RI 8845

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Bureau of Mines Report of Investigations/1984

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UNITED STATES DEPARTMENT OF THE INTERIOR

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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:

Petty, A. V

High-temperature properties of alumina refractory brick impregnated with oxide and salt solutions.

(Bureau of Mines Report of investigations ; 8845)

Bibliography: p. 17-18.

Supt. of Docs. no.: I 28.23:8845.

1. Alumina brick—Thermal properties. 2. Oxides. 3. Salt. I. Title. II. Series: Report of investigations (United States. Bureau of Mines) ; 8845.

TN23.U43 [TA418.26] 622s [620.1'43] 83-600339

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UNIT OF MEASURE ABBREVIATIONS USED IN THIS REPORT

atm	atmosphere	lb/ft^3	pound per cubic foot
°C	degree Celsius	lb/in^2	pound per square inch
°F	degree Fahrenheit	lb/in^3	pound per cubic inch
g/cm^3	gram per cubic centimeter	min	minute
g/L	gram per liter	mm	millimeter
h	hour	pct	percent
in	inch	wt pct	weight percent
kg	kilogram		

HIGH-TEMPERATURE PROPERTIES OF ALUMINA REFRACTORY BRICK IMPREGNATED WITH OXIDE AND SALT SOLUTIONS

By Arthur V. Petty, Jr.[1]

ABSTRACT

The Bureau of Mines has investigated the effect of refractory oxide additions, introduced in soluble form, on the refractory properties of 42-, 58-, and 70-pct-Al_2O_3 brick. Brick having porosities ranging from 12 to 16 pct were impregnated with solutions containing chrome, chrome-iron, zirconium, calcium, magnesium, cobalt, nickel, tin, and manganese ions. Additions of some of these ions provided dramatic improvements to such properties as hot modulus of rupture, hot load, and particularly slag resistance. These improvements can be related to reduction of porosity, amorphous grain boundary phases, formation of more refractory bond phases, and reduction of the wettability of Al_2O_3-containing refractories by metallurgical slags.

Fifty-eight-percent-Al_2O_3 brick, impregnated with chrome, showed hot modulus of rupture, hot load, and slag resistance two to five times better than those of untreated 70-pct-Al_2O_3 brick. This could result in reducing the Nation's dependence on imported refractory-grade bauxite generally required for high-Al_2O_3 brick, as domestic alumina resouces could be used to produce the improved refractories.

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INTRODUCTION

Alumina refractories (Al_2O_3 content ranging from 42 to 99 pct) are being used in nearly all high-temperature metallurgical, glass, and cement processes. The world reserves of refractory-grade bauxite (RGB), which is a primary constituent of high-alumina (>70 pct Al_2O_3) refractories, are known to be quite extensive, but the politico-economic stability of the producing nations remains questionable.

Location of domestic resources in the form of natural mineral deposits or wastes containing >70 pct Al_2O_3, chemical beneficiation of clays and other domestic Al_2O_3-containing resources to obtain a high-Al_2O_3 concentrate, and recycling of high-Al_2O_3 refractories have all been investigated (1-3)[2] as routes to greater self-sufficiency in the area of alumina refractories. Another approach being investigated by the Bureau of Mines is to improve the high-temperature properties of lower Al_2O_3 (42 to 70 pct Al_2O_3) refractories produced from domestic resources to the point where they could be substituted for higher Al_2O_3 refractories requiring imported RGB.

In this study, three commercial refractory bricks, representing 42-, 58-, and 70-pct-Al_2O_3 compositions, were impregnated with saturated or near-saturated solutions of one oxide, two mixtures of oxide and metal salt, and seven different refractory metal salts. Following impregnation and firing to 1,450° C to allow decomposition of the salts and reaction between the resulting oxide(s) and refractory phases present initially, the brick were tested for room temperature compressive strength, hot modulus of rupture (MOR), deformation under load (hot load), and slag resistance. X-ray diffraction was used in mineralogical studies and polished sections prepared for optical and scanning electron microscopy. This report summarizes the results of this work and compares these results to those obtained on identical, but untreated, commercial refractory brick.

REFRACTORY BRICK AND SAMPLE PREPARATION

Three commercially available refractory brick were chosen as representative of those having alumina contents between 42 and 70 pct Al_2O_3 and porosities ranging from 12 to 16 pct. Compositions and properties based on manufacturer's data sheets are summarized in table 1.

Test samples were prepared from the commercial brick in the following manner:

1. Core samples were taken from the center of full-size (9- by 4-1/2- by 3-in) brick for cold compressive strength and polished sections. Cores were sectioned to provide samples 1-1/4 in in diameter and 3/4 in long.

2. Bars measuring 1 by 1 by 9 in were cut from commercial brick according to ASTM C 583-80 (4) for hot MOR tests.

3. Full-size brick were used for hot load tests according to ASTM C 16-77 (5).

4. Wedge-shaped samples were cut from full-size brick for use in rotary slag tests (6).

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

TABLE 1. - Composition and refractory properties of commercial Al_2O_3 refractories

	Commercial refractory brick		
	A	B	C
Chemical analysis, wt pct:			
Alumina (Al_2O_3)........................	41.9	58.0	69.2
Silica (SiO_2)........................	53.2	38.0	26.2
Titania (TiO_2)........................	2.2	2.4	2.9
Iron oxide (Fe_2O_3)..................	1.0	1.3	1.3
Lime (CaO)........................	0.2	0.1	0.1
Magnesia (MgO)........................	0.3	0.1	0.1
Alkalies ($Na_2O + K_2O + Li_2O$)........	1.2	0.1	0.2
Physical property:			
Bulk density................lb/ft^3..	144-148	156-160	157-161
Apparent porosity..............pct..	11.0-14.0	12.0-16.0	15.0-19.0
Cold crushing strength......lb/in^2..	1,800-3,000	7,000-10,000	6,000-9,000
Modulus of rupture (room temperature)..............lb/in^2..	700-1,000	2,300-3,300	1,700-2,400
Hot load test (25 lb/in^2 to 1,450° C (2,640° F)).......pct deformation..	1.0-3.0	0.1-0.5	0.4-1.0

IMPREGNATION--SOLUTIONS, EQUIPMENT, AND TECHNIQUE

There are relatively few mineral commodities that are suitable (i.e., high melting point, mineral stability, and physical and chemical properties) for use in refractory materials to be used above 1,000° C. Alumina easily satisfies all of these requirements and because of its excellent chemical inertness finds many applications in very diverse temperatures and environments. Impurities associated with alumina, including free iron, titania, and alkalies, can have a very detrimental effect on the high-temperature properties of alumina refractories owing to reactions that produce low-melting secondary crystalline phases or glasses, which soften at high temperatures, causing deformation and/or loss of strength. For this reason, these impurities are avoided as much as practical during beneficiation, batching, and forming. Small quantities of these impurities are found in all but the most expensive refractory products and often limit their upper use temperature. Based on the literature from several major refractory producers (7-10), impurity levels in commercial alumina refractories having Al_2O_3 contents from 42 to 70 pct range from 1 to 2 pct iron, 1 to 3 pct titania, and 0.1 to 2.5 pct alkali. If small amounts of other refractory oxides could be added to react with these impurities to form high-temperature solid solutions or crystalline phases or to prevent the formation of amorphous, glassy phases at grain boundaries, then the high-temperature refractory properties, and thus the upper use temperature, could be increased.

A total of 10 solutions were prepared as shown in table 2. Oxide and salts were chosen primarily because of their high water solubilities and relative high-temperature stability. All solutions were prepared using technical-grade materials, when available, or reagent-grade and deionized water.

