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Corrosion Resistance of Ceramic Materials to Hydrochloric Acid

By James P. Bennett



UNITED STATES DEPARTMENT OF THE INTERIOR

Report of Investigations 8807

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UNITED STATES DEPARTMENT OF THE INTERIOR

James G. Watt, Secretary

BUREAU OF MINES

Robert C. Horton, Director

Research at the Tuscaloosa Research Center is carried out under a memorandum of agreement between the Bureau of Mines, U.S. Department of the Interior, and the University of Alabama.

Library of Congress Cataloging in Publication Data:

Bennett, James P. (James Philip), 1951-

Corrosion resistance of ceramic materials to hydrochloric acid.

(Report of investigations ; 8807)

Bibliography: p. 14.

Supt. of Docs. no.: I 28,27:8807.

I. Ceramic materials--Corrosion. 2. Hydrochloric acid. I. Title.
II. Series: Report of investigations (United States. Bureau of Mines) ;
8807.

TN23,U43 [TA455.C43] 622s [620.1'404223] 83-600227

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UNIT OF MEASURE ABBREVIATIONS USED IN THIS REPORT

°C	degree Celsius	mm	millimeter
g/cm ³	gram per cubic centimeter	μm	micrometer
h	hour	pct	percent
in	inch	psi	pound per square inch
L	liter	wt pct	weight percent
min	minute		

CORROSION RESISTANCE OF CERAMIC MATERIALS TO HYDROCHLORIC ACID

By James P. Bennett¹

ABSTRACT

To identify construction materials for emerging technology in chemical and metallurgical processes, the Bureau of Mines investigated the acid resistance of ceramic materials. Eight commercial ceramic materials comprising two red shale, two fire clay, a silica, a five-clay-bonded silicon carbide, a carbon, and a high-alumina brick were evaluated. Samples were exposed for 110 days to 20 wt pct HCl at 50°, 70°, and 90° C and to 30 wt pct HCl at 70° C. Statistically significant changes in cold crushing strength, volume, and weight were generally small or not detected. The leach rates of Al, Ca, Fe, K, Mg, Na, Si, and Ti ions were monitored. The carbon brick sample had the best acid-resistant properties with a maximum total leached ion weight loss of 0.004 wt pct. The silicon carbide, the silica, and one of the fire clay bricks also had excellent acid-resistant properties.

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INTRODUCTION

New mineral processing techniques being investigated by the Bureau of Mines and others, such as processing at elevated temperatures, leaching with acids and bases, chloride leaching, and dissolution in fused-salt baths, may require the use of construction materials that have superior corrosion resistance. One example is the construction material needed to line leaching vessels used in the extraction of alumina from clay using HCl (hydrochloric acid), HNO₃ (nitric acid), or H₂SO₄ (sulfuric acid). In the HCl extraction processes studied by the Bureau, acid concentrations range from 1 to 35 pct (1)² with temperatures from 50° to 900° C (2).

Industrial equipment designers, fabricators, and material suppliers of acid processing systems were surveyed for their recommendations on ceramic construction materials to be used in HCl environments. Although the suppliers recommended acid brick, carbon brick, or dense fire brick, they indicated that they had little experience with HCl environments and advised that brick be tested in an environment simulating actual conditions. In general, the suppliers could say only that their brick would pass ASTM-C279 (3) specifications, which deal with H₂SO₄ rather than HCl.

A general rating of the performance of 17 ceramic materials when subjected to different acids was reported by Campbell and Sherwood (4) in 1967 with no reference to acid concentrations or temperatures. A general ranking of the resistance of 10 ceramic materials to acid attack was made by Lay (5) in 1979 based on data from literature and commercial

manufacturers and on the weight loss of materials exposed to concentrated boiling acid for about 30 min.

Weight loss, modulus of rupture, and cold crushing changes were determined on pulp digester brick exposed to HCl and sulfite pulp mill liquors by Kelly, Mainhardt, and Strandberg (6). The resistance of a reaction-bonded silicon carbide exposed to various acids, bases, molten salts, and metals at temperatures ranging from room temperature to 1,100° C and times of 0.5 to 168 h was listed in a report by Clinton, Lay, and Morrell (7). The chemical resistance was determined by visual appearance and specimen weight loss per unit surface area.

A 1981 literature review by T. A. Clancy (8) on the corrosion of ceramic materials by various aqueous solutions of acids and bases indicated that nearly all the data available refer to glass. Corrosion data on other industrial ceramic products are scarce and based primarily upon supplier information, which often does not cover the specific conditions of interest. This lack of definitive data is partly due to the wide variation in industrial products and their applications. Therefore, engineering data on the corrosion resistance of candidate materials under a variety of conditions are necessary.

This report presents the results of tests to evaluate the resistance of eight commercially available ceramic materials (two red shale, two fire clay, a carbon, a silica, a fire-clay-bonded-silicon carbide, and a high-alumina brick) exposed for 110 days to 20 wt pct HCl at 50°, 70°, and 90° C and to 30 wt pct HCl at 70° C. The effects of acid replenishment or sample replacement on ion leach rates were also determined.

²Underlined numbers in parentheses refer to items in the list of references at the end of this report.

TEST EQUIPMENT AND SAMPLE DESCRIPTION

Test equipment to evaluate changes occurring in ceramic materials under various conditions of exposure was designed and constructed (9). The test unit, shown in figure 1, operates at temperatures up to 250° C. Heat is supplied to the spherical Pyrex³ reaction vessel by heating mantles. The temperature is controlled by means of a variable power source and monitored in the reactor by a type K thermocouple. A peristaltic pump can withdraw, add, or circulate liquid in the system. The system is continuously agitated by a variable-speed stirrer, while a condenser refluxes any vapor and maintains the system at atmospheric

pressure. Samples being tested are placed on a 3/8-in Teflon platform. Grooves cut in the upper surface of the platform allow liquid to circulate under each test specimen. The platform is prevented from moving by embedding the supporting legs in layers of 6-mm glass beads. Bulk density and percent apparent porosity were also measured on each test specimen, using ASTM test C-20 (10).

Atomic absorption was used to measure ion concentration in solution. A vessel containing no test samples was used as a control to monitor background ion concentration.

³Reference to specific products does not imply endorsement by the Bureau of Mines.

