steel ball....	1420	2250	ND	ND
Illium 98......	ND	ND	284	24
Carpenter 20Cb-3........	ND	ND	490	57

ND Not determined.

[1] Test conducted in slurry pot, 170° C, 1.4 m/s peripheral speed (29).

[2] Tests conducted in reactor at foam-slurry interface, 105° to 125° C (30).

The tests by Patterson, for the four materials that can be compared, gave erosion-corrosion rates that were only 8 to 25 pct of those of Oden. The temperature in Patterson's reactor was 65° to 45° C lower, which could account for the lower rates. The much higher wear rates obtained in the larger ball mill, at even lower temperature, must be attributed to erosion effects.

Wieser (31) conducted tests on seven types of stainless steel (none of which was the same as those in table 5) by rotating a disk in an alumina-acid slurry at a peripheral velocity of 5.7 m/s. In 40 pct H_3PO_4 the erosion-corrosion ranged from 20 to 160 mpy, far below the rates obtained for all stainless steels in the 60-cm ball mill tests.

EROSION-CORROSION SYNERGISM

The synergistic effect between erosion and corrosion is evident in data of table 7 and the bar graphs of these data in figure 7. The erosion-corrosion wear rate of all 12 alloys is greater than the sum of erosion and corrosion rates separately. For example, for Hastelloy C-276: the erosion-corrosion rate (phosphate rock milled in gypsum pond water) was 560 mpy, the erosion rate (phosphate rock milled in plain water) was 310 mpy, and the static corrosion rate was less than 1 mpy. These data give a ratio of erosion-corrosion to erosion plus corrosion, EC/E+C, of 1.80. Ratios for the other alloys are seen in table 7 to range from 1.15 for commercial ball material to 2.51 for castable stainless steel, CA6NM. The ranking of the wear rates for erosion-corrosion, erosion, and erosion plus corrosion are seen from table 6 to differ widely.

The combined results of all the tests show that erosion-corrosion rates cannot be predicted from erosion and corrosion data obtained separately. Tests of erosion-corrosion must be conducted under conditions that simulate service conditions very closely. The present laboratory tests show that erosion-corrosion data from the 12-cm ball mill cannot predict results for the 60-cm ball mill. Similarly, the data from the 60-cm ball mill cannot be expected to accurately predict wear in a large commercial mill. However, some trends may be predicted. In a larger mill where the erosion becomes much more severe, the nickel-base alloys and stainless steels would be expected to wear at a greater rate relative to the white cast irons and high-carbon steel (commercial ball material). That is, erosion would tend to dominate over corrosion in larger diameter mills.

TABLE 7. - Comparison of material loss rates

Material	EC[1]		E[2]		C[3]		E + C		Ratio
	mpy	Rank	mpy	Rank	mpy	Rank	mpy	Rank	EC/E+C
Hastelloy C-276......	560	1	310	2	<1	1	311	2	1.80
Incoloy 825..........	935	6	586	11	<1	1	587	7	1.59
Cronifer 1713LCN.....	795	4	448	7	1	3	449	5	1.77
Illium P.............	790	3	440	6	1	3	441	4	1.80
316 stainless steel..	1095	7	581	10	1	3	582	6	1.88
NiResist.............	1470	9	968	12	184	8	1152	11	1.28
NP599 stainless steel	575	2	267	1	1	3	268	1	2.14
CA6NM stainless steel	880	5	326	3	24	7	350	3	2.51
Cr-Mo white iron.....	2465	12	427	5	710	11	1137	10	2.17
NiHard 4 white iron..	1935	10	485	9	590	9	1075	9	1.80
NiHard 1 white iron..	2180	11	409	4	605	10	1014	8	2.15
Commercial steel ball	1420	8	458	8	775	12	1233	12	1.15

[1] Erosion-corrosion rate from milling phosphate rock in gypsum pond water for 1 h in 60-cm mill; initial pH 1.6, final pH 3.0.

[2] Erosion rate from milling phosphate rock in plain water for 1 h in 60-cm mill.

[3] Corrosion rate in stagnant gypsum pond water (phosphoric acid waste water); mean rate for pH 1.6 and pH 3.0 liquors from table 5.

