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High-Temperature Properties of Magnesia-Refractory Brick Treated With Oxide and Salt Solutions

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UNITED STATES DEPARTMENT OF THE INTERIOR

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UNIT OF MEASURE ABBREVIATIONS USED IN THIS REPORT

°C	degree Celsius	min	minute
°F	degree Fahrenheit	pct	percent
g	gram	lb/in^2	pound per square inch
h	hour	lb/ft^3	pound per cubic foot
in	inch	wt pct	weight percent
L	liter		

HIGH-TEMPERATURE PROPERTIES OF MAGNESIA-REFRACTORY BRICK TREATED WITH OXIDE AND SALT SOLUTIONS

By James P. Bennett [1]

ABSTRACT

The Bureau of Mines investigated the effect of refractory oxide additions, introduced in soluble form, on the high-temperature properties of 90- and 98-pct-MgO brick. Brick samples were soaked in solutions containing Al, Ca, Cr, Co, Fe, Mg, Mn, Mo, Ni, Si, Sr, Sn, Ti, or Zr ions. Additions to 98-pct-MgO brick did not generally result in statistically significant property improvements. Statistically significant improvements were noted in hot modulus of rupture (MOR), slag resistance, and spalling resistance of the 90-pct-MgO brick for additions of Al, Mg, or Sn. High-temperature performance of treated 90-pct-MgO refractories was equal to or approached that of 98-pct-MgO brick. The marked improvements due to tin were obtained with additions of only 1.14 wt pct SnO_2.

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INTRODUCTION

Magnesia (MgO) materials are used extensively in basic oxygen and electric arc steelmaking refractories. Greater use of high-MgO materials in problem areas such as the slag-metal interface is limited owing to the superior properties of other materials, such as MgO-chrome or MgO-graphite refractories, both of which require imported critical raw materials, chromite and graphite.

In the United States raw materials for MgO refractories are generally mined as magnesite or processed chemically from brines or seawater as periclase grain. If techniques could be developed to improve MgO brick properties, their increased usage could result in a decreased importation of critical raw materials. Earlier research (1-3)[2] by the Bureau of Mines was directed at improving the properties of the refractory periclase, which is the major component in magnesite refractory products.

More recent Bureau research (4) indicated that certain metallic salt additions to low-alumina refractories improved their high-temperature properties. To determine if similar property improvements might be possible in MgO-based refractories, two commercial MgO refractories (90 and 98 pct MgO) were impregnated with solutions of 14 different metallic salt and oxide solutions. After impregnation, samples were fired to 1,550° C to allow salt decomposition and reaction between the resulting oxide and the refractory phases present in the brick. Subsequently, hot modulus of rupture (MOR), deformation under load at elevated temperature (hot load), thermal spall resistance, and slag resistance tests were conducted. X-ray diffraction (XRD) was used to study the mineral phases that were formed, and energy dispersive spectroscopy (EDS) was used to determine the distribution of the additives. This report summarizes the results and compares them with properties of untreated MgO brick.

REFRACTORY BRICK AND SAMPLE PREPARATION

Chemical and physical properties of two commercial MgO bricks (90 and 98 pct MgO) are listed in table 1. Test samples were prepared from the commercial brick in the following manner:

1. Full-size brick for hot load testing were prepared according to ASTM C 16-81 (5). The 90-pct-MgO brick were tested under a 25 lb/in^2 load to 1,700° C (3,100° F), while the 98-pct-MgO brick

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

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

	Commercial refractory brick	
	90 pct MgO	98 pct MgO
Chemical analysis, wt pct:		
Magnesia (MgO)	89.1	96.5
Alumina (Al_2O_3)	0.38	0.12
Iron oxide (Fe_2O_3)	1.83	0.19
Chromium oxide (Cr_2O_3)	0.42	0.10
Silica (SiO_2)	7.41	1.45
Calcia (CaO)	0.87	1.61
Physical property:		
Bulk density, lb/ft^3	172-178	175-181
Apparent porosity, pct	18-21	17-20
Cold crushing strength, lb/in^2	3,000-5,000	4,000-6,000
Modulus of rupture (room temperature), lb/in^2	1,200-2,000	1,800-3,000

were evaluated under a 25 lb/in^2 load to 1,750° C (3,180° F). Heating rate schedule 5 was followed, as specified in ASTM C 16-81.

2. Bars measuring 1 by 1 by 9 in were prepared according to ASTM C 583-80 (6) for hot MOR tests and were broken at 1,500° C.

3. Wedge-shaped samples, as shown in figure 1, were cut from full-size brick for use in rotary slag tests according to a procedure established by the Bureau in 1980 (7). Slag resistance was determined at 1,600° C using an electric furnace type slag whose composition is given in table 2. Slag-resistance tests were run for 8 h (an initial 2-h heatup, followed by 6 h at 1,600° C). An addition of 400 g of slag was made every 10 min for the first hour after reaching temperature, followed by 200-g additions every 10 min during the remaining 5 h.

