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# Magnesia Refractories Produced From Chemically Modified Periclase Grains and $Mg(OH)_2$ Slurries

By James P. Bennett and Timothy A. Clancy



UNITED STATES DEPARTMENT OF THE INTERIOR

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**UNITED STATES DEPARTMENT OF THE INTERIOR**  
**William P. Clark, Secretary**

**BUREAU OF MINES**  
**Robert C. Horton, Director**

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## CONTENTS

	<u>Page</u>
Abstract.....	1
Introduction.....	2
Raw materials and sample preparation.....	2
Periclase grain study.....	2
Mg(OH) <sub>2</sub> slurry study.....	3
Test procedures.....	4
Periclase grain study.....	4
Mg(OH) <sub>2</sub> slurry study.....	4
Results and discussion.....	5
Periclase grain study.....	5
Mg(OH) <sub>2</sub> slurry study.....	7
Conclusions.....	12
References.....	14

## ILLUSTRATIONS

1. SEM micrographs of elemental distributions for full-size brick sample B-1.	8
2. SEM micrographs of elemental distributions for full-size brick sample S-1.	9
3. SEM micrographs of elemental distributions for brine periclase sample B-Z2	11
4. SEM micrographs of elemental distributions for seawater periclase sample S-M2.....	13

## TABLES

1. Partial chemical analyses of periclase raw materials.....	2
2. Additives and screen analysis of crushed optimized periclase grains.....	3
3. Properties of manufactured bricks.....	3
4. Partial chemical analyses of calcined Mg(OH) <sub>2</sub> slurries.....	3
5. Chemical additions to MgO materials.....	4
6. Physical properties of optimized and commercial MgO bricks.....	5
7. High-temperature properties of optimized and commercial MgO bricks.....	6
8. Mineralogy of periclase samples.....	6
9. Physical properties of Mg(OH) <sub>2</sub> periclase samples.....	7
10. MOR of Mg(OH) <sub>2</sub> periclase samples.....	10
11. Mineralogy of periclase samples.....	12

UNIT OF MEASURE ABBREVIATIONS USED IN THIS REPORT

°C	degree Celsius	lb	pound
cm <sup>3</sup>	cubic centimeter	min	minute
g/cm <sup>3</sup>	gram per cubic centimeter	pct	percent
h	hour	psi	pound per square inch
in	inch	wt pct	weight percent
in <sup>2</sup>	square inch		

# MAGNESIA REFRACTORIES PRODUCED FROM CHEMICALLY MODIFIED PERICLASE GRAINS AND $Mg(OH)_2$ SLURRIES

By James P. Bennett<sup>1</sup> and Timothy A. Clancy<sup>2</sup>

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## ABSTRACT

Based on previous Bureau of Mines research indicating that improved high-temperature properties could be achieved for periclase refractories through chemical additions, the Bureau investigated the properties of full-size bricks produced from chemically modified periclase refractory grains and the suitability of making such chemical additions to  $Mg(OH)_2$  slurries prior to production of the periclase grains. In full-size brick testing, strength values, both hot and cold, for the optimized bricks were superior to those for a commercial 98-wt-pct-MgO refractory. The best results were obtained for a natural magnesite with an adjusted  $CaO:SiO_2$  (C:S) ratio of 3.0 and a 1.0-wt-pct addition of  $ZrO_2$  and for a seawater periclase with an adjusted C:S ratio of 2.5 and a 0.5-wt-pct addition of  $MnO_2$ . For samples produced from chemically modified  $Mg(OH)_2$  slurries, additions of both  $MnO_2$  and  $ZrO_2$  and an increase in C:S ratios produced significant increases in hot flexural strength, similar to those resulting from chemical additions made to periclase grains. The most effective modifications were additions of  $MnO_2$  to brine-derived periclases having a C:S ratio adjusted to 3.0. These results on chemically modified magnesia refractories indicate that such material could potentially substitute for magnesia-chrome refractories containing imported chromite.

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## INTRODUCTION

Improving the performance of refractories produced from domestic magnesia raw materials would reduce the Nation's dependence upon imported refractory raw materials such as chromite.

Refractory-grade periclase grains used to make commercial magnesia refractories are primarily obtained from seawater or well brines by precipitating magnesium hydroxide [Mg(OH)<sub>2</sub>] from a salt solution, filtering the hydroxide to form a cake, calcining the cake to yield MgO powder, and compacting and high-firing MgO briquettes made from these powders in a rotary or shaft kiln. Previous work both within and outside the Bureau of Mines (1-4)<sup>3</sup> has shown that the high-temperature strength properties of refractories made from periclase grains are related to the CaO:SiO<sub>2</sub> (C:S) ratio and the B<sub>2</sub>O<sub>3</sub> content of the grain. Gilpin and Spencer (1) and Jackson and Laming (2) showed that a C:S ratio of at least 2.0 was necessary in order to maximize high-temperature strengths. In addition, Gilpin and Spencer reported that B<sub>2</sub>O<sub>3</sub> contents over 0.1 wt pct were detrimental to high-temperature strengths.

Previous Bureau work (3-4) showed that there was an optimum C:S ratio for specific periclase grains of different origins and compositions. This work also indicated that improvements in the high-temperature strength of the refractories could be obtained by selective addition of zirconium oxide (ZrO<sub>2</sub>). Adjustments to the C:S ratio and addition of ZrO<sub>2</sub> were made to several types of dead-burned periclase grains crushed to minus 200 mesh. These modified powders were then formed into test bars and their high-temperature strengths measured.

This report presents the results of two studies. In the first, the refractory properties of full-size bricks made from modified periclase grains as described above were determined. In the second phase, the modification of periclase grains by chemical additions to Mg(OH)<sub>2</sub> filter cakes was investigated, since this was a more practical technique than using the already fired grain material.

## RAW MATERIALS AND SAMPLE PREPARATION

## PERICLASE GRAIN STUDY

The chemical analyses of the periclase raw materials used for full-size bricks

<sup>3</sup>Underlined numbers in parentheses refer to items in the list of references at the end of this report.

were reported previously (4) and are shown in table 1. Two of the periclase materials were produced from seawater, two from brines, and one from a natural magnesite. Reagent-grade oxide powders (minus 200 mesh in size) of MnO<sub>2</sub>, ZrO<sub>2</sub>, CaO, and SiO<sub>2</sub> were used as additives to produce the optimized grains.

