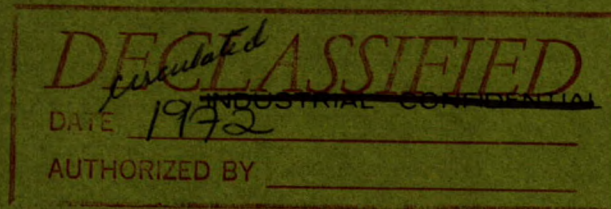


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CANADA

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MINES BRANCH INVESTIGATION REPORT IR 71-17

**EVALUATION OF A SAMPLE
OF A BRITISH COLUMBIA MAGNESITE
AS A REFRACTORY RAW MATERIAL**

by

M. PALFREYMAN

MINERAL PROCESSING DIVISION

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Mines Branch Investigation Report IR 71-17

EVALUATION OF A SAMPLE OF A BRITISH COLUMBIA
MAGNESITE AS A REFRACTORY RAW MATERIAL

by

M. Palfreyman*

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SUMMARY OF RESULTS

A sample of magnesite from Mount Brussilof, B. C. was submitted by Acres Western Limited, Vancouver, B. C. for evaluation as a raw material suitable for the production of dead-burned magnesia.

Investigation has shown that, in a single-stage process in which the raw magnesite was ball-milled, pelletized and fired at 1650 or 1700°C, fired densities of 3.37 g/cm³ were obtained. The fired density was not affected by soaking periods of up to 3 hours.

In a two-stage process, in which the raw magnesite was first calcined between 900 and 1100°C prior to ball-milling, pelletizing and firing at 1650 or 1700°C, the fired densities increased with calcination temperature. Values varied from 3.41 g/cm³ for material calcined at 900°C to 3.48 g/cm³ for a calcination temperature of 1100°C. Identical fired densities were obtained for firing temperatures of 1650 and 1700°C with a 3 hour soaking period.

Hydration stability determination showed that the material could be stabilized by burning as low as 1400°C.

Grain size measurements on the microstructures of pelletized raw and calcined materials showed that after firing for 3 hours at 1650°C the mean grain diameter was about 27µm.

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INTRODUCTION

The sample of magnesite was taken from a deposit on Mount Brussilof, British Columbia, and was submitted in October, 1970, by Mr. K. M. Pople of Acres Western Ltd., Vancouver.

Mount Brussilof is situated in a neck of land about 15 miles wide, lying between the Banff and Kootenay National Parks on the Alberta - British Columbia border. Acres Western Ltd. is interested in developing this deposit, which is reputedly large and of high purity.

Samples of rock previously taken from the western face of Mount Brussilof have been examined by Leech(1) who showed that the magnesite content was either zero or varied from 40 to 99%. The principal impurity was dolomite.

This investigation was concerned with the nature of the material produced after dead-burning the raw magnesite. From the refractories standpoint the important factors in dead-burned, pelletized magnesia are density, crystal size and hydration stability. These factors were determined after the magnesite had been subjected to either a single-stage or a two-stage calcination process. In the single-stage process, the magnesite was comminuted, pelletized and calcined directly to 1650 or 1700°C. In the two-stage process the magnesite was first calcined between 900 and 1100°C, comminuted, pelletized, and subsequently fired to 1650 or 1700°C. On a large scale the single-stage process has obvious economic advantages, provided that the final product meets the required specifications.

PROCEDURE AND RESULTS

Thermogravimetry

After riffing the 10-lb (4.54-k.g) sample, a smaller sample was taken to determine the thermogravimetric behaviour in air. This was carried out using a Stanton thermobalance having a sensitivity of 1 milligram. The sample weight was 1.000 g, and the heating rate was linear at 9°F/minute. Heating was continued until no further weight loss occurred. The weight change/temperature curve is shown in Figure 1. Loss of CO₂ begins at about 450°C and appears to be complete at about 800°C. The total loss in

weight was 51.00%.

Determination of Dead-Burned Data

Single-Stage Process

A sample of the raw magnesite was ball-milled for 6 hours in a 3-gallon (13.5-litre) porcelain ball-mill, using high-alumina grinding media (balls). The charge: media ratio was 1:8. Subsequent attempts to measure the mean particle diameter using a Fisher Sub-Sieve Sizer were unsuccessful. It was not possible to obtain a reading on the instrument, indicating that the mean particle diameter was less than $1\mu\text{m}$.