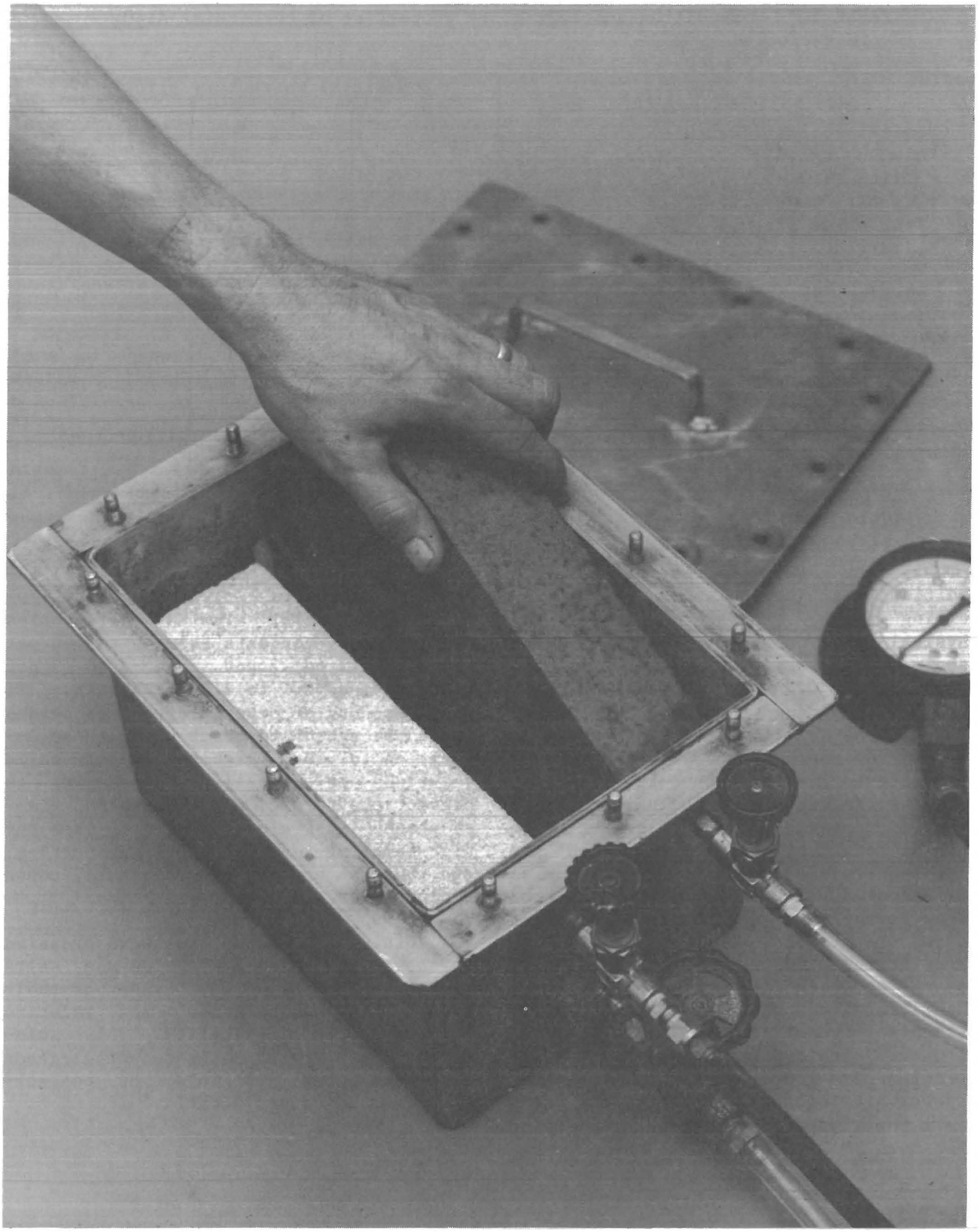

FIGURE 1. - Stainless steel vacuum impregnation chamber.

TABLE 2. - Composition of additives

Salt	Solution concentration, g/L of H_2O	Residual oxide following heating above decomposition temperature
Chromium trioxide (CrO_3)............	1,000	Cr_2O_3.
Chromium trioxide (CrO_3) plus ferric chloride ($FeCl_3 \cdot 6H_2O$).	50--CrO_3, 121.5--$FeCl_3 \cdot 6H_2O$	Cr_2O_3 + Fe_2O_3.
Chromium trioxide (CrO_3) plus ferric chloride ($FeCl_3 \cdot 6H_2O$).	100--CrO_3, 121.5--$FeCl_3 \cdot 6H_2O$	Cr_2O_3 + Fe_2O_3.
Zirconyl chloride ($ZrOCl_2 \cdot XH_2O$).....	500	ZrO_2.
Nickelous chloride ($NiCl_2 \cdot 6H_2O$).....	300	NiO.
Cobalt nitrate ($Co(NO_3)_2 \cdot 6H_2O$)......	500	CoO.
Magnesium nitrate ($Mg(NO_3)_2 \cdot 6H_2O$)...	500	MgO.
Calcium nitrate ($Ca(NO_3)_2 \cdot XH_2O$).....	2,660	CaO.
Stannic chloride ($SnCl_4 \cdot 5H_2O$).......	500	SnO_2.
Manganous nitrate ($Mn(NO_3)_2$)........	200	MnO_2.

A stainless steel vacuum chamber, large enough to impregnate two 9- by 4-1/4- by 3-in brick, was constructed as shown in figure 1. The cylindrical samples, bars, or brick were placed in the chamber on a wire mesh platform. The top was secured, and a mechanical vacuum pump was used to evacuate the chamber. Once minimum pressure of 0.1 Torr was achieved, the pump was run for 20 min to remove air trapped in internal pores of the brick. A valve was then closed, isolating the chamber from the pump, and the chamber was backfilled with solution until the samples were completely submerged. Soaking continued for 15 min, after which the pressure was raised to 1 atm and the liquid was siphoned off. The brick were allowed to drain and air-dry at ambient temperature and pressure for at least 24 h, placed in a dryer at 110° C for an additional 24 h, and then fired in an electric furnace to 1,450° C with a 48-h heating-cooling cycle. Depending on the test, brick were impregnated one, two, or three times with the drying-firing schedule described above completed after each impregnation.

REFRACTORY EVALUATION

PHYSICAL PROPERTIES

Percent absorption, percent apparent porosity, and bulk density were determined on the untreated 1-1/4-in-diameter and 3/4-in-long brick samples using the 5-h boil test, ASTM C 373-72 (11). The results are summarized in table 3 and are in excellent agreement with the ranges furnished by the manufacturer and given in table 1.

Test sets consisting of six cylindrical samples of the 42-, 58-, and 70-pct-Al_2O_3 brick were impregnated three successive times in 1 of 10 solutions, samples of which are shown in figure 2. Following each impregnation, after drying, firing,

TABLE 3. - Absorption, apparent porosity, and bulk density for 42-, 58-, and 70-pct-Al_2O_3 brick

	Brick A, 42 pct Al_2O_3	Brick B, 58 pct Al_2O_3	Brick C, 70 pct Al_2O_3
Absorption..........pct..	5.19	6.43	6.52
Apparent porosity...pct..	12.01	15.61	16.43
Bulk density.....lb/ft^3..	145	153	157

and cooling, the samples were weighed and the percent weight gain was calculated. Similar values were obtained for all three refractory types; table 4 summarizes the average results for the 42-and 70-pct Al_2O_3 refractories. The table indicates several trends to be apparent. First, the weight gain following impregnation is directly related to the molecular weight of the impregnant (i.e., Cr_2O_3 with molecular weight of 152 results in a much larger weight gain than does CaO with a molecular weight of 56).

Second, the weight gain is directly related to the apparent porosity of the brick (i.e., without exception, the 70-pct-Al_2O_3 brick, with an apparent porosity of 16.43 pct, showed a larger weight gain than did the 42-pct-Al_2O_3 brick with an apparent porosity of 12.01 pct).

Third, the weight gain increases linearly with the number of successive impregnations. If impregnations continued, this weight gain should level off as pore volume decreased and bridges formed between interconnected pores.