TABLE 1. - Partial chemical analyses of periclase raw materials, weight percent

Sample No. and source...	B-1, brine	B-2, brine	M-1, natural magnesite	S-1, seawater	S-2, seawater
MgO.....	95.3	95.9	93.5	97.4	93.9
CaO.....	.61	2.30	3.30	.89	.96
SiO <sub>2</sub> .....	.64	.56	1.30	.60	1.80
Fe <sub>2</sub> O <sub>3</sub> .....	.61	.40	.64	.46	.68
Al <sub>2</sub> O <sub>3</sub> .....	.20	.13	.44	.12	.41
B <sub>2</sub> O <sub>3</sub> .....	.11	.02	.02	.05	.13
C:S ratio.....	.95	4.11	2.54	1.48	.53

TABLE 2. - Additives and screen analysis of crushed optimized periclase grains

Sample No. and source...	B-1, brine	B-2, brine	M-1, magnesite	S-1, seawater	S-2, seawater
C:S ratio.....	2.5	3.0	3.0	2.5	3.0
MnO <sub>2</sub> .....wt pct..	0	0	0	0.5	0
ZrO <sub>2</sub> .....wt pct..	2.0	1.0	1.0	0	0
Screen analysis, pct:					
Plus 4 mesh.....	0	Trace	Trace	Trace	Trace
Plus 10 mesh.....	21	23	28	23	21
Minus 10 plus 28 mesh.	31	28	28	31	29
Minus 28 plus 65 mesh.	13	13	12	13	15
Minus 65 mesh.....	35	36	32	33	35
Minus 150 mesh.....	29	29	26	27	27

TABLE 3. - Properties of manufactured bricks

Sample <sup>1</sup> .....	B-1	B-2	M-1	S-1	S-2
Density, g/cm <sup>3</sup> :					
Green.....	2.66	2.58	2.63	2.52	2.58
Dried.....	2.68	2.58	2.63	2.53	2.60
Fired.....	2.75	2.63	2.71	2.56	2.66
Firing shrinkage (fired basis).....pct..	-0.02	-0.01	-0.01	-0.01	-0.01

<sup>1</sup>Each entry is average of 5 tests.

Large quantities of optimized periclase material (250-lb batches) were prepared by combining the periclase (85 pct minus 200 mesh) with additives as shown in table 2. The material was dry mixed for 1 h and pressed at 3,000 psi into 1- by 2- by 5-in bars. These bars were fired at 1,750° C with a 4-h hold in a gas-fired furnace. The fired bars were broken up in a jaw crusher to provide selected grain-size distribution for brick batches as shown in table 2.

A commercial vendor formed and fired full-size bricks from the optimized periclase grains, using the following procedures: The as-received batches were dry mixed for 1 min in a large muller mixer, a magnesium sulfate-water solution was added while mixing, and mixing continued for an additional 3 min. Bricks, 9- by 3-1/2- by 2-1/2-in, were formed on a laboratory hydraulic press at 15,000 psi. The bricks were air-dried at least 8 h and then dried at 180° C for at least 24 h. The bricks were fired at 1,730° C for 10 h.

Test data obtained during manufacture of the bricks are given in table 3.

#### Mg(OH)<sub>2</sub> SLURRY STUDY

Mg(OH)<sub>2</sub> derived from two different domestic sources, brine and seawater, was used. The chemical analysis of each slurry after being calcined at 950° C for 2 h is listed in table 4.

TABLE 4. - Partial chemical analyses of calcined Mg(OH)<sub>2</sub> slurries, weight percent

Oxide	Brine	Seawater
MgO <sup>1</sup> .....	98.62	98.13
CaO.....	.51	.91
SiO <sub>2</sub> .....	.35	.51
Fe <sub>2</sub> O <sub>3</sub> .....	.25	.26
Al <sub>2</sub> O <sub>3</sub> .....	.24	.10
B <sub>2</sub> O <sub>3</sub> .....	.035	.097

<sup>1</sup>By difference.

Reagent-grade oxide additions were made to the Mg(OH)<sub>2</sub> slurries in the amounts listed in table 5. Additions of



TABLE 5. - Chemical additions to MgO materials

Sample	Oxide additions, wt pct			CaO:SiO <sub>2</sub> ratio	Sample	Oxide additions, wt pct			CaO:SiO <sub>2</sub> ratio
	CaO	MnO <sub>2</sub>	ZrO <sub>2</sub>			CaO	MnO <sub>2</sub>	ZrO <sub>2</sub>	
BRINE Mg(OH) <sub>2</sub>					SEAWATER Mg(OH) <sub>2</sub>				
B-A1..	0	0	0	1.5	S-A1..	0	0	0	1.8
B-A2..	.37	0	0	2.5	S-A2..	.36	0	0	2.5
B-A3..	.54	0	0	3.0	S-A3..	.62	0	0	3.0
B-M1..	.54	.54	0	3.0	S-M1..	.61	.54	0	3.0
B-M2..	.53	1.07	0	3.0	S-M2..	.61	1.07	0	3.0
B-M3..	.53	2.13	0	3.0	S-M3..	.60	2.12	0	3.0
B-Z1..	.52	0	3.00	3.0	S-Z1..	.60	0	2.98	3.0
B-Z2..	.51	0	5.87	3.0	S-Z2..	.58	0	5.84	3.0
B-Z3..	.50	0	8.64	3.0	S-Z3..	.56	0	8.59	3.0

CaO, MnO<sub>2</sub>, and ZrO<sub>2</sub> powders (minus 200 mesh in size) were made based on results obtained in an earlier study on the influence of selected additives on the high-temperature strength of MgO refractories (4).

Additions were made to the brine or seawater Mg(OH)<sub>2</sub> slurries using a paddle-blade-type mixer. Samples were mixed for 10 min, dried at 120° C for 48 h, and calcined at 950° C for 2 h to remove

water of hydration. The MgO was then briquetted at 7,000 psi into 1-7/8- by 1- by 0.3-in bars and fired to a dense MgO grain at 1,700° C for 4 h in a gas furnace. The fired MgO grains were then crushed to minus 20 mesh and mixed with 4.8 wt pct of a water solution containing a 10-wt-pct organic binder. Bars 1.75- by 3.5- by 0.5-in were then pressed to 7,000 psi, dried at 120° C for 24 h, and fired at 1,700° C for 4 h.