The ball-milled material was pressed into cylindrical pellets having a cross-sectional area of 1 in.² (6.45 cm²), and about 1/2 in. (1.27 cm) high under a pressure of 25,000 psi (17.6 kg/mm²). To facilitate pressing, 3% water was added to the ball-milled material. The pellets were dried overnight at 80°C, and green densities were determined by weighing and measuring with a Vernier caliper.

Firings were subsequently carried out in a gas-fired furnace at 1650 and 1700°C with no soaking period and at 1700°C with soaking periods of 1 hour and 3 hours.

Fired bulk densities and apparent porosities were determined according to the method given in ASTM C20-70 with the exception that the entrapped air was removed by evacuation instead of by displacement in boiling water. The latter was avoided so as to obviate any problems due to hydration.

The results of these determinations are given in Table 1.

Two-Stage Process

Samples of the raw magnesite were calcined in an electric furnace for 3 hours at 900°C, 2 hours at 1000°C, and 2 hours at 1100°C after which ball-milling was carried out as described for the single-stage process. Attempts to measure the mean particle diameter with the Fisher Sub-Sieve Sizer were again unsuccessful for the reason given above.

Pelletization of the calcined samples and determination of green densities were carried out as in the single-stage process.

The pelletized samples were fired at 1650 and 1700°C in the gas-fired furnace with a soaking time of 3 hours in each case. The fired densities and apparent porosities were determined as previously.