Samples were examined optically, at a magnification of 20, for any structural or mineralogical changes that might be

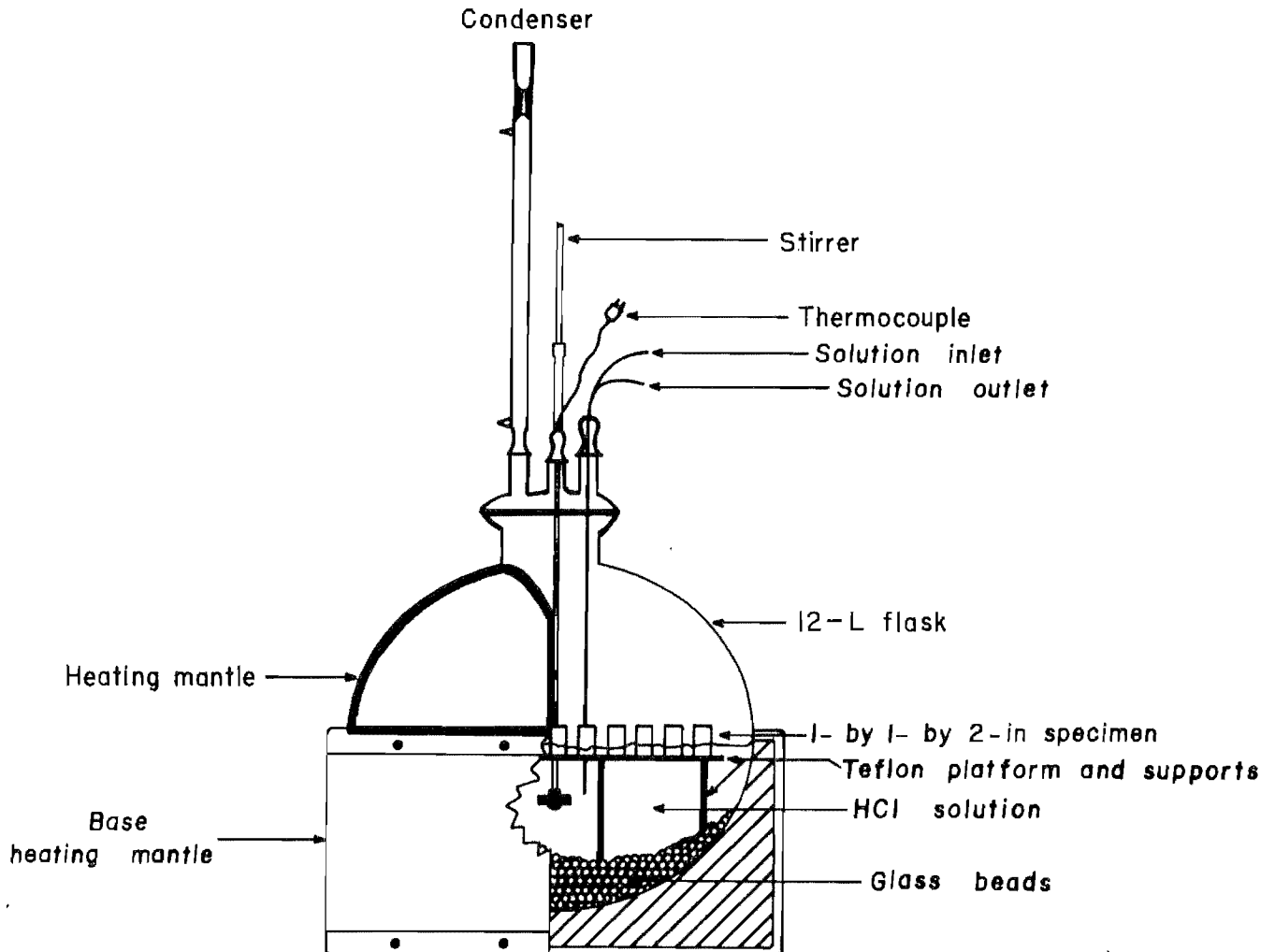


FIGURE 1. - Construction detail of reaction vessel.

TABLE 1. - Chemical and physical properties of commercial ceramic materials

Property	Acid-proof brick				Acid-resistant brick			
	Red shale		Fire clay		SiC (fire clay bonded)	Silica	Carbon	High alumina
	A	B	A	B				
Chemical composition, wt pct:								
SiO ₂	64.6	63.3	59.4	68.6	¹ 9.6	98.4	0.27	8.5
Al ₂ O ₃	20.6	20.7	31.7	22.9	.76	.51	.10	85.6
Fe ₂ O ₃	6.4	5.9	2.0	1.9	.37	.12	.047	.31
K ₂ O.....	3.6	4.6	3.0	1.5	.046	.049	.0037	.07
TiO ₂	1.6	1.6	1.7	1.4	.11	<.05	.0020	.12
MgO.....	.99	1.3	.35	.56	.035	.056	.0083	1.9
Na ₂ O.....	.58	.57	.27	.27	.017	.53	.013	.20
CaO.....	.39	.05	.03	.06	.22	.12	.01	.11
Carbon.....	NA	NA	NA	NA	NA	NA	96.3	NA
Sulfur.....	NA	NA	NA	NA	NA	NA	1.2	NA
SiC.....	NA	NA	NA	NA	¹ 87.9	NA	NA	NA
Apparent porosity....pct..	10.86	3.26	5.66	11.06	10.89	11.91	10.3	.54
Bulk density.....g/cm ³ ..	2.39	2.56	2.38	2.26	2.64	1.90	1.61	3.70

NA Not analyzed.

¹Chemical analysis supplied by manufacturer.

occurring. Electron probe analysis was used to determine locations where ions were leached from the samples.

Properties of four types of brick commonly referred to in industry as acid proof are listed in table 1. The four acid-proof brick are specified as red shale A and B and fire clay A and B. The main chemical differences are in the

alkali and alkaline earth metals present and the iron content. Red shale A and fire clay B brick have high apparent porosity and low bulk density. Table 1 also lists the chemical and physical properties of four ceramic brick classified as acid resistant and labeled as high alumina, carbon, silica, and silicon carbide (SiC).

RESULTS AND DISCUSSION

ACID-PROOF BRICK

Volume changes occurring in the acid-proof brick are listed in table 2. Statistically significant⁴ volume increases occur and increase with increasing temperature or acid concentration, reaching an expansion from 0.25 to 0.44 pct in 20 wt pct HCl at 90° C for red shale brick A and B and fire clay brick B. Fire clay brick A has an initial volume expansion that decreases with increasing

temperature to a volume loss of 0.25 pct in 20 wt pct HCl at 90° C.