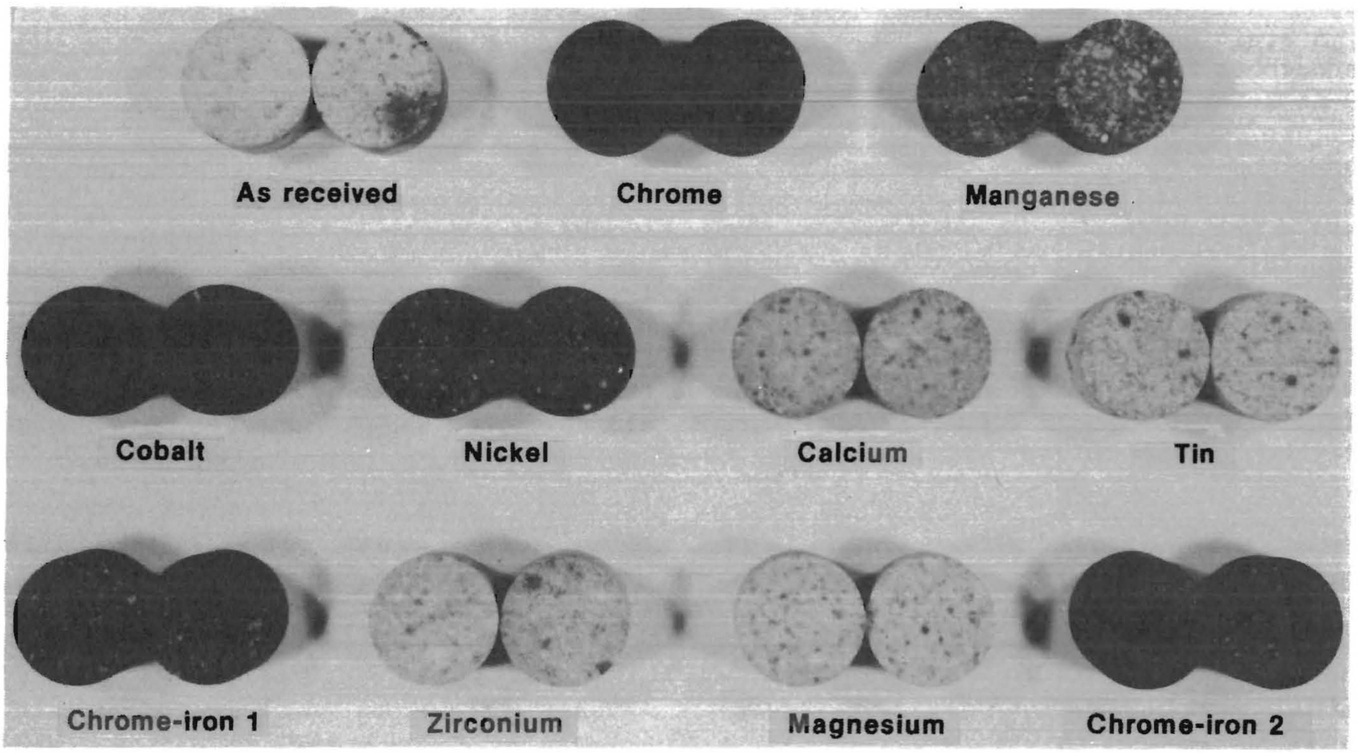

FIGURE 2. - Cylinders measuring 1-1/4 in in diameter by 3/4 in thick of as-received and treated samples.

TABLE 4. - Average weight gain after impregnation of 42- and 70-pct Al_2O_3 brick, percent

Additive	1 impregnation	2 impregnations	3 impregnations
	$42\text{-PCT-}Al_2O_3$ BRICK		
Calcium.............	1.02	1.87	2.75
Chrome..............	2.53	4.45	7.76
Chrome-iron 1.......	1.36	2.83	3.81
Chrome-iron 2.......	2.12	3.76	6.44
Cobalt..............	.70	1.46	2.12
Magnesium...........	.56	.90	1.20
Manganese...........	.71	1.34	2.18
Nickel..............	.78	1.52	2.28
Tin.................	.40	.73	1.01
Zirconium...........	1.11	2.05	2.85
	$70\text{-PCT-}Al_2O_3$ BRICK		
Calcium.............	1.14	2.51	3.78
Chrome..............	2.88	6.21	10.37
Chrome-iron 1.......	1.78	3.40	5.22
Chrome-iron 2.......	2.54	5.30	7.19
Cobalt..............	.89	1.90	2.85
Magnesium...........	.63	1.00	1.64
Manganese...........	.96	1.97	3.35
Nickel..............	.92	1.94	3.13
Tin.................	.47	.92	1.29
Zirconium...........	1.39	2.51	3.93

Following three successive impregnation cycles, cold compressive strength measurements were made on each sample (12). The average results for each as-received and treated brick are given in table 5. Cold compressive strength data, although traditionally reported for refractory products, must be carefully evaluated since they may have little bearing on the high-temperature or service properties of refractories. High room temperature compressive strengths often indicate the formation of excessive glassy phase at grain boundaries, which results in very poor high-temperature properties. Table 5 shows that impregnation has no significant effect on the room temperature strengths of Al_2O_3 refractories.

TABLE 5. - Average cold compressive strength for 42-, 58-, and 70-pct-Al_2O_3 brick, pounds per square inch

Additive	42 pct Al_2O_3	58 pct Al_2O_3	70 pct Al_2O_3
Calcium............	10,900	12,800	13,600
Chrome.............	9,600	17,000	17,400
Chrome-iron 1......	11,000	16,300	11,700
Chrome-iron 2......	9,100	16,600	14,600
Cobalt.............	6,700	13,200	10,100
Magnesium..........	9,400	12,400	13,000
Manganese..........	12,000	12,200	9,700
Nickel.............	9,700	14,800	11,000
None (as-received).	8,400	14,400	10,900
Tin................	7,600	11,600	7,900
Zirconium..........	9,100	11,000	12,000

HOT MODULUS OF RUPTURE

Untreated 42-pct-Al_2O_3 brick samples were broken at 1,250°, 1,300°, 1,350°, and 1,400° C using the high-temperature system shown in figure 3. Average strengths for five-bar sets were similar at 1,250°, 1,300°, and 1,350° C but dropped significantly at 1,400° C. Softening and deformation under load prior to breaking were also noted at 1,400° C, based on the shape of the loading curves. Therefore, 1,350° C was chosen for testing of the 42-pct Al_2O_3 brick. The 58- and 70-pct-Al_2O_3 brick were tested at 1,400° C. Table 6 summarizes the hot MOR data obtained on all as-received and treated brick.

TABLE 6. - Hot modulus of rupture average values for as-received and treated brick, pounds per square inch

Treatment and/or additive	42 pct Al_2O_3, 1,350° C	58 pct Al_2O_3, 1,400° C	70 pct Al_2O_3, 1,400° C
As-received................	530± 70	590±110	370± 50
As-received--heat treatment	560±120	820± 80*	360± 30
Calcium....................	360± 30*	850±120	930± 80*
Chrome.....................	650±100	1,610± 40*	770± 30*
Chrome-iron 1..............	790±130*	990± 70*	700±110*
Chrome-iron 2..............	840±120*	1,540±150*	910±100*
Cobalt.....................	260± 70*	360± 60*	260± 40*
Magnesium..................	370±120	410± 30*	290± 70
Manganese..................	300± 60*	250± 30*	140± 10*
Nickel.....................	470±100	710±180	360± 30
Tin........................	590±100	630± 50*	410± 70
Zirconium..................	600± 90	710± 50	600±110*

*Indicates a statistically significant difference based on t-test with a 99-pct confidence interval.

FIGURE 3. - Hot modulus of rupture test furnace.