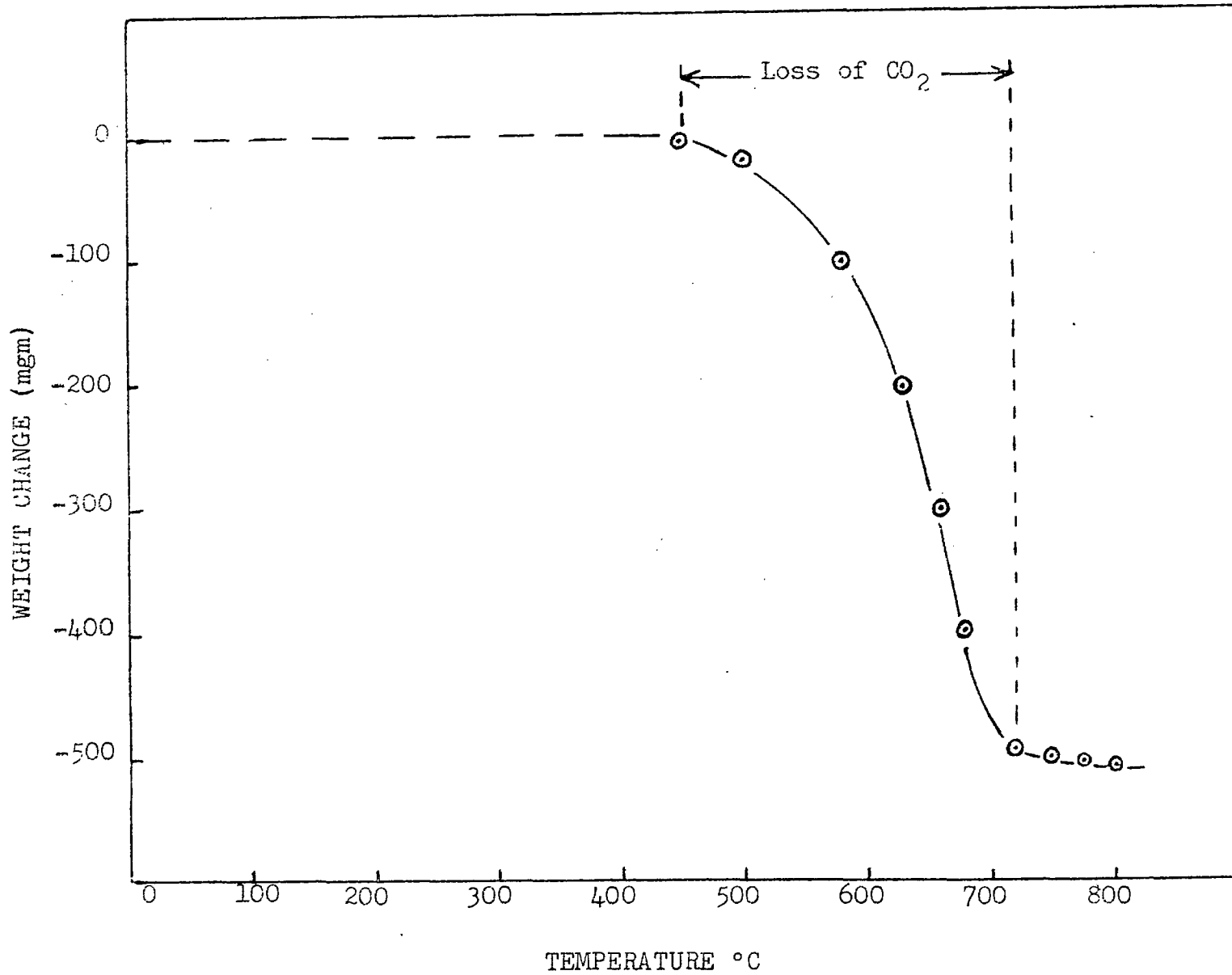


Figure 1. Thermogravimetric Curve of Raw Magnesite

TABLE 1
Dead-Burning Data

Calcination Temp. °C	Calcination Time (Hrs)	Green Bulk Density g/cm ³	Firing Temp. °C	Soak Period (Hrs)	Fired Bulk Density g/cm ³	Apparent Porosity %
Uncalcined	Uncalcined	2.42	1650	-	3.37	0.04
"	"	"	1700	-	3.35	1.04
"	"	"	1700	1	3.37	0.47
"	"	"	1700	3	3.37	0.67
900	3	2.08	1650	3	3.41	0.40
"	"	"	1700	"	3.41	0.42
1000	2	2.24	1650	3	3.42	0.47
"	"	"	1700	"	3.41	0.42
1100	2	2.40	1650	3	3.48	0.04
"	"	"	1700	"	3.48	0.05

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-

The results of these determinations are also given in Table 1.

Determination of Densification Rate On Raw Magnesite

A sample of the raw magnesite was ball-milled and pelletized as described above for the single stage dead-burning process. The pellets were fired in an electric furnace at a heating rate of 200°C/hour up to 1000°C, and 100°C/hour from 1000°C to 1650°C.

Commencing at 1300°C, pellets were withdrawn from the furnace at 50°C intervals up to 1650°C. The final samples were soaked at 1650°C for 3 hours.

Fired bulk densities were determined by means of a mercury balance. This method was adapted in this instance since it was desired to use the same pellets for hydration studies which are described below. A curve for fired bulk density plotted as a function of temperature is shown in Figure 2.

Determination of Hydration Stability

The fired pellets obtained from the densification study, together with pellets from the dead-burning studies were examined for hydration stability by holding in steam for 5 hours and subsequently measuring the loss on ignition. Steaming was carried out by placing the pellets in a household pressure cooker with the valve open so that the internal pressure was essentially atmospheric. Ignition of the steamed pellets was performed by heating for 2 hours at 1000°C in an electric muffle furnace. The results are given in Table 2.

Microstructure of Fired Pellets

Photomicrographs of the internal structure of pellets formed from the raw and calcined materials after firing for 3 hours at 1650°C, are shown in Figures 3 and 4. The surfaces were polished with cerium oxide on a silk lap and subsequently etched for 1 minute in cold 50% HCl. Microscopic examination was carried out using reflected light. The grey areas are periclase grains and the black areas are pores which are probably partly a result of pulling during the polishing operation.

A great deal of microporosity exists as evidenced by the small circular areas within the grains. This is clearly visible at both low and high magnifications.