Weight changes for the acid-proof brick are also listed in table 2. All brick except red shale brick B at 70° C in 20 wt pct HCl show an increasing weight loss with an increase in temperature or acid concentration. The red shale A and fire clay B brick, which have the highest apparent porosity, also have the highest weight losses of 6.13 pct and 6.57 pct respectively when exposed to 20 wt pct HCl at 90° C. Weight losses for red shale brick B and fire clay brick A are less than 1 pct.

⁴Statistically significant changes (Student's t-test) at a 95-pct confidence level, compared with data for untreated specimens (11).

TABLE 2. - Changes in volume and weight of acid-proof brick exposed to HCl for 110 days, percent

Exposure conditions ¹	Red shale		Fire clay	
	Brick A	Brick B	Brick A	Brick B
VOLUME CHANGE				
50° C, 20 HCl.....	-0.12±0.13	+0.05±0.06	+0.10±0.11	+0.10±0.20
70° C, 20 HCl.....	+0.23± .04*	+0.06± .12	+0.08± .04*	+0.13± .02*
90° C, 20 HCl.....	+0.44± .05*	+0.27± .08*	-0.25± .05*	+0.25± .04*
70° C, 30 HCl.....	+0.13± .12	+0.47± .13*	-0.09± .07*	+0.28± .05*
WEIGHT CHANGE				
50° C, 20 HCl.....	-2.25±0.33*	-0.30±0.11*	-0.00±0.02	-0.44±0.07
70° C, 20 HCl.....	-4.08± .26*	+0.09± .02*	-0.03± .04	-1.24± .05*
90° C, 20 HCl.....	-6.13± .33*	-0.95± .32*	-0.90± .07*	-6.57± .32*
70° C, 30 HCl.....	-3.11± .34*	-0.35± .11*	-0.22± .06*	-2.21± .05*

¹HCl in weight percent.

*Statistically significant change at 95-pct confidence level, compared with data for untreated specimen (Student's t-test).

Cold crushing strength data for the acid-proof brick after exposure to various HCl environments are given in table 3. No trends in crushing strength changes are noted for any of the acid-proof brick, in spite of the amount of material leached from several brick. No statistically significant differences were noted between the cold crushing strength values of the top (vapor exposed) or the bottom (liquid exposed) half of the test samples.

The weight percent of ions leached after 110 days from the four types of acid-proof brick are listed in table 4. No silicon was detected as leached from the samples. Generally, the amount of ions leached from the samples increased with increasing temperature or acid concentration to a maximum ion loss in 20 wt pct HCl at 90° C.

TABLE 3. - Cold crushing strength of acid-proof brick exposed to HCl for 110 days, pounds per square inch

Exposure conditions ¹	Red shale		Fire clay	
	Brick A	Brick B	Brick A	Brick B
Unexposed.....	18,800±1,500	20,300±1,700	9,800±1,300	9,700± 650
Top: ²				
50° C, 20 HCl.....	16,200±1,100*	19,100±2,100	12,900±1,600	11,200±2,600
70° C, 20 HCl.....	18,200±1,300	19,400±1,800	10,500±2,100	10,400± 810
90° C, 20 HCl.....	22,400±1,900*	23,000±2,400	8,500±1,000	10,300±1,200
70° C, 30 HCl.....	19,900±1,000	18,900±1,200	9,400±1,500	10,500± 850
Bottom: ³				
50° C, 20 HCl.....	17,500±1,400*	17,600±1,300*	12,400±1,300*	11,000±2,500
70° C, 20 HCl.....	17,500±1,300	19,500±1,510	10,600±1,600	10,000± 920
90° C, 20 HCl.....	19,300±1,500	21,600±1,900	8,100±1,200*	8,800± 920
70° C, 30 HCl.....	21,200±1,700*	20,000±1,700	9,500±1,300	10,300± 920

¹HCl in weight percent.

²Top half of sample, exposed to gas.

³Bottom half of sample, exposed to HCl solution.

*Statistically significant change at 95-pct confidence level, compared with data for untreated specimen (Student's t-test).

TABLE 4. - Ions leached in 110 days from acid-proof brick, weight percent

Brick and exposure conditions ¹	Ion leached							Total ions leached
	Al	Ca	Fe	K	Mg	Na	Ti	
Red shale A:								
50° C, 20 HCl.....	0.081	0.0450	0.97	0.015	0.026	0.0009	0.013	1.15
70° C, 20 HCl.....	.294	.0700	1.80	.065	.074	.0238	.052	2.38
90° C, 20 HCl.....	.972	.0666	2.14	.248	.161	.0554	.103	3.75
70° C, 30 HCl.....	.186	.0593	1.57	.040	.066	.0138	.059	1.99
Red shale B:								
50° C, 20 HCl.....	.031	.0227	.159	.010	.0090	.0031	.0029	.23
70° C, 20 HCl.....	.039	.0141	.153	.018	.0099	.0042	.0050	.24
90° C, 20 HCl.....	.314	.0719	.675	.142	.0568	.0231	.0221	1.31
70° C, 30 HCl.....	.093	.0145	.528	.030	.0240	.0075	.0170	.71
Fire clay A:								
50° C, 20 HCl.....	.006	.00017	.0118	.0009	ND	.00022	.0013	.020
70° C, 20 HCl.....	.023	.00016	.0219	.0025	.00117	.00053	.0051	.054
90° C, 20 HCl.....	.351	.00607	.0667	.0200	.00660	.00435	.0254	.480
70° C, 30 HCl.....	.055	.00024	.0365	.0029	.00241	.00083	.0137	.112
Fire clay B:								
50° C, 20 HCl.....	.03	.0061	.095	.004	.0026	.0022	.015	.16
70° C, 20 HCl.....	.24	.0145	.186	.018	.0114	.0091	.056	.54
90° C, 20 HCl.....	2.22	.0234	.514	.146	.0415	.0506	.147	3.14
70° C, 30 HCl.....	.52	.0254	.359	.031	.0241	.0145	.175	1.15

ND Not detected.

¹HCl in weight percent.