#### TEST PROCEDURES

##### PERICLASE GRAIN STUDY

Room-temperature modulus of rupture (MOR) and cold crushing strengths were determined on the fired full-size bricks per American Society for Testing and Materials (ASTM) standard C133-72. Hot MOR was determined according to ASTM C704-76a, slag attack according to ASTM C874-77, and hot load according to ASTM C16-77. Two slag tests were run, one using a basic oxygen furnace (BOF) type slag and one using a glass composition slag. The first was primarily a CaO-FeO-SiO<sub>2</sub> melt, and the second was primarily a Na<sub>2</sub>O-CaO-SiO<sub>2</sub> melt. Thermal shock resistance was determined following a method developed at the Bethlehem Steel Co. research laboratory. Brick samples cut to 1.0- by 1.0- by 2.5-in dimensions were subjected to five cycles of heating at 1,200° C, held for 10 min at temperature, and removed and cooled in air for 10 min before

another cycle was initiated. Following the completion of the fifth cycle, the room temperature MOR of the samples was determined. The thermal shock resistance was reported as the percentage of loss in MOR compared with values obtained on samples before thermal shock treatment.

Samples of each brick were analyzed by X-ray diffraction for mineralogical composition. Polished section samples were submitted to the Bureau's Albany (OR) Research Center for microstructural characterization by scanning electron microscopy (SEM).

##### Mg(OH)<sub>2</sub> SLURRY STUDY

Fired dimensions and sample weights were measured on the test bars and used to calculate fired bulk density and firing shrinkage. The bars were cut into 0.5- by 0.5- by 3.5-in samples for hot

(1,500° C) and cold (25° C) MOR measurements. Five samples of each composition were tested at each temperature. Samples

were examined for mineral phases present using X-ray diffraction analysis and for microstructure using SEM.

## RESULTS AND DISCUSSION

### PERICLASE GRAIN STUDY

The chemical analyses of the periclase starting materials indicated C:S ratios ranging from 0.53 to 4.11. Minor amounts of Fe<sub>2</sub>O<sub>3</sub> and Al<sub>2</sub>O<sub>3</sub> also were present. Two of the starting materials, B-1 and S-2, had B<sub>2</sub>O<sub>3</sub> contents exceeding a level (0.1 wt pct) earlier found to be detrimental to hot MOR of refractory-grade magnesia (4).

The physical properties of the optimized full-size MgO bricks are compared with properties of commercial refractories in table 6. The fired bulk densities of the optimized bricks were 0.1 to 0.3 g/cm<sup>3</sup> lower than the density of a normal 98-wt-pct-MgO commercial refractory (3.1 g/cm<sup>3</sup>). This difference probably results from lower grain densities produced in the laboratory compared with grain densities achievable in commercial periclase shaft kiln practice. However, the strength properties of the optimized bricks were superior to those for a 98-wt-pct-MgO refractory. These strength data were evaluated statistically (5). All of the cold crushing strengths and four of the five MOR values were significantly greater than those determined for

a commercial brick. However, results of the Bethlehem Steel thermal shock tests indicated that the optimized brick lost a greater proportion of flexural strength owing to thermal shock. All of the optimized bricks demonstrated better abrasion resistance than that obtained for a 98-wt-pct-MgO commercial brick. Previous abrasion resistance testing at Tuscaloosa Research Center of commercial refractories had shown that abrasion resistance results coincide with cold crushing strength data.

High-temperature properties of the optimized full-size MgO bricks are compared with those for commercial refractories in table 7. All of the 1,300° and 1,500° C MOR values for the five optimized periclase materials were significantly higher than the value obtained for a 98-wt-pct-MgO commercial refractory. The average hot MOR for the 10 conditions of composition and temperature was 648 psi with an overall standard deviation of 256.5. All five of the optimized periclase materials exhibited less hot load deformation at 1,700° C than that obtained for the 98-wt-pct-MgO commercial refractory. The 1,650° C BOF slag resistances of the optimized MgO bricks were similar to that

TABLE 6. - Physical properties of optimized and commercial MgO bricks

Sample	Cold crushing strength, psi	MOR at 25° C, psi	Thermal-shocked MOR, psi	Strength loss, pct	Abrasion resistance, vol loss, cm <sup>3</sup>
B-1.....	*11,200±800	2,420±370	363±290	85±15	2.6
B-2.....	*9,510±690	*3,100±320	195±125	94±5	3.0
M-1.....	*10,740±620	*3,470±230	728±265	79±3	2.7
S-1.....	*8,730±940	*3,020±80	146±99	95±4	3.2
S-2.....	*9,470±880	*2,940±540	123±35	96±2	3.2
98-wt-pct-MgO commercial refractory.....	4,880±910	2,070±330	1,327±205	36±12	4.0

\*Significant difference compared with 98-wt-pct-MgO commercial refractory at 99-pct confidence level.

NOTE.--Figures preceded by ± are 95-pct standard deviation intervals.

TABLE 7. - High-temperature properties of optimized and commercial MgO bricks

Sample	MOR, psi		Hot load (1,700° C, 25 psi) deformation, pct	Slag resistance, vol loss, in <sup>2</sup>	
	1,300° C	1,500° C		1,650° C, BOF slag	1,600° C, glass slag
B-1.....	*360±134	*110±15	0	1.80	1.45
B-2.....	*800±132	*690±106	-.03	2.11	.96
M-1.....	*930±133	*810±105	0	2.08	1.64
S-1.....	*700±25	*790±132	+.92	2.20	1.55
S-2.....	*800±205	*490±179	+.89	2.00	1.78
98-wt-pct-MgO com- mercial refractory	120±20	40±10	-.27	1.88	.94

\*Significant difference compared with 98-wt-pct-MgO commercial refractory at 99-pct confidence level.

NOTE.--Figures preceded by ± are 95-pct standard deviation intervals.

obtained for the commercial 98-wt-pct MgO refractory with only one value (that for B-1) better than for the commercial bricks.

Comparing high-temperature properties of the five optimized materials, sample M-1 (with a C:S of 3.0 and a 1.0-wt-pct-ZrO<sub>2</sub> addition) exhibited the highest MOR values at both 1,300° and 1,500° C and showed no measurable hot load deformation. Sample S-1 (with a C:S of 2.5 and a 0.5-wt-pct-MnO<sub>2</sub> addition) had the second highest 1,500° C MOR (790 psi versus 810 psi) and showed a positive change under hot load testing. The weakest material both at 1,300° and 1,500° C was

sample B-1 (with a C:S of 2.5 and a 2.0-wt-pct-addition of ZrO<sub>2</sub>).