4. Samples 1-1/4 by 1-1/2 by 9 in were cut from full-size brick for thermal spall testing using a procedure described

TABLE 2. - Chemical analysis of slag used in rotary slag test, weight percent

Fe_2O_3	35.0
CaO	20.7
SiO_2	20.7
MgO	20.6
MnO_2	3.0
Total	100.0

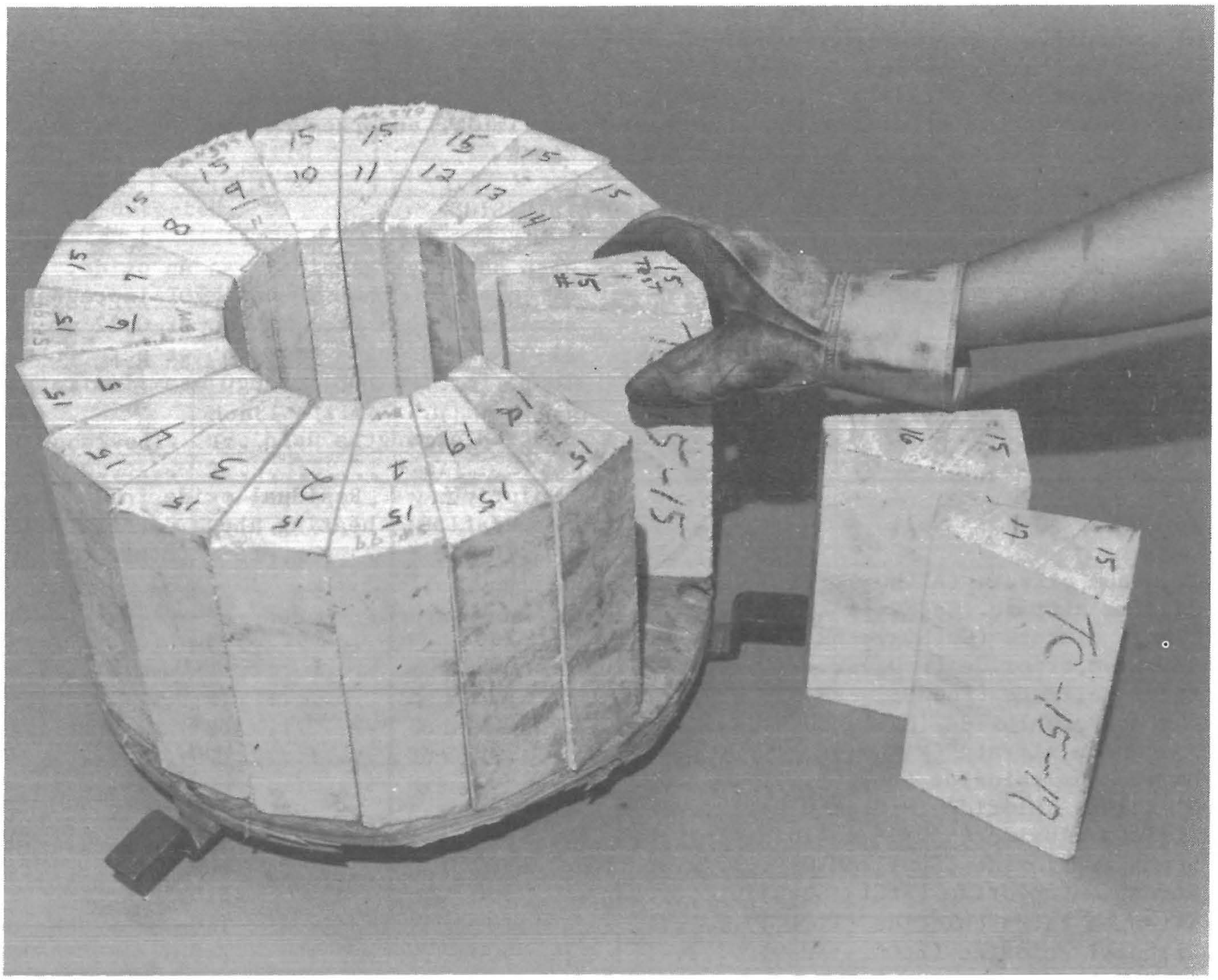

FIGURE 1. - Arrangement of refractory specimens before placement in rotary slag test drum.

by Semler (8). The samples were subjected to five cycles of heating to 1,100° C for 10 min followed by cooling to 75° C for 10 min. Modulus of elasticity (MOE) measurements of thermally shocked and unshocked samples were made with a James V-meter.[3] The percent MOE retained was used to determine the thermal spall resistance of the material.

5. Mineralogical, chemical, and microstructural analyses were conducted on specimens obtained from hot MOR bars.

TREATMENT PROCEDURE--SOLUTIONS AND TECHNIQUES

All salts or oxides used to treat MgO bricks were dissolved in deionized water, with the exception of molybdenum trioxide (MoO_3), which was dissolved in ammonium hydroxide (NH_4OH). All impregnation solutions were reagent-grade chemicals that formed oxides upon firing. The starting salts, solution concentrations used to impregnate test samples, and their residual oxides are listed in table 3.

Magnesia brick samples were submerged in the different solutions at 25° C for 24 h. The brick samples were drained at room temperature for 24 h, then dried at 120° C for 24 h. After drying, the samples were fired in a gas kiln at 1,550° C for 2 h. Treated samples were used for XRD phase identification, chemical analysis, scanning electron microscopic (SEM) examination, and EDS analysis of the element distribution. Treated samples were also used for hot MOR, hot load, thermal spall, and rotary slag testing.