The structures appear to be two-phase, in each case; this seems particularly evident at low magnification (Figure 3 (a), (b), (c) and (d)). The two phases appear to be present in roughly equal proportions. Chemical analysis showed the material

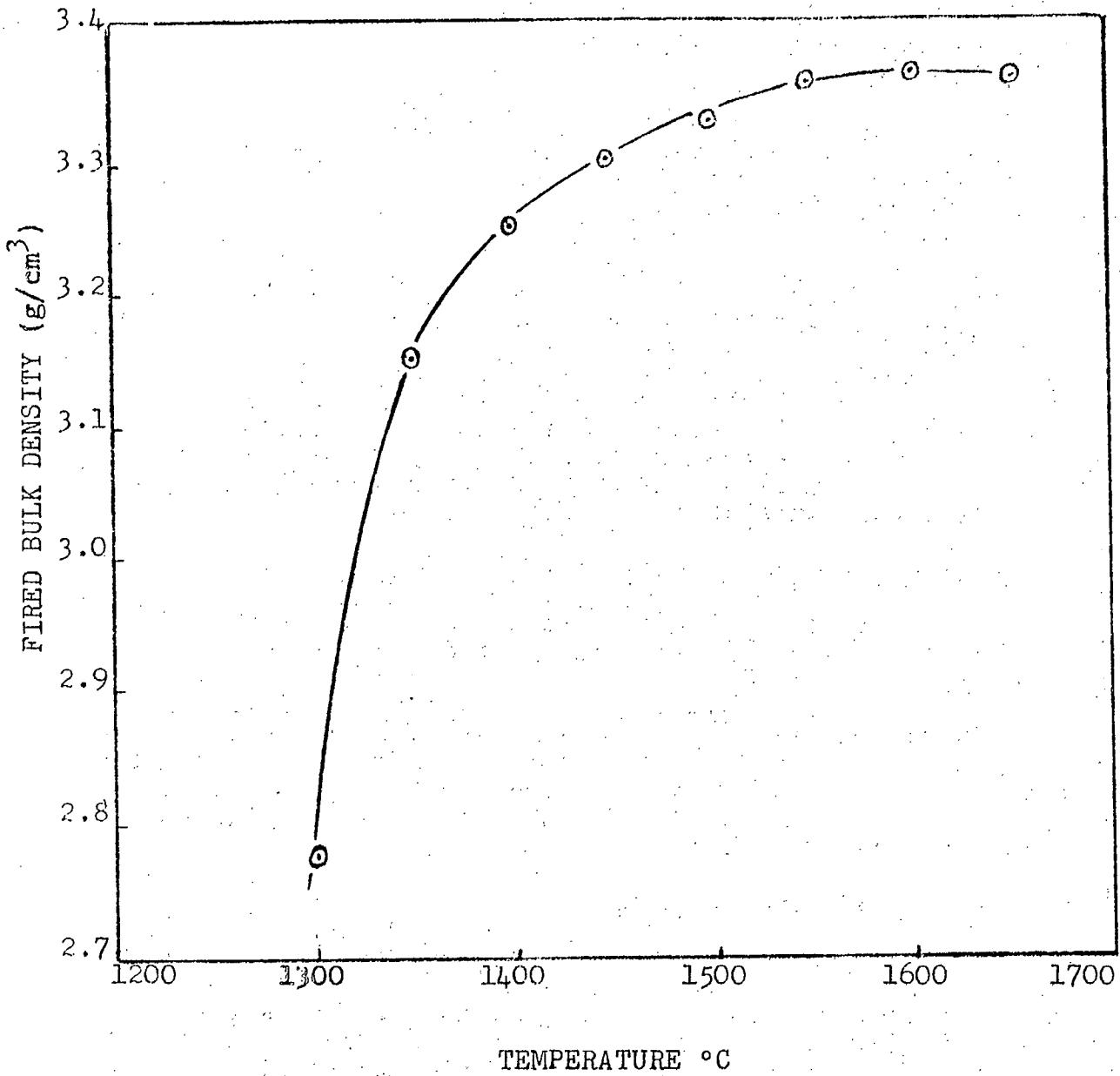


Figure 2. Densification of Pelletized Raw Magnesite

TABLE 2
Hydration Stability Data

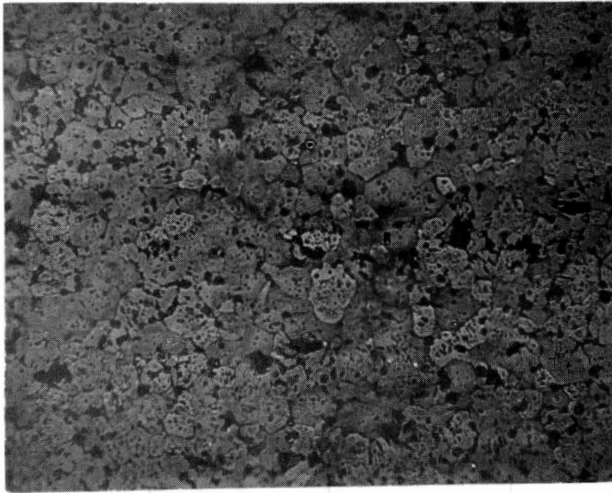
Calcination Temp. °C	Calcination Time (Hrs)	Firing Temp. °C	Soak Period (Hrs)	Hydration Stability (% L.O.I.)
Uncalcined	Uncalcined	1300	-	14.903
"	"	1350	-	7.824
"	"	1400	-	1.491
"	"	1450	-	0.777
"	"	1500	-	0.069
"	"	1550	-	0.041
"	"	1650	-	0.010
"	"	1650	3	0.013
900	3	1650	3	0.016
1000	2	"	"	0.020
1100	2	"	"	0.051
900	3	1700	3	0.010
1000	2	"	"	0.010
1100	2	"	"	0.006