The results of mineralogical analyses of the optimized periclase bricks are shown in table 8. Periclase was the predominant phase in all five materials. The as-received materials contained minor amounts of monticellite (CaO·MgO·SiO<sub>2</sub>) and merwinite (3CaO·MgO·2SiO<sub>2</sub>). Both samples with additions of ZrO<sub>2</sub> (M-1 and B-1) had minor amounts of calcium zirconate (CaZrO<sub>3</sub>) present. This is a refractory phase with a melting point of 2,340° C (while the original phases of monticellite and merwinite have melting points of 1,487° C and 1,577° C,

TABLE 8. - Mineralogy of periclase samples

Sample	Peri- clase, MgO	Monticellite, CaO·MgO·SiO <sub>2</sub>	Merwinite, 3CaO·MgO·2SiO <sub>2</sub>	α-dicalcium silicate, 2CaO·SiO <sub>2</sub>	CaZrO <sub>3</sub>	Cubic ZrO <sub>2</sub>	Cubic Mn phase
B-1.....	Maj	Min	ND	ND	ND	ND	ND
B-1 (optimized)	Maj	Tr	Tr	ND	Min	Min	ND
B-2.....	Maj	ND	ND	Tr	ND	ND	ND
B-2 (optimized)	Maj	ND	ND	Min	ND	ND	ND
M-1.....	Maj	ND	Min	Min	ND	ND	ND
M-1 (optimized)	Maj	ND	ND	Min	Min	ND	ND
S-1.....	Maj	ND	Min	ND	ND	ND	ND
S-1 (optimized)	Maj	ND	ND	Min	ND	ND	Tr
S-2.....	Maj	Min	ND	ND	ND	ND	ND
S-2 (optimized)	Maj	ND	ND	Min	ND	ND	Tr

ND Not detected. Maj Major. Min Minor. Tr Trace.

respectively). All of the optimized periclases, except B-1, indicated small amounts of dicalcium silicate ( $2CaO \cdot SiO_2$ ), with a melting point of  $2,130^\circ C$ . One of the samples (B-1) with a 2.0-wt-pct addition of  $ZrO_2$  exhibited a minor amount of cubic zirconia.

The SEM micrographs indicate the distribution of the elements added to each magnesia material. Figure 1 contains micrographs of brine periclase sample B-1, which had a C:S of 2.5 and a  $ZrO_2$  addition of 2.0 wt pct. The micrographs show that the individual periclase grains were rounded, with low internal porosity and a medium degree of direct grain-to-grain bonding. Comparing the Mg, Ca, and Si distribution micrographs, it is clear that the intergrain areas were composed predominantly of calcium silicate phases. The Zr distribution micrograph reveals that a substantial amount of zirconium was located in these areas, presumably as calcium zirconate. Additions of zirconium had the effect of reducing the amount of calcium in solution in MgO. The Al distribution micrograph indicates that some of the intergrain areas contained aluminum as well.

Figure 2 shows micrographs of seawater periclase sample S-1, which had a C:S of 2.5 and an  $MnO_2$  addition of 0.5 wt pct. The periclase grains in this SEM micrograph were more angular, with some internal porosity. Once again, based upon the Ca and Si distribution, the intergrain areas were composed of calcium silicates. The Mn distribution micrograph indicates that the manganese was widely disseminated throughout the periclase grains. This broad distribution is to be expected because manganese can be taken into solid solution in periclase.

#### Mg(OH)<sub>2</sub> SLURRY STUDY

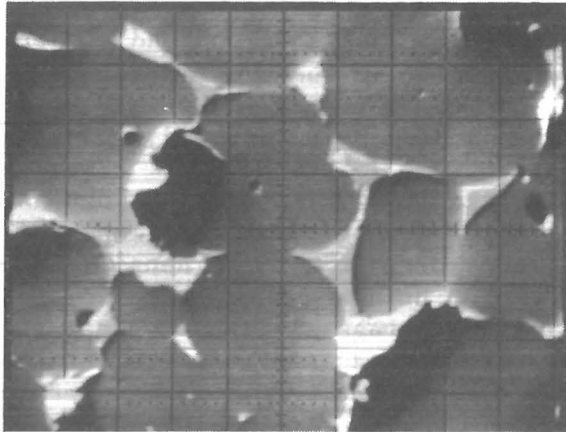
Fired bulk density and fired shrinkage for brine and seawater periclase samples are given in table 9. Bulk densities for all samples ranged from 2.37 to 2.63 g/cm<sup>3</sup> and are lower than values reported

for commercial firing conditions. Brine-based periclase samples had higher fired bulk densities than comparable seawater-based compositions in eight out of the nine sample mixtures. Adjusting the C:S ratio from 1.5 to 3.0 for brine samples resulted in a bulk density increase from 2.48 to 2.56 g/cm<sup>3</sup>. Additions of  $ZrO_2$  also resulted in bulk density increases for the brine-based periclase samples. Similar increases in bulk density in the seawater-based samples were observed in the case of both  $MnO_2$  and  $ZrO_2$  additions.

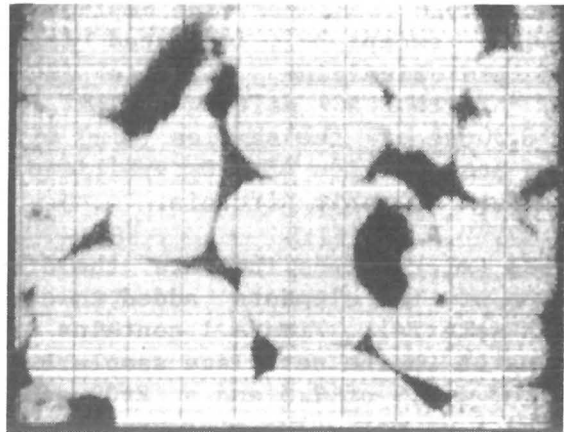
TABLE 9. - Physical properties of Mg(OH)<sub>2</sub> periclase samples

Sample	Fired bulk density, g/cm <sup>3</sup>	Firing shrinkage, pct
BRINE Mg(OH) <sub>2</sub>		
B-A1.....	2.48	-0.59
B-A2.....	2.49	-.55
B-A3.....	2.56	-.59
B-M1.....	2.46	-.54
B-M2.....	2.58	-.56
B-M3.....	2.52	-.54
B-Z1.....	2.57	-1.10
B-Z2.....	2.50	-.92
B-Z3.....	2.63	-1.14
SEAWATER Mg(OH) <sub>2</sub>		
S-A1.....	2.41	-0.74
S-A2.....	2.37	-.75
S-A3.....	2.42	-.76
S-M1.....	2.45	-.90
S-M2.....	2.45	-1.02
S-M3.....	2.45	-1.16
S-Z1.....	2.53	-1.16
S-Z2.....	2.55	-1.09
S-Z3.....	2.58	-1.13