A set of 90- and 98-pct-MgO reference samples was soaked in deionized water, dried, and fired at 1,550° C for 2 h, following the treatment procedure established for oxide additions.

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

RESULTS AND DISCUSSION

CHEMICAL, MINERALOGICAL, AND MICROSTRUCTURAL PHASE ANALYSIS

Chemical analyses of treated brick, listed in table 4, indicate the amount of each additive retained as an oxide. Additions to the 90-pct-MgO impregnated samples ranged from a low of 0.22 wt pct Al_2O_3 to a high of 4.55 wt pct Cr_2O_3. Those for the 98-pct-MgO samples ranged

TABLE 3. - Additives and solution strengths used

Salt	Solution concentration, g/L	Residual oxide following heating above decomposition temperature
Aluminum nitrate ($Al(NO_3)_3 \cdot 9H_2O$.........	500	Al_2O_3.
Calcium nitrate ($Ca(NO_3)_2 \cdot XH_2O$).........	500	CaO.
Cobalt nitrate ($Co(NO_3)_2 \cdot 6H_2O$)..........	250	CoO.
Chromium trioxide (CrO_3)................	1,000	Cr_2O_3.
Ferric nitrate ($Fe(NO_3)_3 \cdot 9H_2O$...........	500	Fe_2O_3.
Magnesium chloride ($MgCl_2 \cdot 6H_2O$).........	1,000	MgO.
Manganous nitrate ($Mn(NO_3)_2$)[1]...........	250	MnO.
Molybdenum trioxide (MoO_3)[2].............	200	MoO_3.
Nickelous chloride ($NiCl_2 \cdot 6H_2O$).........	300	NiO.
Silicon dioxide (SiO_2 - colloidal)[1].....	300	SiO_2.
Stannic chloride ($SnCl_4 \cdot 5H_2O$)...........	500	SnO_2.
Strontium chloride ($SrCl_2 \cdot 6H_2O$).........	500	SrO.
Titanium tetra chloride ($TiCl_4$)[1]........	100	TiO_2.
Zirconyl chloride ($ZrOCl_2 \cdot XH_2O$).........	500	ZrO_2.

[1]Commercial solution. [2]NH_4OH solution.

from a low of 0.16 wt pct Al_2O_3 to a high of 2.39 wt pct Cr_2O_3.

Phases, identified in the 90- and 98-pct-MgO brick before and after treatment and firing to 1,550° C, are listed in table 5, with the exception of periclase, the predominant phase.

In the 90-pct-MgO brick, a minor amount of fosterite ($2MgO{\cdot}SiO_2$, MP 1,890° C) and a trace amount of monticellite ($MgO{\cdot}CaO{\cdot}SiO_2$, MP 1,485° C) were present. The addition of either strontium or titanium resulted in the formation of the more refractory phases dicalcium silicate ($2CaO{\cdot}SiO_2$, MP 2,130° C) and calcium titanate ($CaTiO_3$, MP 1,970° C), respectively. Other identified phases formed from additions to 90-pct-MgO brick were as follows: aluminum → $MgAl_2O_4$, chromium → $MgCr_2O_4$-$FeCr_2O_4$, manganese → Mn spinel, molybdenum → $CaMoO_4$, tin → Mg_2SnO_4, and zirconium → ZrO_2.

The addition of calcium to 98-pct-MgO brick resulted in the conversion of monticellite into the slightly more refractory phase merwinite ($3CaO{\cdot}MgO{\cdot}2SiO_2$, MP

TABLE 4. - Amount[1] of oxide additions after treatment of 90- and 98-pct-MgO brick

Additive	Amount of oxide added, wt pct		Additive	Amount of oxide added, wt pct	
	90-pct-MgO brick	98-pct-MgO brick		90-pct-MgO brick	98-pct-MgO brick
Al........	0.22	0.16	Mo........	1.50	1.35
Ca........	.53	.35	Ni........	.89	.83
Co........	.64	.42	Si........	1.57	1.33
Cr........	4.55	2.39	Sn........	1.14	.25
Fe........	.67	.65	Sr........	.72	.59
Mg........	1.10	ND	Ti........	.40	.22
Mn........	1.68	1.42	Zr........	1.38	1.45

ND Not detected.
[1]Adjusted by difference in chemical analysis reported in table 1.