Since the impregnation process involved heating the samples to 1,450° C to decompose the salt and allow reactions to occur, as-received brick of each type were tested with and without heat treatment to see if the heat treatment itself affected strength. No significant difference was found for the 42- or 70-pct-Al_2O_3 brick; however, heat treatment alone did increase the strength of as-received 58-pct-Al_2O_3 brick significantly, as shown in table 6. Based on this, all impregnated samples were compared to the as-received bars for 42- and 70-pct-Al_2O_3 brick and to the heat-treated 58-pct-Al_2O_3 brick.

From table 6 it is noted that nickel, cobalt, magnesium, tin, and manganese impregnation resulted in either no effect or a detrimental effect on each type of refractory; these solutions were eliminated from further tests. Solutions of chrome or mixtures of chrome and iron consistently improved the hot MOR properties of each type of refractory. Additions of these salts resulted in twofold to threefold improvements. Zirconium and calcium significantly improved the hot MOR properties of the 70-pct-Al_2O_3 brick while having little effect on the 42- and 58-pct Al_2O_3 brick.

HOT LOAD

All treatments resulting in improvements to the hot MOR of the 42-, 58-, and 70-pct-Al_2O_3 brick were used to prepare samples for deformation under load tests run according to ASTM C 16-77 (5). Hot MOR tests run on samples impregnated one, two, or three times showed only marginal improvement of hot strength between the second and third impregnations. As a result, samples prepared for hot load, and all subsequent, tests were only impregnated twice successively instead of three times. This results in smaller additions of secondary oxide, as shown in table 4.

The equipment used is shown in figure 4, and the results are summarized in table 7. It should be noted that these were very severe tests. Each brick was subjected to temperatures much higher than the upper use limit recommended for that particular composition. Manufacturers' hot load values shown in table 1 were obtained for brick heated to only 1,450° C (2,640° F) (ASTM 16-77, schedule 3), as compared to 1,680° C (3,060° F), 1,725° C (3,140° F), and 1,760° C (3,195° F) (ASTM 16-77, schedule 5) in this evaluation for the 42-, 58-, and 70-pct-Al_2O_3 brick, respectively. Higher temperature test conditions were used because initial tests to 1,450° C (2,640° F) resulted in such minimal deformation that comparisons between treated and untreated brick were impossible. Higher temperatures greatly magnified these differences. Generally, the chrome improved the resistance to deformation under load for each type of refractory, while the addition of zirconium and calcium to the 70-pct-Al_2O_3 refractory had a very deleterious effect. Figure 5 shows the as-received, calcium-treated, and chrome-treated 70-pct-Al_2O_3 test brick. As indicated in table 7, the chrome treatment led to a 50-pct reduction in deformation while the addition of calcium resulted in a fourfold increase.

TABLE 7. - Hot load average values for as-received and treated brick

Treatment and/or additive	Average deformation,[1] pct		
	42 pct Al_2O_3 to 1,680° C	58 pct Al_2O_3 to 1,725° C	70 pct Al_2O_3 to 1,760° C
As-received................	4.5±0.6	2.2±0.5	4.1±0.3
As-received--heat treatment	NAp	1.1± .4	NAp
Calcium....................	NAp	NAp	15.6±1.7
Chrome.....................	3.6±1.0	2.0± .5	2.2± .3
Chrome-iron 1..............	5.4±1.1	2.3± .2	6.0± .8
Chrome-iron 2..............	5.8±1.3	3.2± .3	8.5± .1
Zirconium..................	NAp	NAp	9.6± .7

NAp Not applicable. [1]ASTM C 16-77, schedule 5.

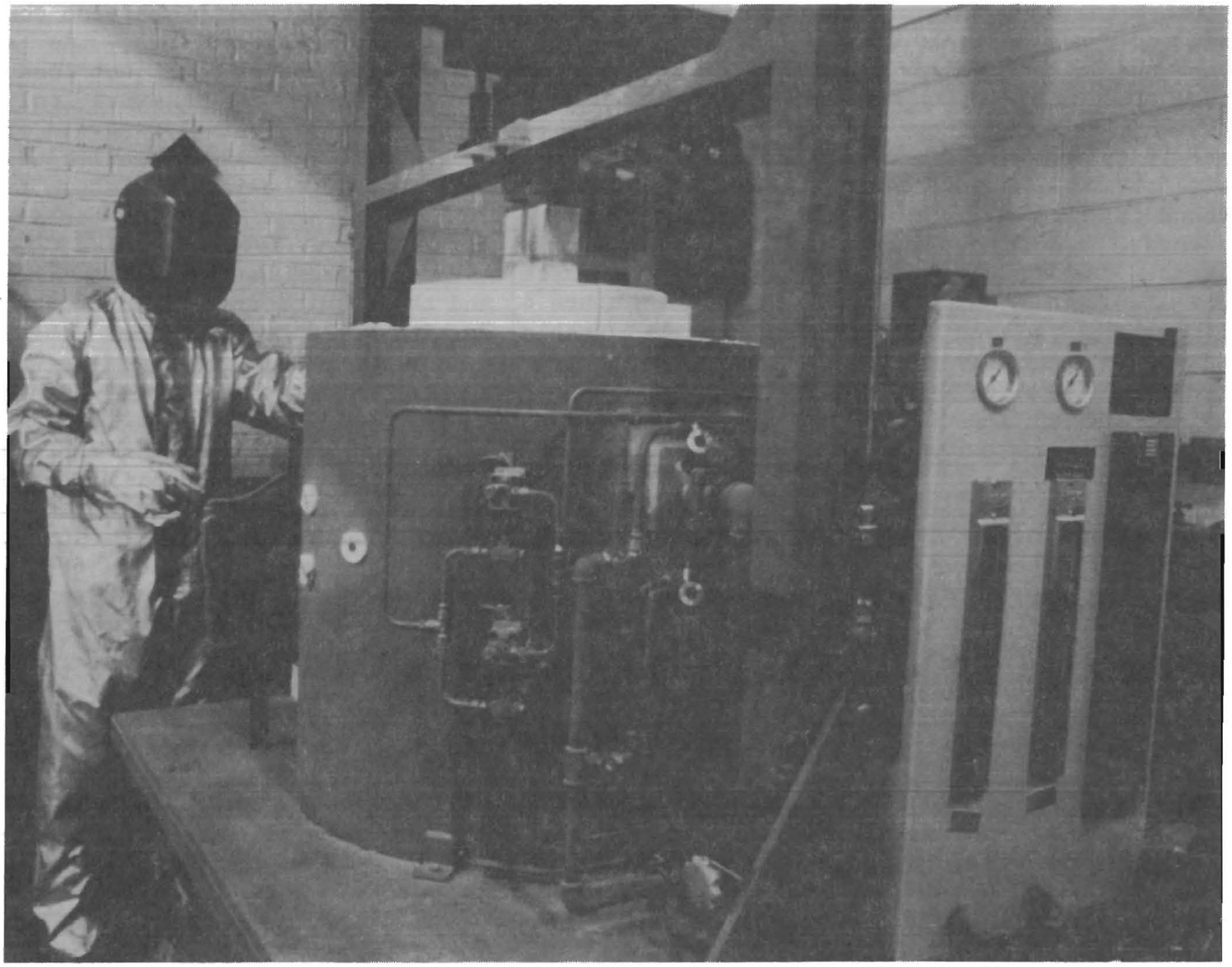

FIGURE 4. - Hot load test furnace.

SLAG RESISTANCE

For alumina refractories used in the presence of molten slags, numerous reactions can occur, particularly at the ternary interface of refractory, slag, and atmosphere. Due to the high mobility of various species in the liquid and gaseous states, chemical corrosion can be severe and rapid. Corrosion can be related, to a large extent, to the wettability of the refractory by the liquid phase (13-15). If secondary refractory oxides uniformly coat the alumina or mullite grains and reduce wettability or react to form more stable crystalline phases at grain boundaries, then the slag resistance would be greatly improved.