During the leaching period of 110 days, the rate at which ions were leached from the samples at any given temperature and acid condition tended to follow a second-order parabolic equation, in its general form listed as

$$y = a_1 + a_2x + a_3x^2,$$

where y = ion concentration in solution, x = days, and a_1 , a_2 , a_3 = constants. Out of 117 curves, 101 yielded coefficients of correlation above 0.95.

Red shale brick A lost mainly Fe (2.14 wt pct) and Al (0.97 wt pct) in 20 wt pct HCl at 90° C, with 0.1 wt pct or less of either Ca, Na, or Ti removed.

Red shale brick B had 0.68 wt pct Fe and 0.31 wt pct Al leached when exposed to 20 wt pct HCl at 90° C. Ca, Mg, Na, and Ti ions were removed at levels below

0.1 wt pct. The lower leach values for red shale brick B compared with red shale brick A are probably due to the lower porosity of the former.

With the two fire clay bricks A and B, the Al ion was leached at the highest rate, followed by Fe, Ti, and K. The amount of Al ion leached increased from 0.03 to 2.22 wt pct for brick B and from 0.006 to 0.351 wt pct for brick A with increasing temperature in 20 wt pct HCl. The amount of Al ion removed from fire clay brick B was the highest level of any ion removed from the eight acid-proof or acid-resistant brick tested. Changing acid concentration from 20 to 30 wt pct HCl at 70° C resulted in an increase in the leached levels of all ions. The higher leach rates for each ion of fire clay brick B are probably due to the higher porosity of this brick versus fire clay brick A.

Figure 2 shows the total weight percent of ions removed from the acid-proof brick after 110 days of exposure to 20 wt pct HCl at 50°, 70°, and 90° C. Both the red shale and fire clay brick show an increase in the amount of total ion leached from the samples with an increase in temperature. Red shale brick A has the most ions leached, reaching 3.75 wt pct at 90° C. As mentioned previously, those samples with the highest porosity have the highest rate of ion removal.

The general trend of increasing ion weight loss with increasing temperature or acid concentration coincided with decreasing sample weight changes in the acid-proof brick.

In spite of the amount of ions leached from both the fire clay and red shale brick, no correlation exists between increased leaching and cold crushing strength values. This may be due to the

lack of silicon ion removal from any of the specimens, indicating that the silicate-rich bonding phase in the brick was not weakened.

It was observed that the acid-proof brick samples were bleached to lighter colors after exposure to the various HCl environments. The red shale brick changed from a red color to a light pink when exposed to the most severe corrosion condition of 20 wt pct HCl at 90° C. This was caused primarily by the removal of iron from the samples. The fire clay brick changed in appearance from a buff to a light cream color.

The leaching of iron occurring as hematite was visible in the microstructure of all acid-proof brick except fire clay brick A. Optical micrographs of red shale brick A before and after exposure to 20 wt pct HCl at 90° C for 110 days are shown in figure 3. Micrograph A is

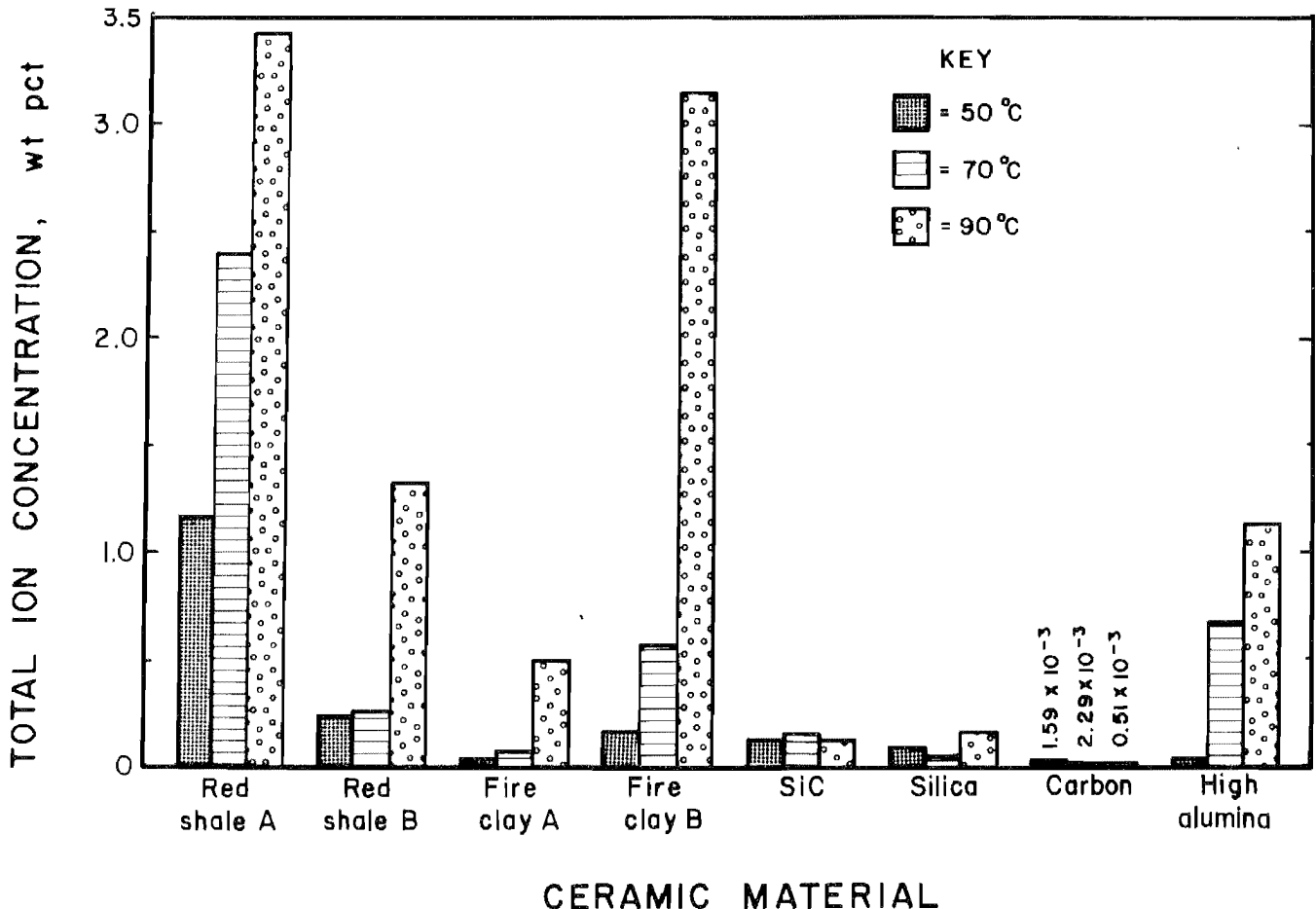


FIGURE 2. - Total ion leached from ceramic samples in 110 days in 20 wt pct HCl.