TABLE 5. - Mineral identification for as-received and treated 90- and 98-pct-MgO brick

Treatment	90-pct-MgO brick[1]		98-pct-MgO brick[2]		
	Monticellite	Other phases	Monticellite	Merwinite	Other phases
As-received..	Tr..........	None...........	Tr-m........	Tr-m.....	ND.
Al...........	Tr..........	$MgAl_2O_4$ (Tr)...	Tr-m........	Tr-m.....	ND.
Ca...........	Tr-m........	None...........	ND..........	Tr-m.....	ND.
Co...........	Tr..........	None...........	Tr-m........	Tr-m.....	ND.
Cr...........	Tr..........	$MgCr_2O_4$-$FeCr_2O_4$ (m).	Tr..........	Tr.......	$MgCr_2O_4$-$FeCr_2O_4$ (Tr).
Fe...........	Tr..........	None...........	Tr-m........	Tr-m.....	ND.
Mg...........	Tr..........	None...........	Tr..........	Tr.......	ND.
Mn...........	Tr..........	Mn spinel (Tr).	Tr..........	Tr.......	ND.
Mo...........	ND..........	$CaMoO_4$ (m).....	Tr..........	Tr.......	$CaMoO_4$ (m).
Ni...........	Tr..........	None...........	Tr-m........	Tr-m.....	ND.
Si...........	Tr..........	None...........	Tr-m........	ND.......	ND.
Sn...........	Tr..........	$MgSnO_4$ (Tr-m)..	Tr-m........	Tr-m.....	Mg_2SnO_4(Tr).
Sr...........	ND..........	Ca_2SiO_4 (Tr-m).	ND..........	ND.......	ND.
Ti...........	ND..........	$CaTiO_3$ (Tr-m)..	Tr..........	ND.......	$CaTiO_3$ (Tr).
Zr...........	Tr..........	ZrO_2 (cubic) (m).	Tr-m........	Tr.......	ZrO_2 (cubic) (m).

ND Not detected. m minor. Tr Trace.
[1]Minor fosterite; merwinite not detected.
[2]Fosterite not detected.

= 1,575° C). Other identified phases formed from additions to 98-pct-MgO brick were as follows: chromium → $MgCr_2O_4$-$FeCr_2O_4$, molybdenum → $CaMoO_4$, tin → Mg_2SnO_4, titanium → $CaTiO_3$, and zirconium → ZrO_2.

Elemental mapping analysis using EDS indicated that the additives were generally uniformly distributed throughout a sample. An example is strontium additions to a 98-pct-MgO brick, shown in figure 2. No strontium phases were identified by XRD (table 5).

In the case of chromium, however, EDS examination for a 90-pct-MgO sample indicated a concentration of the chromium between MgO grains, as illustrated in figure 3. X-ray phase analysis indicated that a $MgCr_2O_4$-$FeCr_2O_4$ solid solution was formed (table 5).

HOT MODULUS OF RUPTURE

The results of hot MOR testing of treated and untreated brick are listed in table 6. Statistically significant strength increases occurred in 90-pct-MgO samples with Al, Ca, Cr, Co, Mg, Si, Sn, and Zr additions compared with strength of the untreated brick. The largest strength increase, from 200 to 650 lb/in^2, resulted from silicon additions. The strength increases were apparently due to the formation of more refractory bond phases. Titanium additions caused a strength decrease, although a more refractory phase ($CaTiO_3$) was formed. It is possible that, owing to the formation of $CaTiO_3$, the $CaO:SiO_2$ ratio in the bond phase was affected.