The slag resistance of as-received and treated brick was evaluated using a rotary slag test facility (shown in figure 6) developed by the Bureau of Mines, Tuscaloosa Research Center, and previously described by Cobble and Sadler (6). As in the hot load test, samples were impregnated twice. Tests were conducted using a highly reactive furnace slag having the composition shown in table 8. The tests were run for 8 h (an initial 2-h heat-up, followed by 6 h at 1,500°, 1,550°, and 1,600° C for the 42-, 58-, and 70-pct-Al_2O_3 brick). Four-hundred-gram slag additions were made every 10 min during the first hour after reaching temperature, followed by 200-g additions every 10 min for the remaining 5 h. Total slag introduced was 8.4 kg.

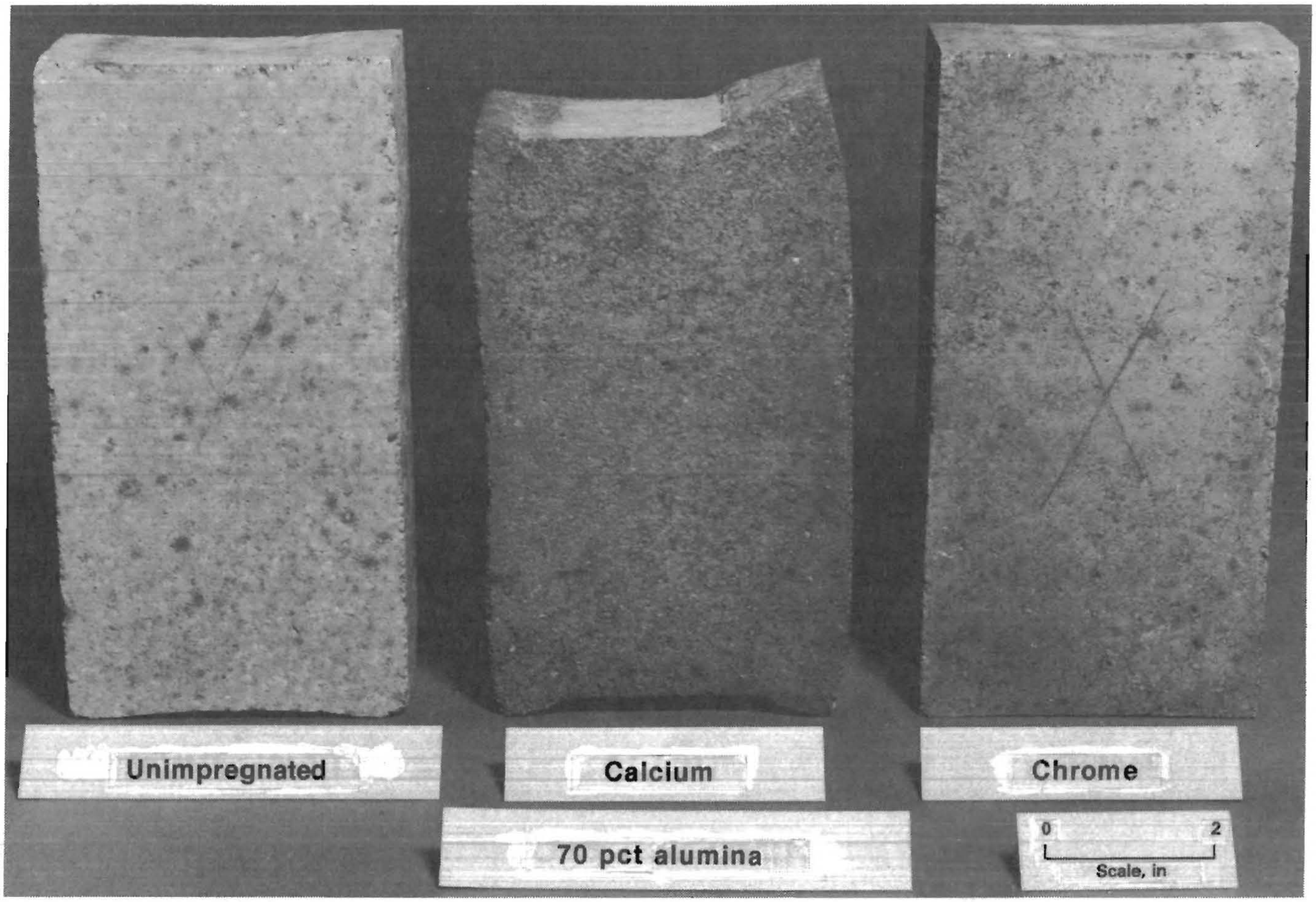

FIGURE 5. - Seventy-percent-Al_2O_3 hot load test specimens. Brick on left is an as-received sample heated to 3,195° F. Brick in middle and on right represent similar brick tested after treatment with calcium- and chromium-containing solutions.

TABLE 8. - Chemical analysis of slag used in rotary slag test, weight percent

CaO	33
SiO_2	33
Fe_2O_3	20
MgO	5
MnO	5
Al_2O_3	4
Total	100

The average area change for each specimen tested was obtained in the following manner: The straight (4.5- by 9-in) and slant (4.7- by 9-in) side faces of each specimen were traced on a piece of white posterboard before and after testing to represent the initial and final areas of the faces. The area difference was determined using a computerized image analysis system. Average percent area change was determined by averaging the area changes for the two sides. A summary of results is given in table 9. In every case except the 70-pct-Al_2O_3 brick impregnated with zirconium, statistically significant improvement in the slag resistance resulted from impregnation. Improvement was dramatic, representing twofold to fivefold improvements, for all brick impregnated with chrome-containing solutions. Figure 7 shows an as-received and a chrome-iron-treated 58-pct-Al_2O_3 brick after rotary slag testing at 1,550° C.