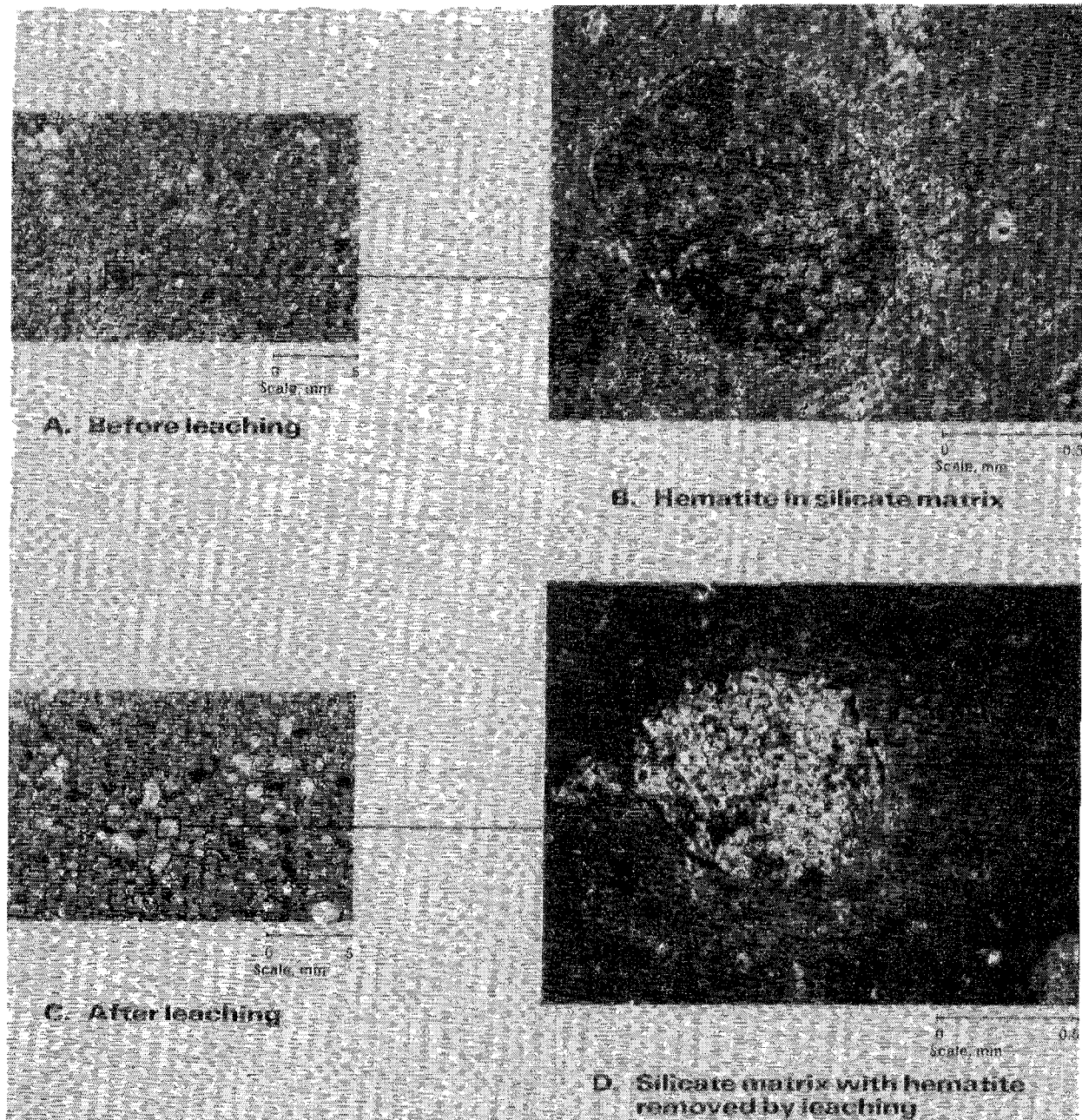


FIGURE 3. - Red shale brick A before and after exposure to 20 wt pct HCl at 90° C for 110 days.

an overall view of the sample before exposure to acid. Dark areas such as the spot shown in the enlarged micrograph B contain hematite in a silicate matrix. Micrograph C is an overall sample view after acid exposure; the sample contains a large number of bleached grains, also shown in the enlarged micrograph D. The hematite is leached from the sample, leaving voids in the silicate matrix but leaving the grain intact and consequently not weakening the structure.

ACID-RESISTANT BRICK

Statistically significant volume changes occur in an inconsistent manner for all acid-resistant brick, as shown in table 5. No trends were observed with changes in acid concentration or temperature, and the reason for the variable results is not known.

Statistically significant weight changes occurring in the acid-resistant brick

TABLE 5. - Changes in volume and weight of acid-resistant brick exposed to HCl for 110 days, percent

Exposure conditions ¹	SiC	Silica	Carbon	High alumina
VOLUME CHANGE				
50° C, 20 HCl.....	+0.34±0.09*	+0.17±0.10*	-0.26±0.04*	-0.34±0.04
70° C, 20 HCl.....	-.12± .03*	+.01± .04	-.06± .07	+.17± .03*
90° C, 20 HCl.....	-.01± .05	+.70± .18*	+.03± .04	-.09± .04*
70° C, 30 HCl.....	-.10± .05*	-.27± .06*	+.38± .18*	-.28± .08*
WEIGHT CHANGE				
50° C, 20 HCl.....	-0.29±0.04*	-0.30±0.02*	+0.40±0.04*	-0.07±0.02*
70° C, 20 HCl.....	-.24± .02*	-.20± .02*	+.75± .01*	-1.36± .05*
90° C, 20 HCl.....	-.19± .02*	-.61± .03*	+.99± .07*	-1.98± .08*
70° C, 30 HCl.....	-.25± .02*	-.44± .04*	+1.50± .10*	-.90± .10*

¹HCl in weight percent.