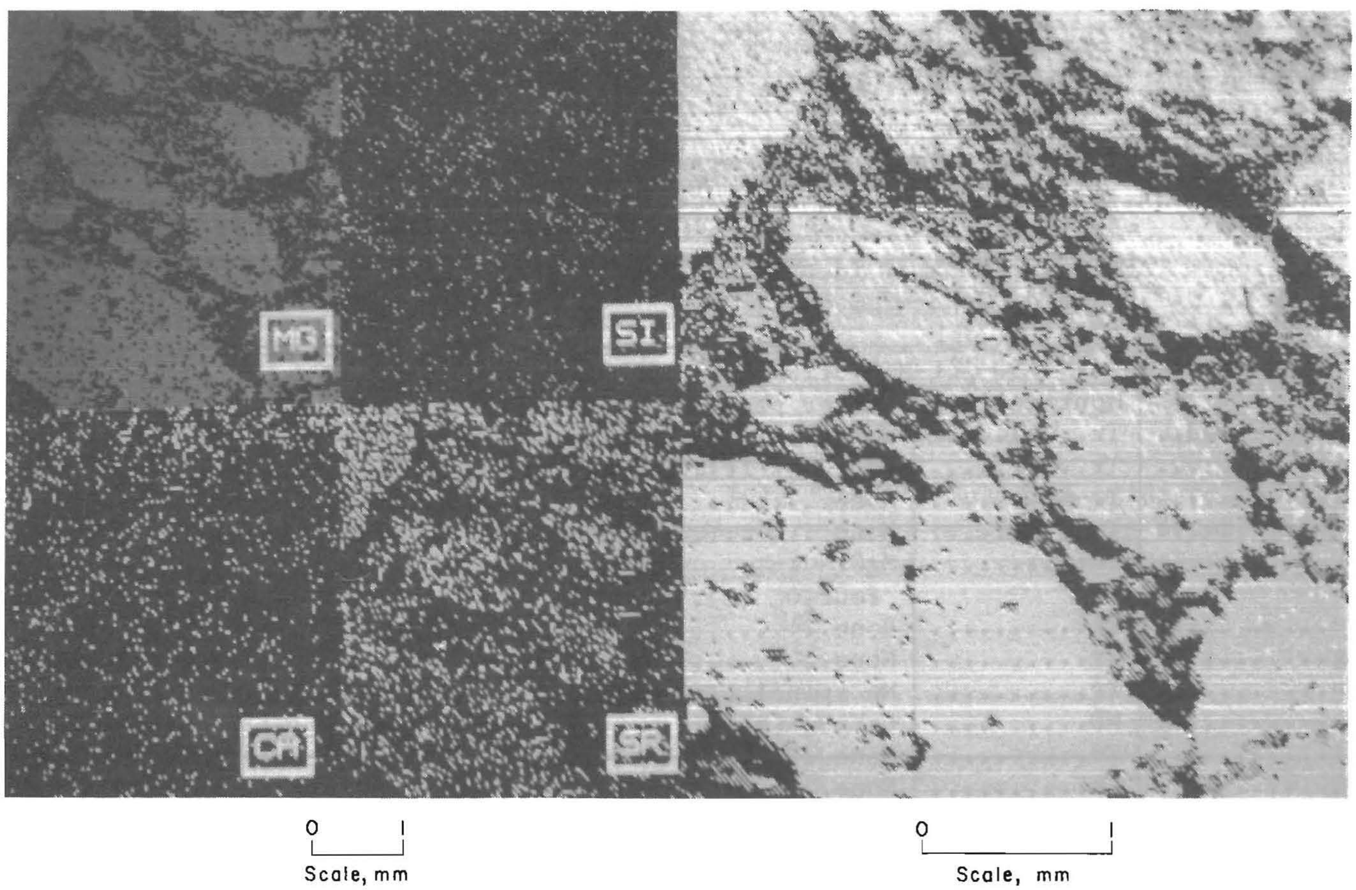

FIGURE 2. - SEM micrograph of elemental distributions of a 98-pct-MgO brick with strontium additions.

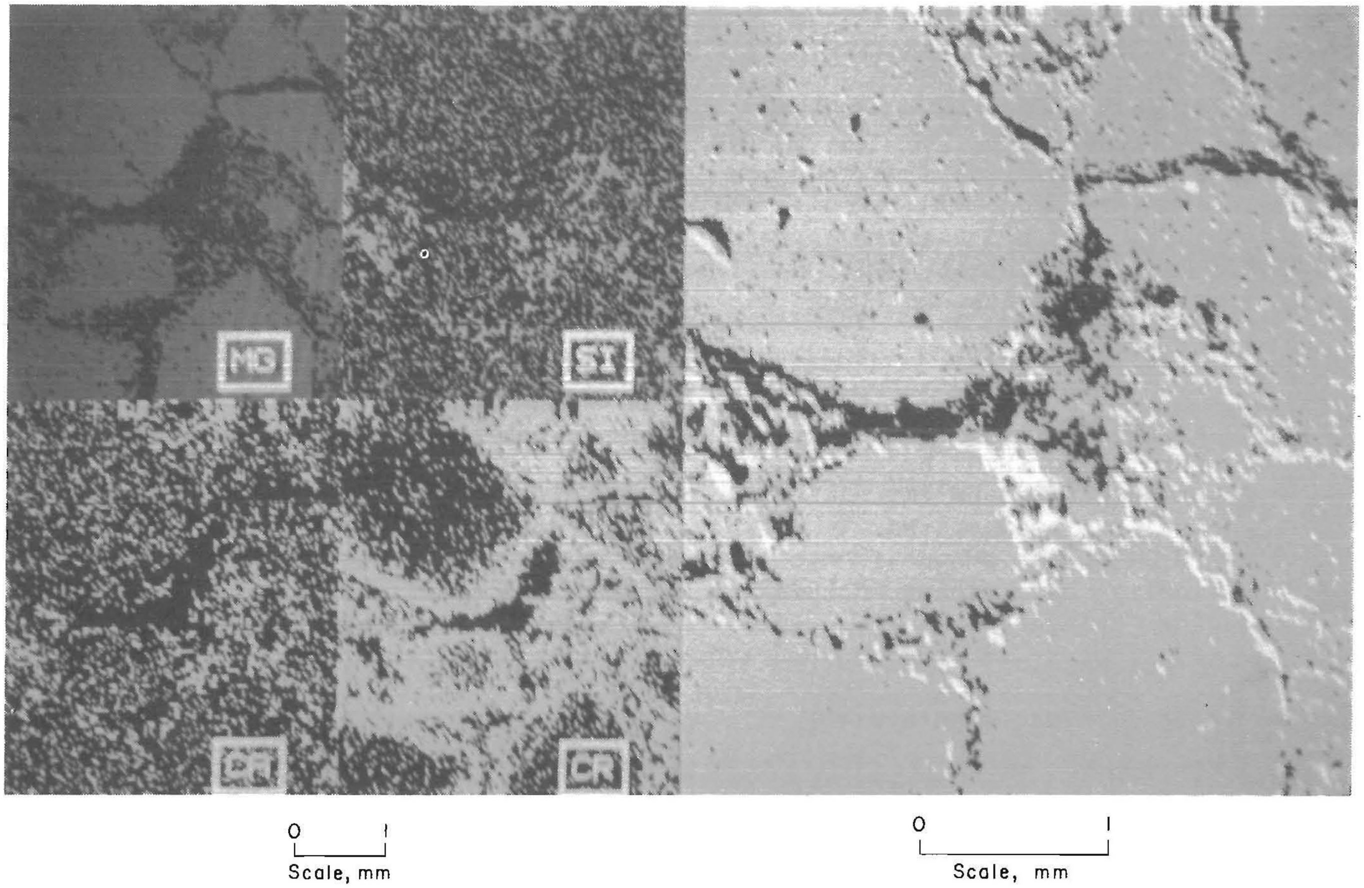

FIGURE 3. - SEM micrograph of elemental distributions of a 90-pct-MgO brick with chromium additions.