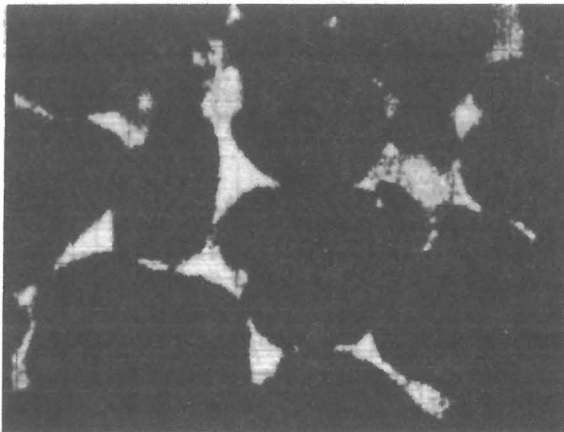
The firing shrinkages of seawater samples were generally higher than those of the comparable brine-based compositions. Increasing the C:S ratio for the brine- and seawater-based samples did not have a noticeable effect on firing shrinkages. Firing shrinkage was largest in the case of  $ZrO_2$  additions to the brine- and seawater-based samples, while  $MnO_2$  additions resulted in shrinkage increases in only seawater periclase samples.



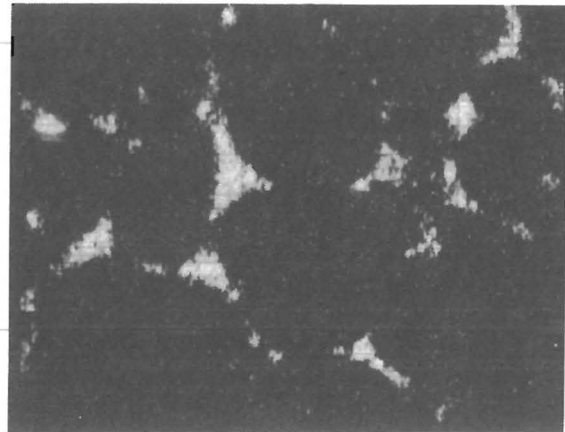
**SEM micrograph**



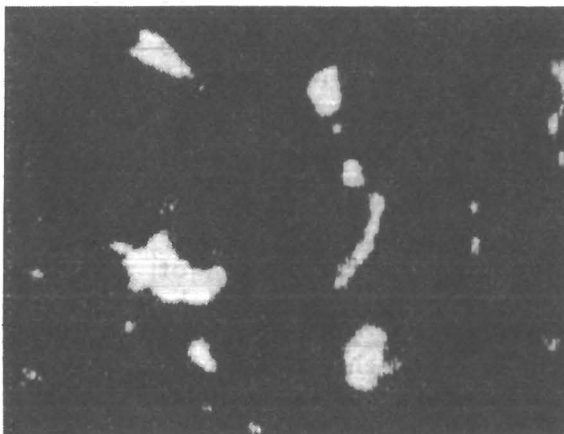
**Mg distribution**



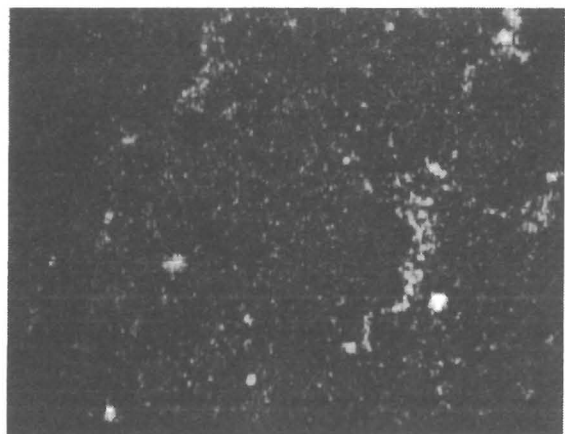
**Ca distribution**



**Si distribution**



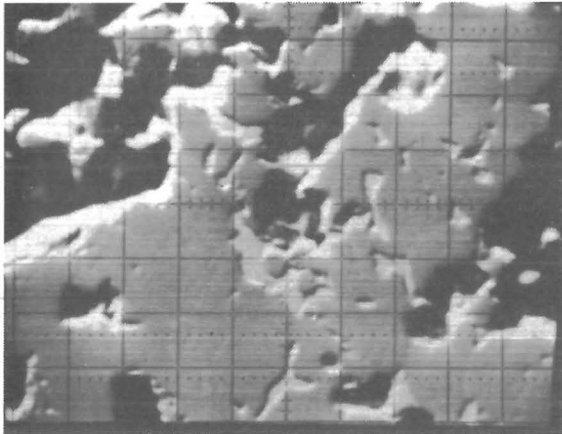
**Zr distribution**



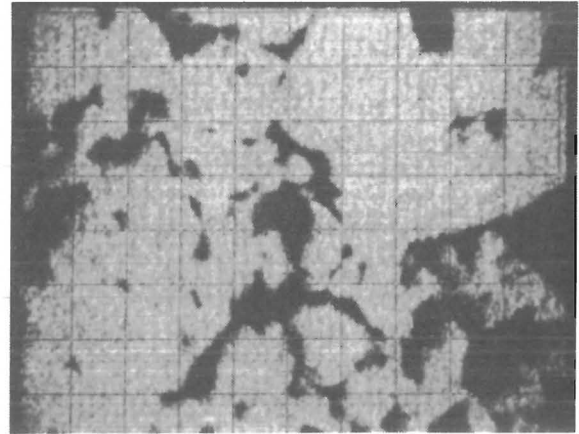
**Al distribution**

0 40  
Scale,  $\mu\text{m}$

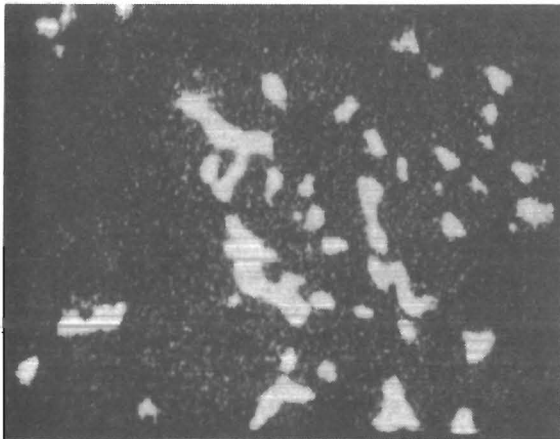
FIGURE 1. - SEM micrographs of elemental distributions for full-size brick sample B-1.