*Statistically significant change at 95-pct confidence level, compared with data for untreated specimen (Student's t-test).

are also listed in table 5. The silica and high-alumina brick show an increase in weight loss with an increase in temperature or acid concentration. The silica brick had a maximum weight loss of 0.61 pct in 20 wt pct HCl at 90° C, and the high-alumina brick a maximum loss of 1.98 wt pct. The SiC brick samples had an average weight loss of about 0.25 wt pct under all the test conditions. The carbon brick, in contrast, showed an increase in weight with increasing temperature in 20 wt pct HCl, changing from 0.40 wt pct at 50° C to 1.50 wt pct at 90° C. This was the only brick tested that showed a consistent weight gain, probably caused by the adsorption of ions on carbon surfaces.

Cold crushing strength values for the acid-resistant brick are given in table 6. The silica brick show small statistically significant increases in crushing strength when exposed to increasing temperature or acid concentration. The carbon brick exhibits a decrease in crushing strength with increasing temperature when compared with the value of 8,000 psi for unexposed samples. The SiC and high-alumina bricks' crushing strength tended to remain constant with changes in temperature or acid concentration. No significant differences exist between cold crushing strength values of the top

(vapor exposed) and bottom (liquid exposed) half of the test samples.

The weight percent of ions leached after 110 days of brick exposure to various HCl environments are listed in table 7. As was noted with the acid-proof brick, no silicon was detected as leached from the samples.

The SiC brick has less than 0.02 wt pct of each of the Al, Ca, Mg, Na, K, and Ti ions leached from it in all HCl environments tested. Only the Fe ion was leached at a rate of about 0.1 wt pct. The constant amount of ions leached at all temperatures and acid concentrations was in agreement with the constant weight change results listed in table 5. The few statistically significant changes in cold crushing strength observed for this brick also support the low leach rates.

The silica brick leach data in table 7 indicated an increase in the weight percent of ions leached with increasing acid concentration or temperature. In 20 wt pct HCl at 90° C, the maximum total ion removal amounts to 0.16 wt pct. The ion leach data changes are in good agreement with the small weight changes noted in table 5 for the silica samples and the slight increase in cold crushing strength noted in table 6.

TABLE 6. - Cold crushing strength of acid-resistant brick exposed to HCl for 110 days, pounds per square inch

Exposure conditions ¹	SiC	Silica	Carbon	High alumina
Unexposed.....	14,400±1,000	4,100±340	8,000±470	58,500± 8,100
Top: ²				
50° C, 20 HCl.....	13,000± 900	3,700±200	7,200±700*	68,400±10,000
70° C, 20 HCl.....	13,400±1,000*	4,700±310*	5,800±450*	65,000± 6,010
90° C, 20 HCl.....	10,900± 930*	4,100±390	5,900±510*	78,600± 2,900*
70° C, 30 HCl.....	13,500± 880	4,700±270*	8,570±460	63,300± 8,000
Bottom: ³				
50° C, 20 HCl.....	12,400± 700*	3,600±100*	7,400±700	68,100±10,000
70° C, 20 HCl.....	14,700±1,400	5,000±380*	5,600±410*	62,000± 4,800
90° C, 20 HCl.....	10,300± 800*	3,800±380	5,800±520*	79,700± 2,800*
70° C, 30 HCl.....	13,800± 720	4,800±320*	8,900±380*	59,700± 9,600

¹HCl in weight percent.

²Top half of sample, exposed to gas.

³Bottom half of sample, exposed to HCl solution.

*Statistically significant change at 95-pct confidence level, compared with data for untreated specimen (Student's t-test).

TABLE 7. - Ions leached in 110 days from acid-resistant brick, weight-percent

Brick and exposure conditions ¹	Ion leached							Total ions leached
	Al	Ca	Fe	K	Mg	Na	Ti	
SiC:								
50° C, 20 HCl..	0.00432	0.00120	0.096	0.000425	0.000705	0.000341	0.0163	0.119
70° C, 20 HCl..	.00563	.00141	.118	.000409	.000725	.000180	.0055	.132
90° C, 20 HCl..	.00884	.00121	.109	.000296	.000574	.000354	ND	.120
70° C, 30 HCl..	.00375	.00080	.095	.000140	.000799	.000639	.0152	.116
Silica:								
50° C, 20 HCl..	.0178	.0103	.0368	.00326	.0056	.00094	.000207	.075
70° C, 20 HCl..	.0037	.0017	.0089	.00104	.0015	.00002	.000036	.017
90° C, 20 HCl..	.0543	.0291	.0578	.00497	.0110	.00272	ND	.160
70° C, 30 HCl..	.0264	.0117	.0215	.00125	.0056	.00087	ND	.067
Carbon:								
50° C, 20 HCl..	.00005	.00015	.00136	ND	ND	.000026	ND	.00159
70° C, 20 HCl..	.00012	ND	.00215	ND	.00002	ND	ND	.00229
90° C, 20 HCl..	ND	ND	.00051	ND	ND	ND	ND	.00051
70° C, 30 HCl..	.00092	ND	.00340	.0000334	.000053	ND	ND	.00441
High alumina:								
50° C, 20 HCl..	.006	.003	ND	.0001	ND	.0011	ND	.01
70° C, 20 HCl..	.410	.206	.00139	.0072	.0060	.0429	.00086	.67
90° C, 20 HCl..	.693	.327	.00383	.0123	.0245	.0672	.00121	1.13
70° C, 30 HCl..	.295	.159	.00112	.0053	.0050	.0313	.00067	.50

ND Not detected.

¹HCl in weight percent.

The carbon brick had few or no ions removed under all temperature and HCl conditions evaluated. The rate for Fe, which had the highest ion leach rate of all ions monitored, was below 0.0035 wt pct. In contrast, weight changes listed in table 5 indicated weight gains of up to 1.5 pct, and cold crushing values in table 6 indicated a general strength decrease.

The high-alumina brick samples showed a maximum of 0.693 wt pct Al and 0.327 wt pct Ca leached in 20 wt pct HCl at 90° C. As the temperature was increased from 50° to 90° C, the amount of ions removed increased. All other ions leached and analyzed for were at levels lower than 0.07 wt pct. At 70° C when the acid concentration was increased from 20 to 30 wt pct, the amount of ions removed decreased, in good agreement with the weight loss data listed in table 5. No correlation of total ion weight loss with cold crushing strength data was found.