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

Treatment and/or additive	90 pct MgO	98 pct MgO	Treatment and/or additive	90 pct MgO	98 pct MgO
As-received......	200± 30	240± 40	Mo...............	160± 40	90± 20*
Al...............	260± 50*	170± 40*	Ni...............	220± 30	220± 40
Ca...............	350± 70*	890±150*	Si...............	650± 30*	570± 80*
Co...............	270± 40*	220± 50	Sn...............	450± 50*	229± 30
Cr...............	450± 80*	290± 30*	Sr...............	300±100	610± 86*
Fe...............	220± 40	190± 20*	Ti...............	150± 10*	160± 30*
Mg...............	400±110*	210± 40	Zr...............	300± 30*	220± 70
Mn...............	200± 20	210± 30			

*Indicates a statistically significant difference based on t-test with a 95-pct confidence interval. Sample population = 5.

NOTE.--Plus-minus (±) values are standard deviation.

Additions of Ca, Cr, Si, and Sr resulted in statistically significant strength increases in 98-pct-MgO brick. Calcium additions produced the largest strength increase, from 240 to 890 lb/in^2. Large increases in strength also were noted for silicon (570 lb/in^2) and strontium (610 lb/in^2) additions at 1,500° C. Additions of Al, Fe, and Ti caused a strength decrease at 1,500° C.

HOT LOAD

Hot load testing was conducted at 1,700° C for 90-pct-MgO brick and at 1,750° C for 98-pct-MgO brick. Both firing schedules followed the No. 5 heating rate of ASTM C-16. As shown in table 7, no statistically significant changes in hot load for treated versus untreated samples were noted in the 90-pct-MgO brick. Statistically significant increases in deformation occurred in the 98-pct-MgO brick from additions of aluminum (0.27-pct deformation) and molybdenum (brick failure). The type of failure observed in the 98-pct-MgO brick with molybdenum additions is shown in figure 4.

SLAG RESISTANCE

The results of the slag resistance evaluation tests using an electric furnace type slag on treated and untreated samples at 1,600° C are listed in table 8. Statistically significant decreases in sample area loss from the as-received condition were noted for Al, Mg, Mn, Mo, Si, and Sn additions to 90-pct-MgO samples. The best slag resistance, a decrease in area loss from 1.59 to 0.29 pct, was noted with magnesium additions.

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

Treatment and/or additive	Average deformation, pct		Treatment and/or additive	Average deformation, pct	
	90 pct MgO to 1,700° C	98 pct MgO to 1,750° C		90 pct MgO to 1,700° C	98 pct MgO to 1,750° C
As-received....	0.91±0.50	0.12±0.05	Mn.............	0.72±0.21	0.11±0.07
Al.............	.42± .09	.27± .03*	Mo.............	.20± .01	Failed*
Ca.............	1.00± .45	.14± .04	Si.............	.22± .03	.05± .06
Co.............	.40± .01	.11± .04	Sn.............	.46± .01	.26± .05
Cr.............	.16± .02	.10± .02	Sr.............	1.22± .57	.13± .01
Mg.............	.49± .02	.37± .13	Zr.............	.59± .27	.16± .06

*Indicates a statistically significant difference based on t-test with a 95-pct confidence interval. Sample population = 2.

NOTE.--Plus-minus (±) values are standard deviation.

TABLE 8. - Area removed by slag attack, percent

Treatment and/or additive	Area removed, pct		Treatment and/or additive	Area removed, pct	
	90 pct MgO	98 pct MgO		90 pct MgO	98 pct MgO
As-received....	-1.59±0.76	-0.77±0.47	Mn.............	-0.60±0.48*	-0.77±0.35
Al.............	-.61± .48*	-.70± .53	Mo.............	-.30± .25*	-.32± .21
Ca.............	-2.57± .91	-1.22± .33	Si.............	-.63± .30*	-1.23± .57
Co.............	-1.17± .68	-.82± .39	Sn.............	-.82± .45*	-.65± .40
Cr.............	-1.07± .65	-.86± .36	Sr.............	-1.28± .75	-1.41± .62
Mg.............	-.29± .44*	-.64± .45	Zr.............	-1.47± .56	-.91± .34

*Indicates a statistically significant difference based on t-test with a 95-pct confidence interval. Sample population = 6 sides.

NOTE.--Plus-minus (±) values are standard deviation.