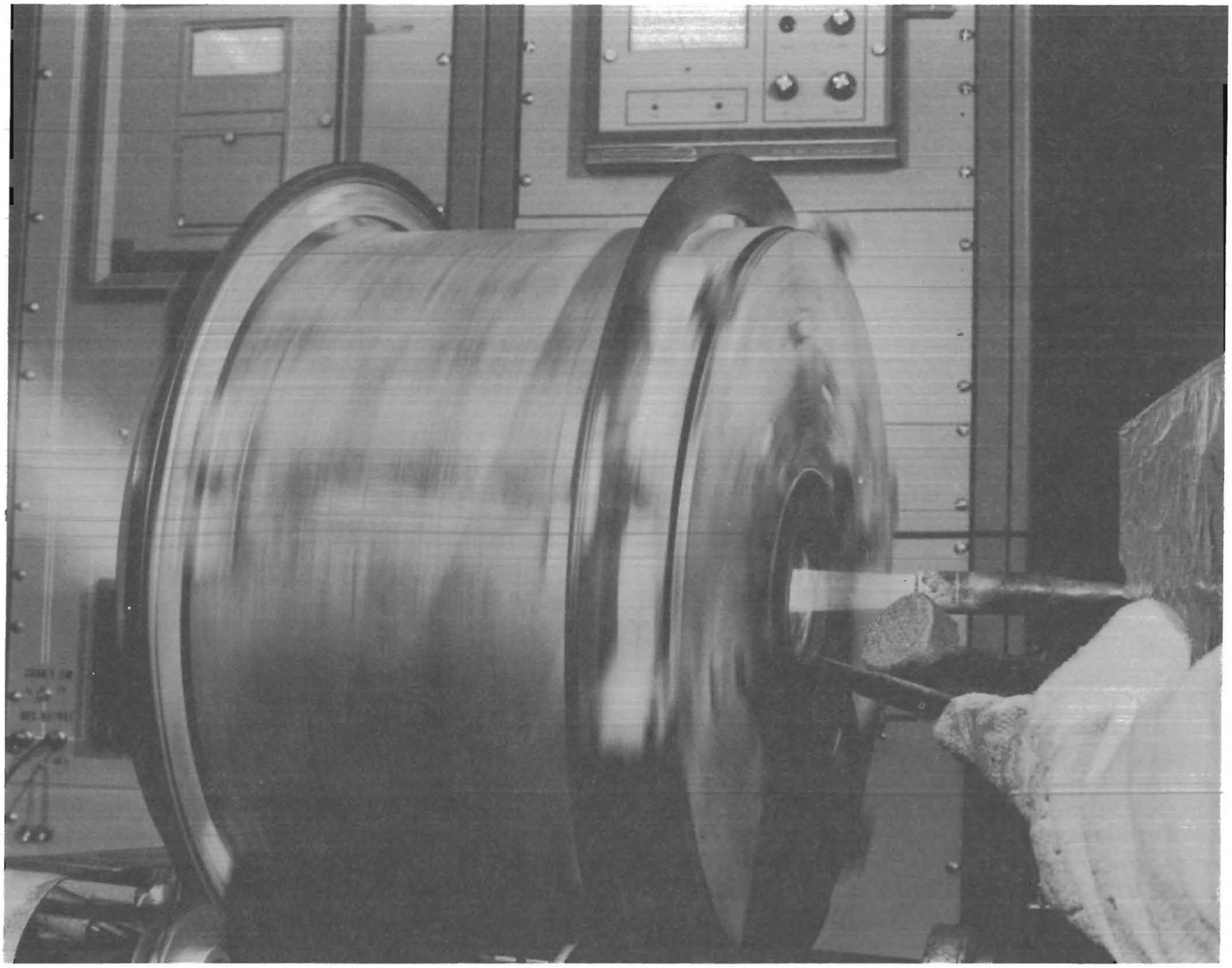

FIGURE 6. - Rotary slag test facility.

TABLE 9. -- Average area change for brick following rotary slag test, percent

Treatment and/or additive	42 pct Al_2O_3, 1,500° C	58 pct Al_2O_3, 1,550° C	70 pct Al_2O_3, 1,600° C
As-received................	[1]11.4±5.0	10.2±1.6	11.0±0.8
As-received--heat treatment	NAp	9.3± .3	NAp
Calcium....................	NAp	NAp	7.5±1.0*
Chrome.....................	4.1± .9*	2.2±1.1*	3.0± .4*
Chrome-iron 1..............	6.2±1.0*	3.0± .8*	6.0± .9*
Chrome-iron 2..............	6.1±1.0*	1.6± .6*	4.1± .2*
Zirconium..................	NAp	NAp	8.1±1.6

ND Not determined.

[1]19 brick are required for construction of a rotary slag test drum. Values given in the table are average values of 3, 4, or 5 brick depending on the drum configuration for each particular test.

*Indicates a statistically significant difference based on t-test with a 99-pct confidence interval.

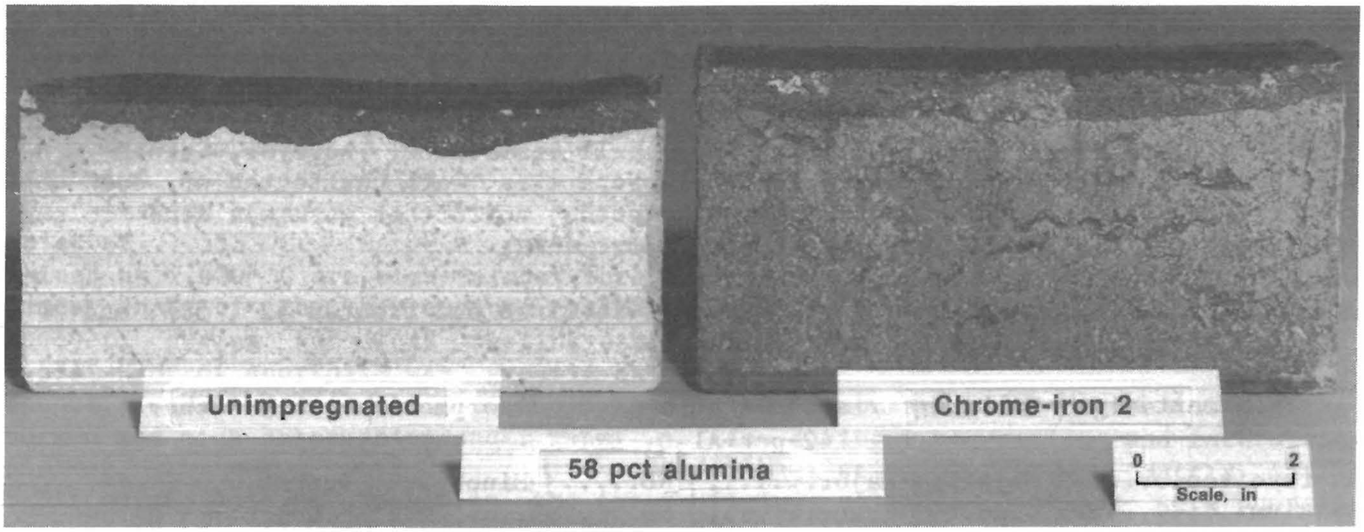

FIGURE 7. - Comparison of as-received (left) and chrome-iron-treated (right) 58-pct-Al_2O_3 brick.

The improved slag resistance can be attributed to several factors. The addition of chrome or chrome-iron mixtures to alumina-containing refractories causes increased bulk density and corresponding decreased porosity. As an example, additions of chrome or chrome-iron mixtures to a 58-pct-Al_2O_3 brick increase the density from 2.45 to 2.64 g/cm^3. This decreased porosity reduces penetration of the brick by the liquid slag. The formation of $Al_2O_3 \cdot Cr_2O_3$ or $Al_2O_3 \cdot Fe_2O_3 \cdot Cr_2O_3$ solid solutions, as discussed in the following section, results in phases more chemically inert than Al_2O_3 to iron-containing slags. The presence of Cr_2O_3 also reduces the wettability of iron-containing slags, as evidenced by reduced penetration and almost no residual slag on the surface of the brick following the rotary slag test. Residual slag adhering to the untreated brick was two to three times as thick.

X-RAY DIFFRACTION AND MINERALOGY

In all alumina refractories containing 42 to 70 pct Al_2O_3, the bulk of the remaining material is silica (SiO_2). At high temperatures (either during forming or in use) there is a reaction between SiO_2 and Al_2O_3 resulting in the formation of mullite ($3Al_2O_3 \cdot 2SiO_2$), which has a melting point of 1,850° C. As the Al_2O_3 content drops below 70 pct, there is more and more excess SiO_2, which may be in the form of alpha quartz, cristobalite, or combined with impurities to form an amorphous glassy phase. If the excess silica is present in the form of quartz it does not pose a serious problem, but in the form of a glass, as discussed above, it can limit the high-temperature properties (16). In the presence of mineralizers the quartz can be converted to cristobalite at temperatures above 1,200° C, which is within the typical temperature range of these refractories. The presence of cristobalite can be very detrimental since it undergoes a low-temperature inversion, accompanied by a 1-pct linear expansion, which results in poor spall resistance. If small amounts of secondary refractory oxides can stabilize the quartz phase and prevent cristobalite formation, then the thermal shock resistance of the refractory could be greatly improved.

X-ray diffraction analyses were used to provide mineral phase identification for the as-received and treated samples of 42-, 58-, and 70-pct-Al_2O_3 brick. The results are summarized in table 10. The addition of solutions containing chromium results in all cases in the formation of $Al_2O_3 \cdot Cr_2O_3$ or $Al_2O_3 \cdot Cr_2O_3 \cdot Fe_2O_3$ solid solutions. Zirconium additions result in the formation of zircon ($ZrSiO_4$) and monoclinic zirconia accompanied by reduction of the cristobalite phase. Addition of calcium to the 58- and 70-pct-Al_2O_3 brick results in the formation of anorthite accompanied by elimination of cristobalite.