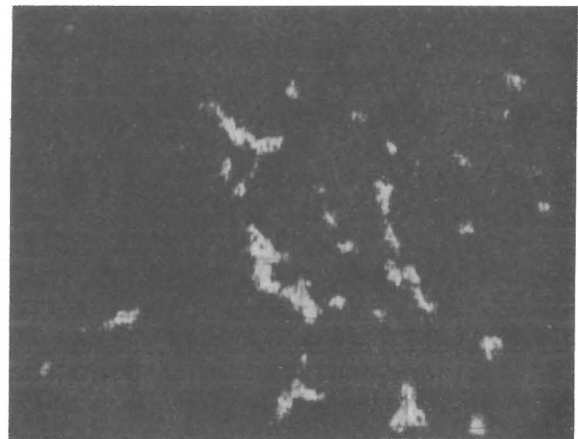
**SEM micrograph**



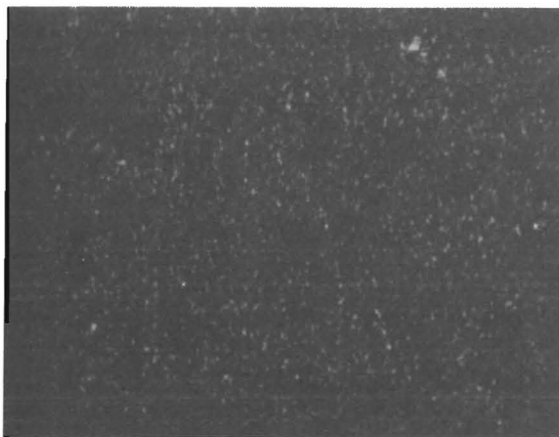
**Mg distribution**



**Ca distribution**



**Si distribution**



**Mn distribution**

0 40  
Scale,  $\mu\text{m}$

FIGURE 2. - SEM micrographs of elemental distributions for full-size brick sample S-1.

MOR strengths measured at room temperature (25° C) and 1,500° C for brine- and seawater-based periclase samples are listed in table 10. All hot MOR strength values of the brine-based mixes were greater than those for corresponding seawater mixes. The greater hot MOR values for the brine-based materials can probably be related to the lower B<sub>2</sub>O<sub>3</sub> content of these samples (approximately one-third that of the seawater-based samples). Prior studies have shown that the formation of low-melting borate phases is particularly detrimental to high-temperature strength of periclase materials.

All additives to the brine mixes produced a statistically significant increase in hot and cold MOR strength, except for the cold strength values of sample B-A3. The 1,500° C MOR strength values were higher in all samples in which an addition of ZrO<sub>2</sub> or MnO<sub>2</sub> or an increase in C:S ratio was made. An increase in 1,500° C MOR strength was statistically significant for all seawater

periclase samples with additives, except S-Z2. Generally, the increase of C:S ratio to 2.5 or 3.0 produced hot MOR strength increases equivalent to those in samples with MnO<sub>2</sub> and ZrO<sub>2</sub> additions and C:S ratios of 3.0.

Mineralogical phase analyses of brine- and seawater-based periclase samples are listed in table 11. The phases present in comparable brine- and seawater-based compositions were generally the same. Periclase was the predominant crystalline phase present in all materials tested.

Adjustment of the C:S ratio in all periclase samples from 1.5 to 2.5 and 3.0 resulted in the formation of refractory dicalcium silicate and the disappearance of monticellite and merwinite. A C:S ratio of at least 2.5 or higher is necessary to form high-melting phases such as dicalcium silicate instead of the lower melting compounds, monticellite and merwinite. Additions of MnO<sub>2</sub> at an adjusted C:S ratio of 3.0 in all periclase samples resulted in the formation of an unidentifiable cubic manganese phase and dicalcium silicate. Analysis of crystalline phases in samples containing zirconia additions indicated the presence of cubic zirconia, calcium zirconate, and monticellite.

The elimination of the low-melting crystalline phases such as monticellite and merwinite and the formation of refractory phases such as dicalcium silicate and calcium zirconate improved the hot strengths.

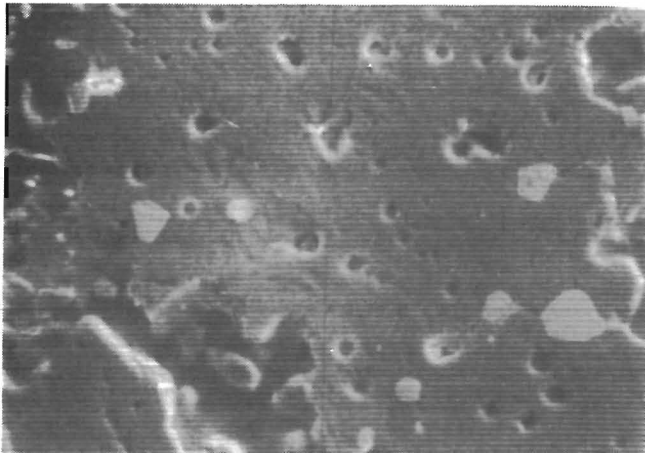
SEM examination of fired brine and seawater samples indicated thorough mixing of Ca, Mn, and Zr additives and a higher porosity in seawater than in brine grains.

Figure 3 is an SEM micrograph of sample B-Z2, a brine-based periclase with CaO and ZrO<sub>2</sub> additions. Comparison of elemental maps of Mg, Zr, Ca, and Si in the micrographs indicates individual particles of unreacted ZrO<sub>2</sub> confirmed by X-ray diffraction analysis. An overlap of Ca

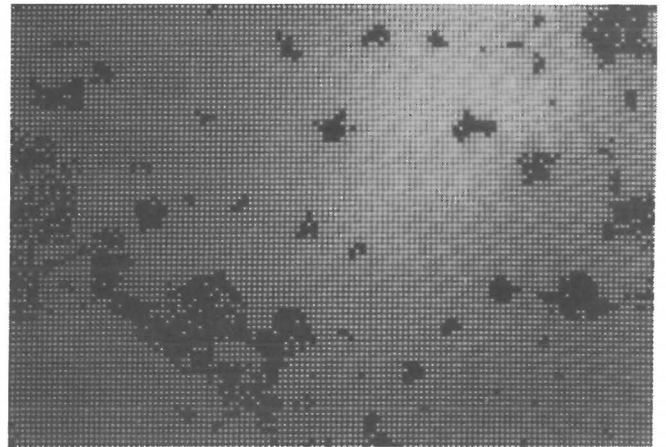
TABLE 10. - MOR of Mg(OH)<sub>2</sub> periclase samples