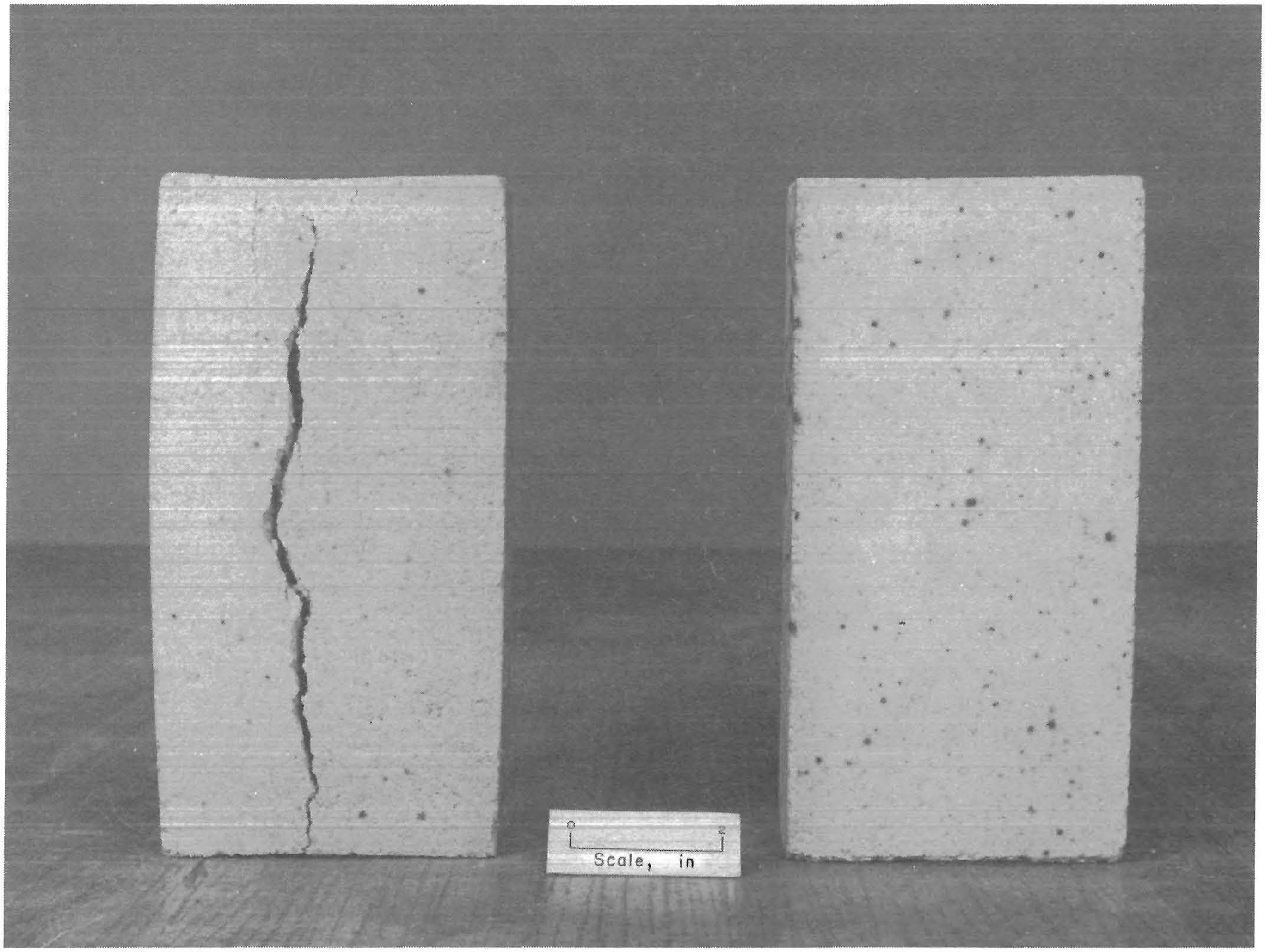

FIGURE 4. - Comparison of hot load failure occurring at 1,750° C in a 98-pct-MgO brick after molybdenum treatment (left) with the untreated sample (right).

None of the 98-pct-MgO brick showed significant changes in slag resistance with ion additions.

THERMAL SPALL RESISTANCE

The thermal spall resistance of samples was determined by the percent MOE retained before and after thermal cycling of the samples five times between 75° and 1,100° C. Loading of the thermal spall furnace for sample testing is shown in figure 5. Results are given in table 9. Reductions in elastic modulus indicate a weakening of the refractory bond. Additions of Al, Co, Cr, Mg, Sn, and Zr to the 90-pct-MgO refractory samples resulted in a greater percentage of original MOE retained in the treated samples than in the untreated samples. This indicates that these additives would improve the spalling resistance of 90-pct-MgO refractories.

The 98-pct-MgO materials with ion additions generally did not show statistically significant changes in MOE values. A significant improvement in spalling resistance was observed with manganese additions (87 pct MOE retained versus 76 pct for the untreated sample), and a significant decrease in spalling resistance for chromium addition (59 pct MOE retained versus 76 pct).