Several other additions lead to the formation of aluminates (cobalt, melting point [MP] 1,960° C; nickel, MP 2,209° C), cordierite, MP 1,540° C, or oxide (tin, MP 1,127° C). Still other mineral phases may be present, but owing to the small weight percent additions of certain additives (table 4) may not be detectable by X-ray diffraction. As in the case of calcium and zirconium additions, several other additives resulted in the reduction of cristobalite, which could improve spall resistance; however, since other properties were unaffected or even worsened, no further work was done to support this.

TABLE 10. - Mineral identification for as-received and treated 42-, 58-, and 70-pct-Al_2O_3 brick

Treatment	Mullite	Cristobalite	α-Al_2O_3	Amorphous	Other
		42-pct-Al_2O_3 BRICK			
As-received.......	Major..	Major.......	ND.....	Minor....	Quartz.
Calcium...........	..do...	Trace.......	ND.....	..do.....	Do.
Chrome............	..do...	Major.......	ND.....	..do.....	$Cr_2O_3 \cdot Al_2O_3$, ss.
Chrome-iron 1.....	..do...	..do........	ND.....	..do.....	$Cr_2O_3 \cdot Fe_2O_3 \cdot Al_2O_3$, ss.
Chrome iron 2.....	..do...	..do........	ND.....	..do.....	$Cr_2O_3 \cdot Fe_2O_3 \cdot Al_2O_3$, ss.
Cobalt............	..do...	Minor.......	ND.....	..do.....	$CoAl_2O_4$.
Magnesium.........	..do...	..do........	ND.....	..do.....	None.
Manganese.........	..do...	..do........	ND.....	..do.....	None.
Nickel............	..do...	Major.......	ND.....	..do.....	$NiAl_2O_4$.
Tin...............	..do...	..do........	ND.....	..do.....	SnO_2.
Zirconium.........	..do...	..do........	ND.....	..do.....	Zircon + zirconia (monoclinic).
		58-pct-Al_2O_3 BRICK			
As-received.......	Major..	Trace.......	ND.....	Minor....	Rutile.
As-received--heat treated.	..do...	Major.......	ND.....	ND.......	Do.
Calcium...........	..do...	Minor.......	ND.....	Minor....	Anorthite.
Chrome............	..do...	..do........	ND.....	ND.......	$Al_2O_3 \cdot Cr_2O_3$, ss, quartz, rutile.
Chrome-iron 1.....	..do...	..do........	Trace..	ND.......	$Al_2O_3 \cdot Cr_2O_3$, ss.
Chrome iron 2.....	..do...	..do........	..do...	ND.......	$Al_2O_3 \cdot Cr_2O_3$, ss.
Cobalt............	..do...	..do........	ND.....	Minor....	Rutile.
Magnesium.........	..do...	..do........	Trace..	..do.....	Do.
Manganese.........	..do...	..do........	ND.....	..do.....	Do.
Nickel............	..do...	..do........	ND.....	..do.....	Do.
Tin...............	..do...	..do........	ND.....	..do.....	Do.
Zirconium.........	..do...	Trace.......	ND.....	Trace....	Zircon.
		70-pct-Al_2O_3 BRICK			
As-received.......	Major..	Minor.......	Trace..	ND.......	Quartz.
Calcium...........	..do...	ND..........	Minor..	Minor....	Anorthite.
Chrome............	..do...	Minor.......	Trace..	ND.......	$Al_2O_3 \cdot Cr_2O_3$, ss.
Chrome-iron 1.....	..do...	..do........	..do...	ND.......	$Al_2O_3 \cdot Cr_2O_3$, ss.
Chrome iron 2.....	..do...	..do........	..do...	ND.......	$Al_2O_3 \cdot Cr_2O_3$, ss.
Cobalt............	..do...	Trace.......	..do...	ND.......	$CoAl_2O_4$.
Magnesium.........	..do...	..do........	..do...	ND.......	α-$Mg_2Al_4Si_5O_{18}$.
Manganese.........	..do...	ND..........	..do...	ND.......	None.
Nickel............	..do...	Minor.......	..do...	ND.......	$NiAl_2O_4$.
Tin...............	..do...	Trace.......	..do...	ND.......	$(Sn \cdot Fe)O_2$, quartz.
Zirconium.........	..do...	..do........	..do...	ND.......	Zircon + zirconia (monoclinic).

ND Not detected. ss Solid solution.

The X-ray data can be used to explain inconsistencies between the hot MOR values obtained at 1,400° C and hot load data obtained at 1,750° C for 70-pct-Al_2O_3 brick impregnated with calcium and zirconium. Calcium additions result in the formation of anorthite with a melting point of 1,553° C. Hot MOR values obtained at 1,400° C are high--almost three times that of the as-received brick. However, during hot load testing the 1,553° C MP of anorthite was greatly exceeded, resulting in a fluid liquid being formed and high deformation under load.

Zirconium additions result in the formation of zircon, which ties up free SiO_2 and results in high MOR values at 1,400° C--almost twice that of the as-received brick. However, during hot load testing above 1,600° C, the zircon dissociates into refractory zirconia and silica, which at these temperatures can soften and, in the presence of other impurities (iron, titania, and alkalies), form low-viscosity melts resulting in high deformation under load. This would indicate improved properties for these refractories when used to temperatures not exceeding 1,550° C.

To demonstrate the degree of penetration during impregnation and interaction with existing refractory matrix during firing, polished sections were prepared from the center of treated 58-pct-Al_2O_3 brick. Figures 8 and 9 show backscattered X-ray images of the surface