EFFECTS OF VARIABLES

Multiple linear regression analysis was used to determine the significant factors that cause erosion-corrosion in the larger ball mill. The dependent factor was the erosion-corrosion rate for each material. Independent factors for the balls were hardness, static corrosion rate, erosion rate (phosphate rock in plain water), and eight elements of composition, namely, C, Mn, Si, Fe, Ni, Cr, Mo, and Cu. The significant factors were found to be hardness, static corrosion rate, erosion rate, carbon content, and silicon content. Silicon additions caused a decrease in erosion-corrosion rates; the other seven additions caused increases.

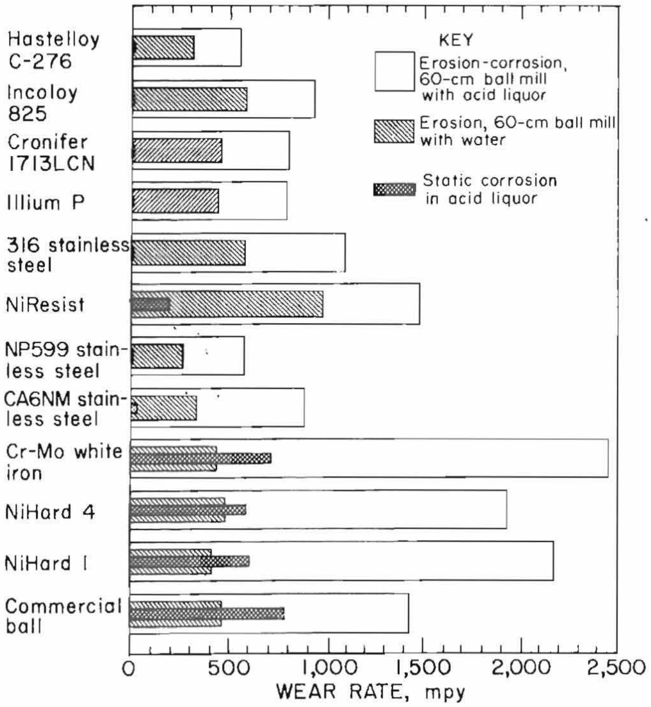

FIGURE 7. - Comparative wear, corrosion, and erosion-corrosion rates.

PRACTICAL CONSIDERATIONS

The relative cost of grinding media consumed for a given grinding time is presented in table 8. The costs were calculated from the erosion and erosion-corrosion rates of table 7 and the relative costs as given in table 1. In plain water, the present results show that the commercial ball material is the cheapest--a result that gives credence to the present experiments. In mill pond water, the commercial ball steel is still the cheapest, but the NP599 stainless steel is a very close second. The castable CA6NM stainless is about 30 pct more costly. The other stainless steels and white cast irons are two to three times more costly, and the nickel alloys are about five times as costly. As the mill diameter is increased, the proportion of erosion to corrosion could increase; therefore, the more corrosion-resistant alloys would be proportionately less cost effective. The difference between cost of commercial steel ball consumption and that of NP599 stainless would probably increase. Thus, it is believed that commercial steel balls are the most cost effective alloy for milling in low-pH conditions in large commercial ball mills.

TABLE 8. - Relative cost of alloys consumed during ball milling of phosphate rock concentrate

(Calculated values based on relative costs from table 1 and material loss rates from table 6)

Material	Milled in--	
	Plain water	Gypsum pond water
Commercial steel ball.	1	3.1
NP599 stainless steel.	1.5	3.1
CA6NM stainless steel.	1.6	4.2
Illium P.............	3.5	6.4
Cronifer 1713LCN......	4.1	7.3
NiHard 1 white iron...	1.4	7.6
NiHard 4 white iron...	2.1	8.4
316 stainless steel...	4.6	8.6
NiResist..............	6.3	9.6
Cr-Mo white iron......	2.0	11.3
Incoloy 825...........	8.7	13.9
Hastelloy C-276.......	8.8	15.9

Using commercial steel ball material in the 60-cm ball mill resulted in 3.1 times greater wear rate when grinding in phosphoric acid waste liquor than in water. A larger diameter commercial ball mill, in which the corrosion is reduced relative to erosion, would experience a cost factor less than 3.1 times the present cost. Whether or not this would be a cost effective way of disposing of gypsum pond water depends upon many other economic factors. The added metal contamination of the phosphate rock from corrosion could be disadvantageous, depending on the downstream effects on acidulation and fertilizer quality.