Sample	25° C	1,500° C
BRINE Mg(OH) <sub>2</sub>		
B-A1.....	610±320	76±30
B-A2.....	*1,060±90	*450±190
B-A3.....	860±240	*193±40
B-M1.....	*1,200±50	*550±160
B-M2.....	*1,080±90	*171±30
B-M3.....	*1,190±160	*400±200
B-Z1.....	*1,590±190	*180±20
B-Z2.....	*1,490±210	*170±60
B-Z3.....	*1,400±360	*190±40
SEAWATER Mg(OH) <sub>2</sub>		
S-A1.....	650±240	33±3
S-A2.....	540±100	*98±14
S-A3.....	580±60	*78±30
S-M1.....	560±210	*71±19
S-M2.....	510±220	*69±1
S-M3.....	770±100	*77±6
S-Z1.....	*870±80	*74±9
S-Z2.....	770±30	54±34
S-Z3.....	760±260	*62±16

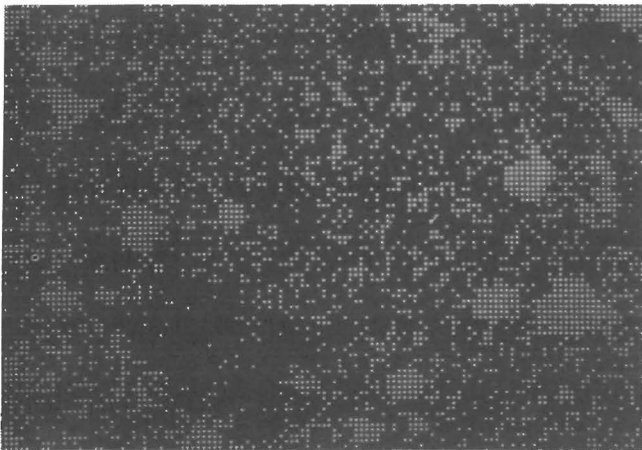
\*Significant difference compared with untreated sample data at 99-pct confidence level.



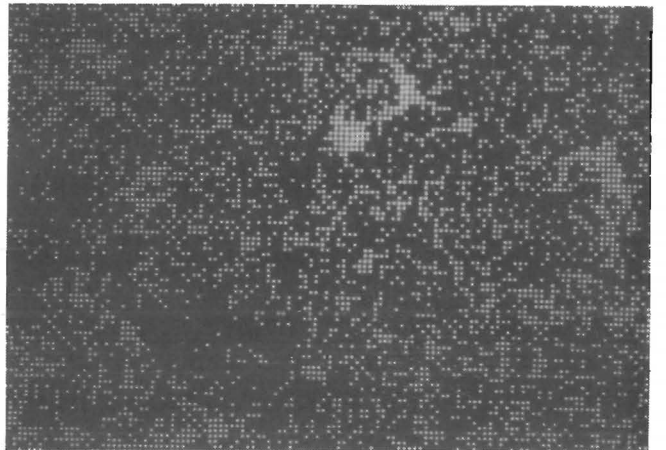
**SEM micrograph**



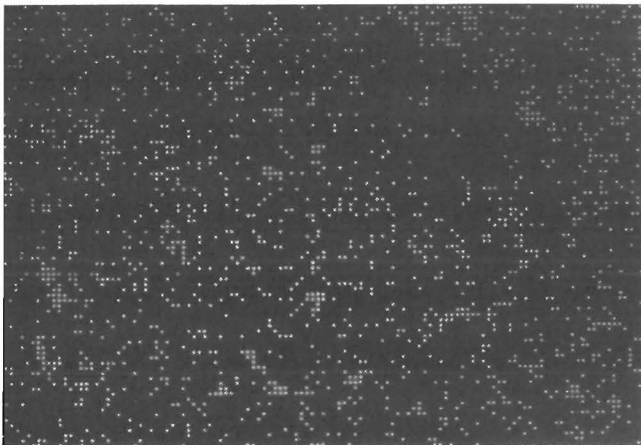
**Mg distribution**



**Zr distribution**



**Ca distribution**



**Si distribution**

0 40  
Scale,  $\mu\text{m}$

FIGURE 3. - SEM micrographs of elemental distributions for brine periclase sample B-Z2.



TABLE 11. - Mineralogy of periclase samples

Sample	Periclase, MgO	Monticellite, CaO·MgO·SiO <sub>2</sub>	Merwinite, 3CaO·MgO·2SiO <sub>2</sub>	α-dicalcium silicate, 2CaO·SiO <sub>2</sub>	CaZrO <sub>3</sub>	Cubic ZrO <sub>2</sub>	Cubic Mn phase
BRINE Mg(OH) <sub>2</sub>							
B-A1..	Maj	Tr	Tr	ND	ND	ND	ND
B-A2..	Maj	ND	ND	Tr	ND	ND	ND
B-A3..	Maj	ND	ND	Tr	ND	ND	ND
B-M1..	Maj	ND	Tr	Tr	ND	ND	Tr
B-M2..	Maj	ND	Tr	Tr	ND	ND	Tr
B-M3..	Maj	ND	Tr	Tr	ND	ND	Tr
B-Z1..	Maj	Tr	ND	ND	Min	Min	ND
B-Z2..	Maj	Tr	ND	ND	Tr	Min-maj	ND
B-Z3..	Maj	Tr	ND	ND	ND	Min-maj	ND
SEAWATER Mg(OH) <sub>2</sub>							
S-A1..	Maj	Tr	Tr	ND	ND	ND	ND
S-A2..	Maj	ND	Tr	Tr	ND	ND	ND
S-A3..	Maj	ND	ND	Tr	ND	ND	ND
S-M1..	Maj	ND	ND	Tr	ND	ND	Tr
S-M2..	Maj	ND	ND	Tr	ND	ND	Tr
S-M3..	Maj	ND	ND	Tr	ND	ND	Tr
S-Z1..	Maj	Tr	ND	Tr	Tr-min	Min	ND
S-Z2..	Maj	Tr	ND	ND	ND	Min	ND
S-Z3..	Maj	Tr	ND	ND	ND	Min	ND

ND Not detected. Maj Major. Min Minor. Tr Trace.

and Zr and of Ca and Si concentrations reaffirm the presence of calcium zirconate and monticellite phases reported in table 11. Pores are also visible throughout the grain.

The SEM examination in figure 4 is of sample S-M2, a seawater-based periclase material with CaO and MnO<sub>2</sub> additions. An examination of the micrographs showing

the Mn, Ca, and Si distributions indicates no Mn segregation. Some segregation of Ca occurs with Si, reaffirming the trace quantities of dicalcium silicate and merwinite reported by X-ray analysis in table 11. A greater grain porosity is noted in seawater sample S-M2, which was true for all seawater samples.