During the 110-day leach cycle, the ion removal rate from the brick samples tended to fit the second-order parabolic equation discussed in the previous section on acid-proof brick. Sixty-eight out of 90 curves yielded coefficients of correlation above 0.90.

A plot of the total weight percent of ions removed from the acid-resistant brick in 110 days of exposure to 20 wt pct HCl is given in figure 2. Only the high-alumina brick showed a large increase in the weight percent of ions leached with increasing temperature, changing from 0.01 wt pct in 20 wt pct HCl at 50° C to 1.13 wt pct at 90° C. The loss, as mentioned earlier, is primarily due to leaching of Al and Ca ions.

The carbon, SiC, and silica brick show little change in the total amount of material leached into solution with changes in temperature or acid concentration. The carbon brick averages 0.001 wt pct total ions leached, the SiC brick about 0.12 wt pct, and the silica brick below 0.16 wt pct.

Scanning electron micrograph examinations of the microstructure of the acid-resistant brick revealed no visible changes except for the high-alumina brick. Figure 4 shows microstructural changes that occurred in the high-alumina brick after exposure to 20 wt pct HCl for 110 days at 90° C. Micrograph A of a cross section of a corner of a brick sample shows a lighter colored outer zone, about 4 mm thick, and a darker interior area. The leached exterior zone, shown in micrograph B, has a noticeable increase in small pores when compared with the interior of the sample, shown in micrograph C. This increase in porosity, due to removal of material at grain boundaries, had no immediate adverse effect on cold crushing strength values but may have one over longer exposure times.

SPECIAL LEACH TESTS--RED SHALE BRICK A

To determine if the increasing ion concentration in the leach liquors over a 110-day period affected the ion leach rates, two special tests were conducted in 20 wt pct HCl at 90° C using red shale brick A, which had demonstrated high levels of ion leaching. One test consisted of set of 30 samples exposed to a 20 wt pct HCl test solution that was changed every 30 days; the other test retained the same leach solution but the 30 test samples were replaced every 30 days.

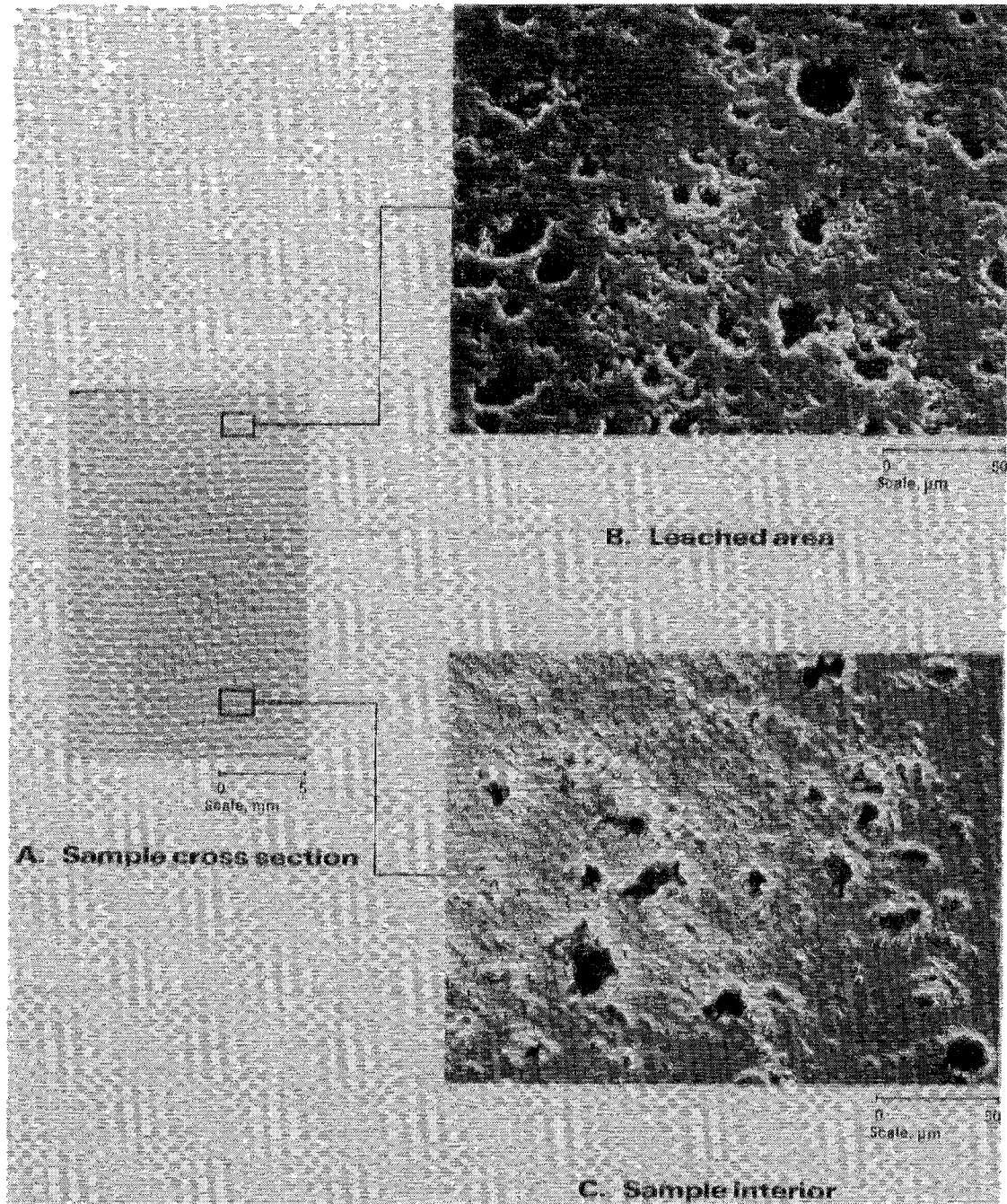


FIGURE 4. - High-alumina brick after exposure to 20 wt pct HCl at 90° C for 110 days.

Table 8 lists the quantity of ions leached from 30 samples of red shale brick A at 30-day increments when fresh acid solutions were introduced. The test environment was maintained at 90° C and 20 wt pct HCl. Two ions, Fe and Ca, tended to decrease in the amount leached from the samples over the test period. The Fe concentration in solution changed from 2.01 wt pct after the first 30-day

period to 0.38 wt pct during the fourth 30-day period. The Ca ion changed from 0.0336 wt pct ion leached to 0.0013 wt pct over the same time period. The Mg, Na, and Ti ions appear to be leached at a generally constant rate from the samples, while Al and K show a gradual increase in the quantity of ion removed during each 30-day increment.