The mill liners and shells of commercial ball mills may present problems if gypsum pond water is used. Liner materials used at present may be satisfactory although their lifetime would be reduced. The shell of the ball mill would definitely need protection from phosphoric acid because corrosion of the shell could cause the entire mill to collapse. Because there is no abrasion on the shell, a highly corrosion-resistant alloy such as stainless steel or nickel alloy could be used. The corrosion rate would be about 1 mpy or less. An alternative is a rubber lining between the mill liners and the shell, including seals around the liner bolts, to keep acid from contacting the shell.

SUMMARY

Twelve alloys were evaluated for their wear rates by erosion-corrosion during ball milling of phosphate rock in gypsum pond water (phosphoric acid waste water) with a starting pH of 1.6. The alloyed white cast irons, normally very abrasion resistant, lost about 2,000 mpy or more. Commercial steel ball material currently used by the phosphate industry lost about 1,400 mpy. NiResist was about the same. The stainless steels and nickel-base alloys lost less than 1,100 mpy. The lowest losses, under 600 mpy, were found for Hastelloy C-276 and Armco NP599.

Separate tests of erosion (ball milling of phosphate rock in plain water) and static corrosion (in gypsum pond water) were conducted. For all alloys, the erosion-corrosion wear rate in the 60-cm ball mill was greater than the sum of erosion and corrosion rates. The erosion-corrosion synergism was particularly strong for the white cast irons. The nickel-base alloys had very low static corrosion rates (~1 mpy) but nevertheless displayed appreciable erosion-corrosion synergism. In the 12-cm mill, however, the erosion-corrosion rates differed greatly among the alloys because the reduced erosion allowed corrosion to become rate controlling.

It is estimated that the cost of grinding media when grinding in gypsum pond water would be no more than three times the cost of grinding in water as done at present. The overall cost effectiveness of disposing of the gypsum pond water by recycling it into the ball mills depends upon a number of other economic factors.

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APPENDIX.--ANALYZED COMPOSITION AND HARDNESS OF ALLOYS EVALUATED IN 12-CM BALL MILL

(Buttons were arc-melted and heat treated)

Material	Composition, wt pct								HB[1]
	C	Cr	Fe	Mn	Mo	Ni	Si	Other	
Ni alloy, Hastelloy C-276	0.027	15.6	10.05	0.85	15.3	54.5	0.05	3.57 W, 0.04 Co	170
Ni alloy, Incoloy 825	.04	22.9	30.01	.29	2.42	41.7	.11	1.56 Cu, 0.90 Ti	137
Stainless steel, Cronifer 1713LCN	.013	17.4	62.58	1.73	4.22	13.3	.23	0.41 Cu, 0.12 N	156
High Cr-Ni steel Superalloy, Illium P.	.19	27.1	58.06	.55	3.19	7.60	.40	2.91 Cu	241
Stainless steel, type 316	<.01	18.3	65.07	1.82	2.29	12.0	.52	NA	149
Ni-Cu-Cr steel alloy, NiResist	2.97	3.34	70.2	.54	NA	14.9	1.88	6.17 Cu	197
Stainless steel, Armco NP599	.087	15.9	72.56	8.28	NA	2.31	.44	0.31 Cu, 0.11 N	207
Stainless steel, castable, CA6NM	<.01	13.5	81.76	.009	.76	3.95	<.01	NA	229
High Cr-Mo white cast iron	2.48	16.1	79.19	.54	1.27	.30	.12	NA	578
Ni-Cr white cast iron, NiHard 4	3.51	9.23	78.75	1.05	.22	5.48	1.76	NA	653
Ni white cast iron, NiHard 1	3.45	3.58	87.42	.62	.03	4.30	.60	NA	578
High-carbon steel, commercial ball	.86	.12	98.20	.57	.039	.07	.06	0.08 CU	477

NA Not available.

[1] Brinell hardness number.

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