#### CONCLUSIONS

Based on the results of tests described herein, the following conclusions can be made:

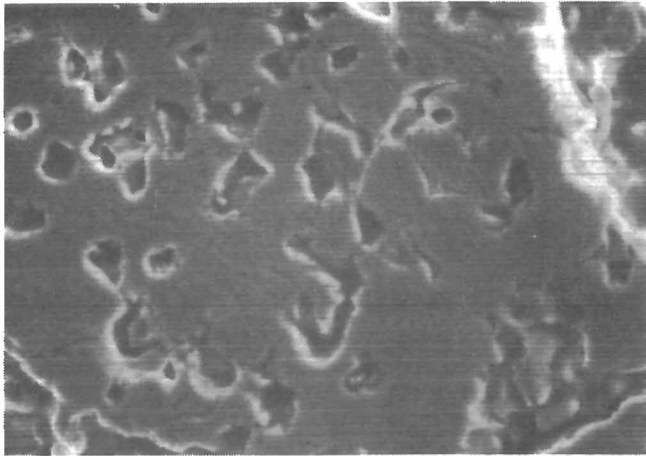
1. The high-temperature MOR and hot load properties for the optimized periclase grain bricks were superior to those for a commercial 98-wt-pct-MgO refractory. However, the optimized bricks suffered greater losses in strength following thermal shock exposure.

2. Improvements in hot strength were attributed both to increases in C:S

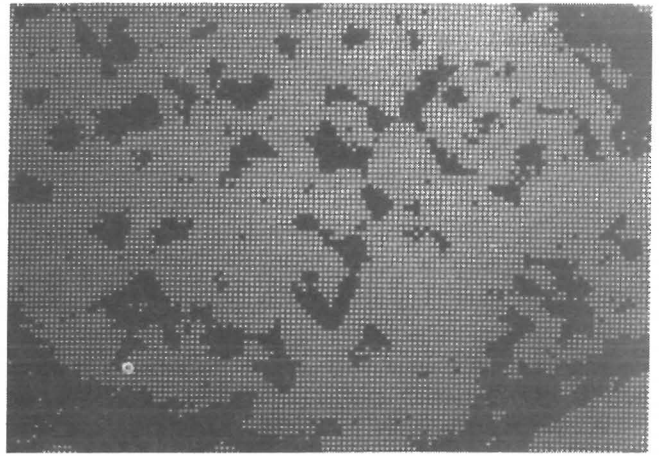
ratio and/or to additions of ZrO<sub>2</sub> or MnO<sub>2</sub>. The optimum additions were found to be different for each particular raw material.

3. The hot strength improvements resulted from formation of the refractory phases of dicalcium silicate and calcium zirconate in place of the lower melting silicates, monticellite and merwinite.

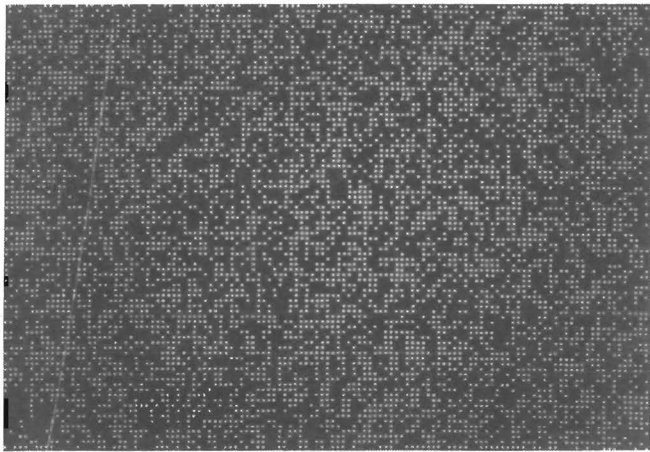
4. Additions of oxide materials and C:S adjustments to Mg(OH)<sub>2</sub> slurry resulted in physical property changes



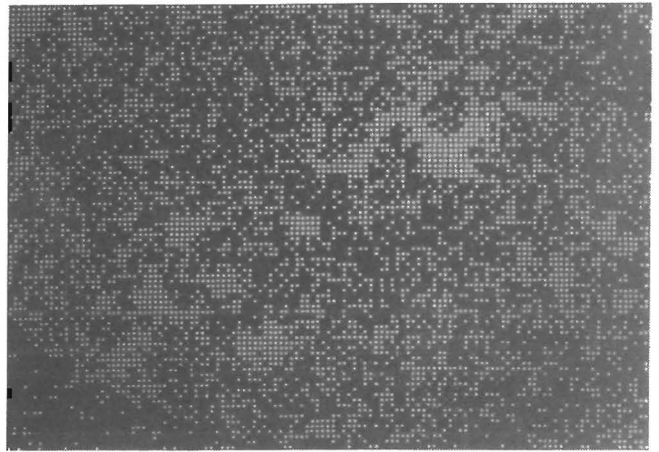
**SEM micrograph**



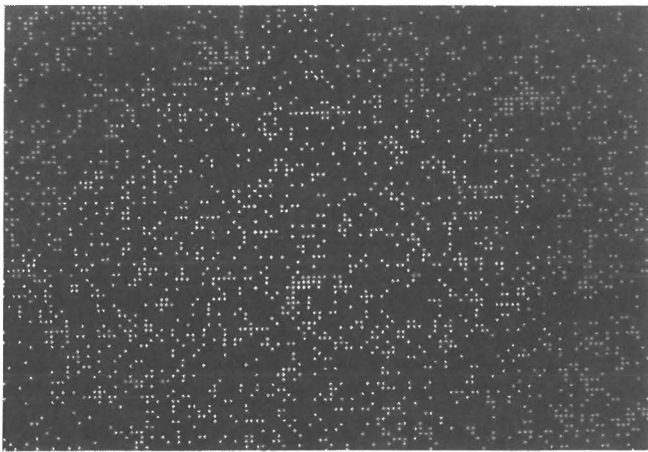
**Mg distribution**



**Mn distribution**



**Ca distribution**



**Si distribution**

0 40  
Scale,  $\mu\text{m}$

FIGURE 4. - SEM micrographs of elemental distributions for seawater periclase sample S-M2.

similar to those achieved with additions to dense fired periclase grain. This indicates that in commercial practice, adjustments can be made at the slurry stage of periclase grain processing.

5. Properties of the improved chemically modified periclase grains indicated that they could serve as substitutes for magnesia-chrome products, reducing the need for imported chromite.

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