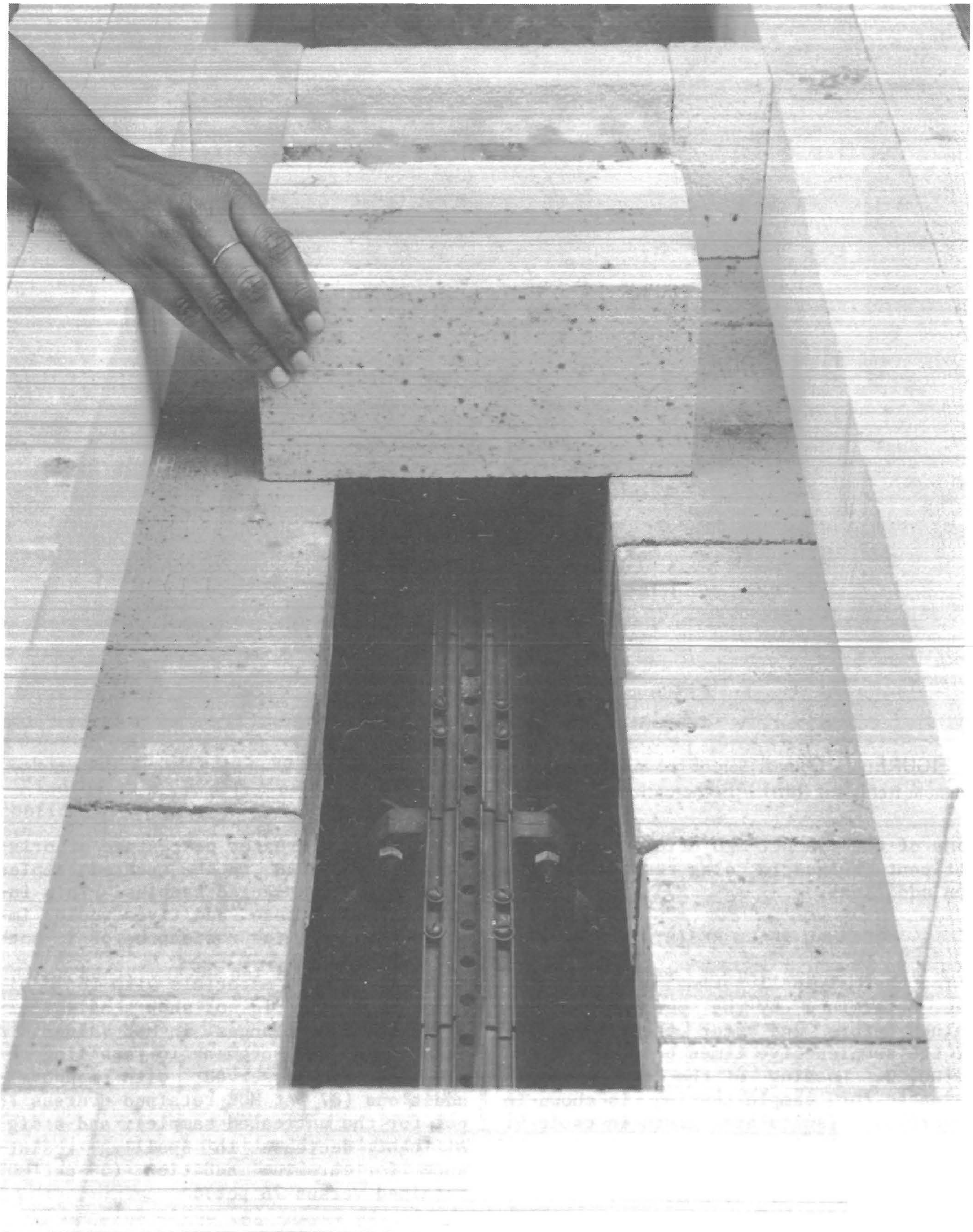

FIGURE 5. - Loading of samples in the thermal spall test facility.

TABLE 9. - Modulus of elasticity retained, percent

Treatment and/or additive	MOE retained, pct		Treatment and/or additive	MOE retained, pct	
	90 pct MgO	98 pct MgO		90 pct MgO	98 pct MgO
As-received.....	39± 3	76±10	Mn..............	40±14	87± 5*
Al..............	58±10*	75± 6	Mo..............	30± 4*	81± 5
Ca..............	46±10	79± 4	Si..............	47±15	77± 7
Co..............	49± 9*	78± 8	Sn..............	52±12*	83± 6
Cr..............	46± 6*	59± 6*	Sr..............	38±10	75± 3
Mg..............	55± 5*	72± 9	Zr..............	45± 5*	81± 5

*Indicates a statistically significant difference based on t-test with a 95-pct confidence interval. Sample population = 5.

NOTE.--Plus-minus (±) values are standard deviation.

CONCLUSIONS

Based on the results of this study the following conclusions can be made:

1. Additions to 98-pct-MgO brick did not generally result in statistically significant improvements.

2. Additions of Al, Mg, or Sn to 90-pct-MgO brick resulted in statistically significant improvements in hot MOR, slag resistance, and spalling resistance properties. The addition of only 1.14 wt pct SnO_2 resulted in dramatic improvements of hot MOR (200 lb/in^2 to 450 lb/in^2 at 1,500° C), slagging resistance (1.59 pct area removed to 0.82 pct), and spalling resistance (39 pct MOE retained to 52 pct retained).

3. The high-temperature properties of 90-pct-MgO brick with additions of Al, Mg, or Sn are equal to or approach those of 98-pct-MgO brick.

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