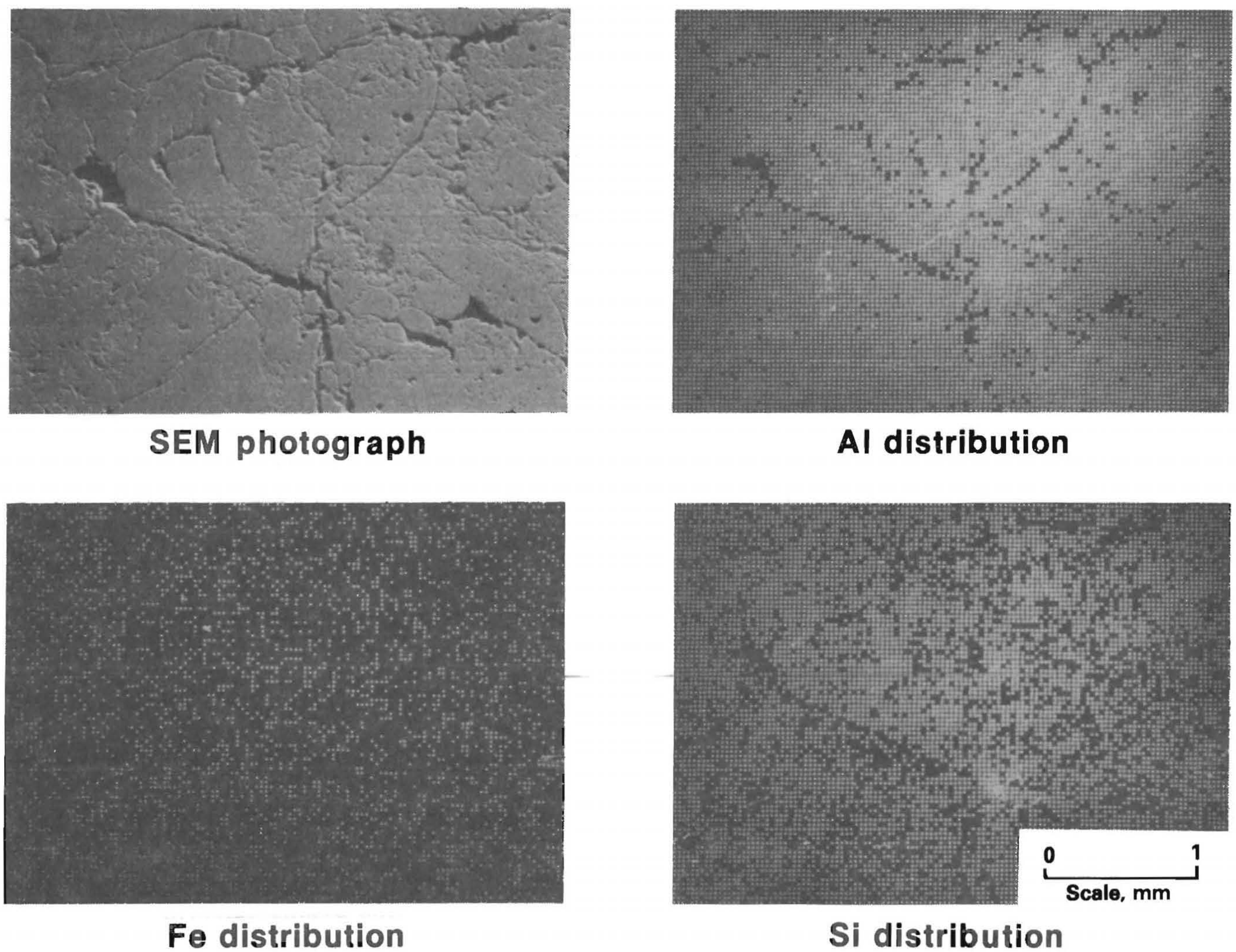

FIGURE 8. - SEM micrographs of elemental distribution for untreated 58-pct-Al_2O_3 brick.

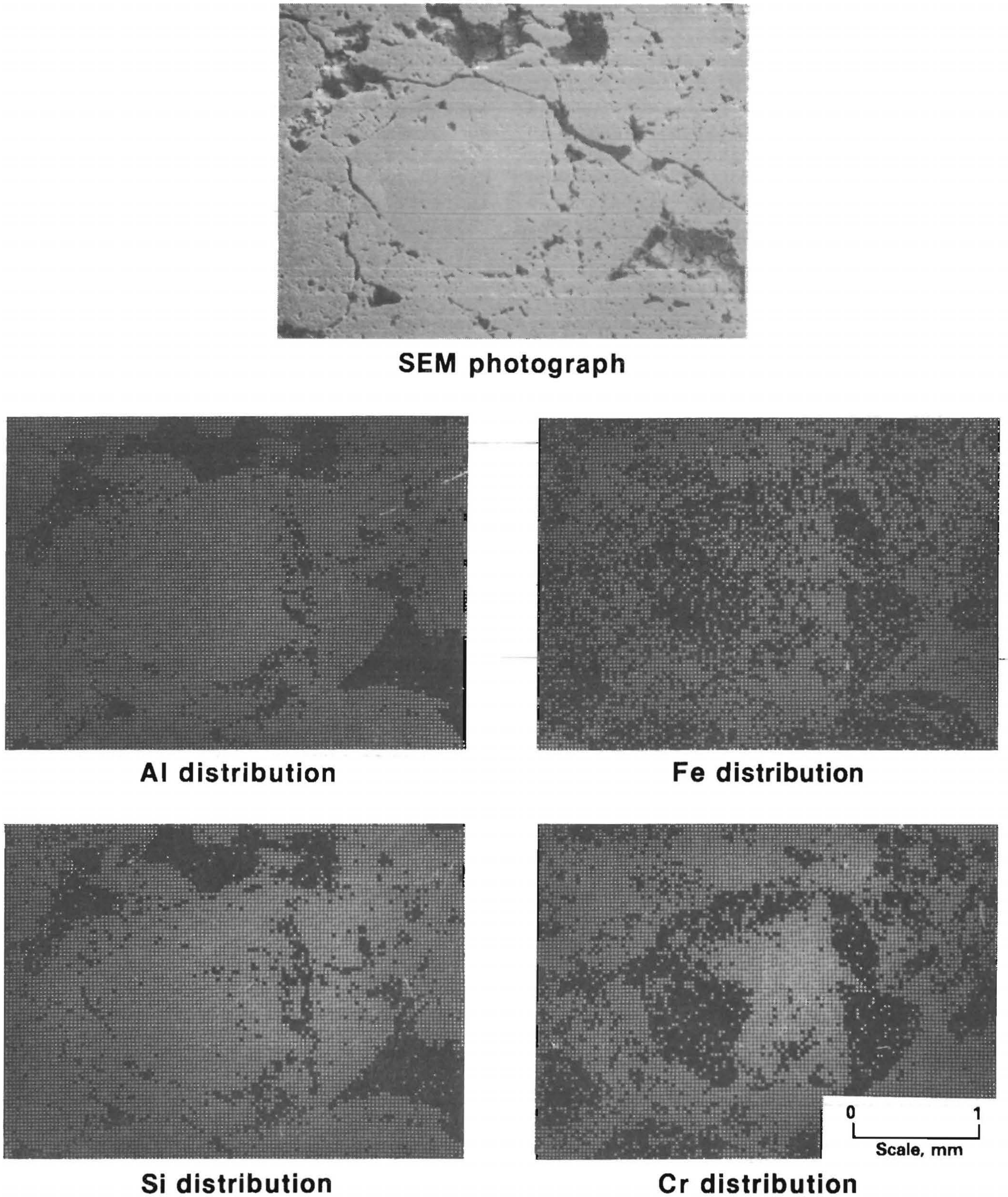

FIGURE 9. - SEM micrographs of elemental distribution for chrome-iron-treated 58-pct-Al_2O_3 brick.

profile and elemental maps for Al, Si, Fe, and Cr for the untreated and chrome-iron-treated refractories. Comparing the two figures, it is noted that the Al_2O_3 and SiO_2 occur together throughout both the treated and untreated samples. The small amount of Fe_2O_3 found in the untreated brick is uniformly distributed throughout the refractory matrix. Following treatment, a dramatic and uniform increase in the chrome and iron distribution is noted in figure 9. Both the chrome and iron have penetrated the dense mullite grains as well as appearing in voids and grain boundaries.

SUMMARY AND CONCLUSIONS

Brick containing 42, 58, and 70 pct Al_2O_3 and having apparent porosities ranging from 12 to 16 pct were vacuum-impregnated with solutions containing chrome, chrome-iron, zirconium, nickel, cobalt, magnesium, calcium, tin, and manganese. After drying and firing to 1,450° C, weight gains ranged from 1 to 10 wt pct. Impregnation had little, if any, effect on the cold compressive strength of the refractories; however, some very significant improvements were noted for the hot MOR, hot load, and slag resistance of the alumina brick. Additions of chrome or chrome-iron mixtures resulted in general improvement to hot load resistance and very dramatic improvement to the hot MOR and slag resistance of all the brick. Fivefold improvements to the slag resistance were noted due to decreased porosity, increased chemical inertness, and decreased wetting of the refractory by high-iron slags. These improvements resulted from additions as small as 3 wt pct.

Calcium and zirconium additions, which improved the hot MOR of 70-pct-Al_2O_3 brick at 1,400° C, resulted in only marginal improvement in the slag resistance at 1,600° C and caused severe deformation under load at 1,750° C owing to the formation of fluid liquid phases above 1,550° C.

Additions of nickel, cobalt, magnesium, tin, and manganese had a negative influence on the high-temperature properties of Al_2O_3-containing refractories, primarily owing to the formation of low-melting glassy phases above 1,350° C.

Hot MOR, hot load, and slag resistance measurements on 42-and 58-pct-Al_2O_3 brick indicated these properties were superior to those of untreated brick with significantly higher Al_2O_3 contents. Fifty-eight-percent-Al_2O_3 brick impregnated with chrome had values two to five times better than values obtained for untreated 70-pct-Al_2O_3 brick. This could reduce the Nation's dependence on imported refractory-grade bauxite generally required for high-Al_2O_3 brick, as domestic alumina resources could be used to produce the improved refractories.

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