TABLE 8. - Ion concentrations in 20-wt-pct-HCl solution at 90° C for red shale brick A after 30-day acid replacement and 30-day sample replacement intervals, weight percent

Ion leached	Interval			
	1st	2d	3d	4th
ACID REPLACED AT 30-DAY INTERVALS				
Al.....	0.305	0.283	0.367	.505
Ca.....	.0336	.0015	.0013	.0013
Fe.....	2.01	.53	.45	.38
K.....	.060	.054	.073	.105
Mg.....	.0643	.0424	.0482	.0497
Na.....	.0270	.0169	.0183	.0249
Ti.....	.0503	.0395	.426	.0403
SAMPLE REPLACED AT 30-DAY INTERVALS ¹				
Al.....	0.38 ¹	0.71	1.17	1.64
	(.38)	(.33)	(.46)	(.47)
Ca.....	.039	.091	.171	.249
	(.039)	(.052)	(.080)	(.078)
Fe.....	2.26	4.07	5.95	7.95
	(2.26)	(1.81)	(1.88)	(2.00)
K.....	.077	.161	.243	.349
	(.077)	(.084)	(.082)	(.106)
Mg.....	.080	.168	.250	.320
	(.080)	(.088)	(.082)	(.070)
Na.....	.032	.068	.098	.147
	(.032)	(.036)	(.030)	(.049)
Ti.....	.063	.115	.148	.190
	(.063)	(.052)	(.033)	(.042)

¹Numbers in parentheses refer to the amount of ions in solution removed from a particular set of samples.

Apparently ions that are easily leached from compounds, such as Fe from hematite, are rapidly removed from the red shale brick A, giving rise to high initial leach rates. The increase in the leach rate for Al and K ions if continued over a long period of time may result in physical property changes in the brick.

The quantity of ions leached from red shale brick A when a set of 30 test samples was replaced every 30 days in the

same leach solution is given in table 8. Ion concentrations listed are for the 30th day of sample exposure, when samples were changed. Al, Fe, Mg, Na, K, and Ti show about the same levels of ions leached from each set of 30 brick samples regardless of ion concentration in solution. The amount of Ca ion leached at the end of the fourth 30-day leach period was 0.078 wt pct, a slight increase compared to 0.039 wt pct for the first 30-day period.

CONCLUSIONS

A study of the effects of 20 wt pct HCl at 50°, 70°, and 90° C and of 30 wt pct HCl at 70° C on two red shale, two fire clay, a carbon, a silica, a fire-clay-bonded silicon carbide and a high-alumina brick after 110 days of exposure indicated the following:

1. Carbon brick had the best acid-resistant properties with a maximum total leached ion weight loss of 0.004 wt pct.

2. Silicon carbide and silica brick had excellent acid-resistant properties with total leached ion weight losses of 0.132 and 0.160 wt pct respectively.

3. Fire clay brick A and good acid-resistant properties with a total leached ion weight loss of 0.480 wt pct, which is better than the high-alumina brick, which had a 1.129-wt-pct loss.

4. Statistically significant physical property changes in strength and weight for all the evaluated materials were small, or were not detected. Volume increases were noted for two of the red shale, one of the fire clay, and the silica brick.

5. The silicon ion was not leached from any samples, indicating that the siliceous bond or silicate mineral phases were not affected; this may explain why

physical property changes were small or not observed.

6. In general, the Fe and Al ions have the highest ion removal rates, with Ca, Mg, Na, K, and Ti removal being minor.

7. Increasing temperature or acid concentration generally increased ion leach rates and sample weight loss values.

8. The parabolic nature of the leach rate curves appears not to be affected by the ion concentrations in the leach solutions, but to be controlled by the acid resistance of different bond and mineral phases of the brick.

REFERENCES

1. Eisele, J. A. Producing Alumina From Clay by the Hydrochloric Acid Process, A Bench-Scale Study. BuMines RI 8476, 1980, 21 pp.
2. Bengton, K. B., P. Chuberka, L. E. Malm, A. E. McLaughlin, R. F. Nunn, and D. L. Stein. Alumina Process Feasibility Study and Preliminary Pilot Plant Design. Task 1 Final Report. Comparison of Six Processes (contract J0265048, Kaiser Engineers). BuMines OFR 18-78, 1977, 253 pp.; NTIS PB 286/638.
3. American Society for Testing and Materials. Standard Specifications for Chemical-Resistant Masonry Units. C279-79 in 1981 Annual Book of ASTM Standards: Part 17, Refractories, Glass, Ceramic Materials; Carbon and Graphite Products. Philadelphia, PA, 1981, pp. 217-219.
4. Campbell, I. E., and E. M. Sherwood. High-Temperature Materials and Technology. John Wiley & Sons, Inc., New York, 1967, 1022 pp.
5. Lay, L. A. The Resistance of Ceramics to Chemical Attack. Nat. Phys. Lab. (Teddington, Middlesex, England), NPL Rept. CHEM 96, January 1979, pp. 1-27; available from National Technical Information Service, Springfield, VA, N79-26219.
6. Kelly, H. J., R. Mainhardt, and K. G. Strandberg. Factors Influencing
7. Premature Failure of Ceramic Digester Linings in Sulfite Pulp Mills. J. Am. Ceram. Soc., v. 36, No. 1, 1953, pp. 18-26.
8. Clancy, T. A. High-Temperature Corrosion Resistance of Ceramic Materials. BuMines IC 8843, 1981, 31 pp.
9. Bennett, J. P. Corrosion Resistance of Ceramic Materials to Hydrochloric Acid (20 Wt-Pct at 50° C). BuMines RI 8650, 1982, 11 pp.
10. American Society for Testing and Materials. Standard Test Methods for Apparent Porosity, Water Absorption, Apparent Specific Gravity, and Bulk Density of Burned Refractory Brick and Shapes by Boiling Water. C20-80a in 1981 Annual Book of ASTM Standards: Part 17, Refractories, Glass, Ceramic Materials; Carbon and Graphite Products. Philadelphia, PA, 1981, pp. 6-8.
11. Miller, I., and J. E. Freund. Probability and Statistics for Engineers. Prentice-Hall, Englewood Cliffs, NJ, 1965, 432 pp.