to contain 3.12% CaO, 0.26% SiO₂ and 0.29% Fe₂O₃,⁽²⁾ in which case the material would contain free lime due to the high CaO:SiO₂ ratio. However, this would not be expected to account for the structures observed.

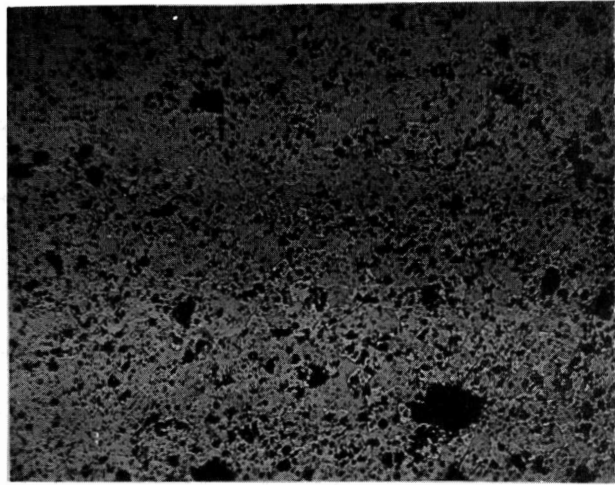
X-Ray Diffraction Analyses

X-ray diffraction analysis of the as-received raw material showed that the principal constituent was magnesite (MgCO₃) accompanied by very small amounts of dolomite (CaMg(CO₃)₂), quartz (SiO₂), and pyrite (FeS₂).

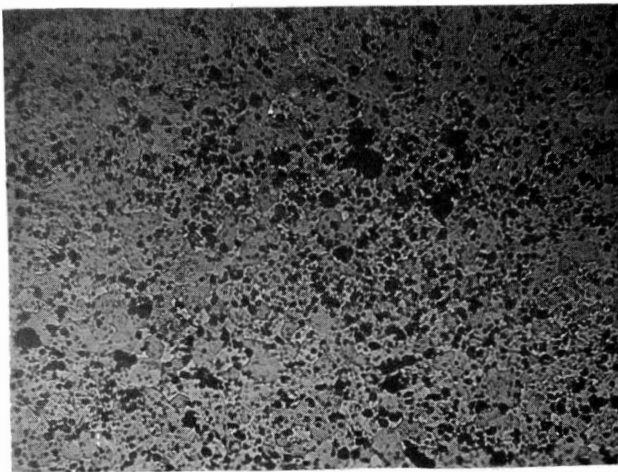
X-ray diffraction analyses of the pelletized materials fired for 3 hours at 1650°C (Figures 3 and 4), showed them to be practically entirely periclase. Some diffuse lines indicated the presence of lime (CaO), and unconverted magnesite.



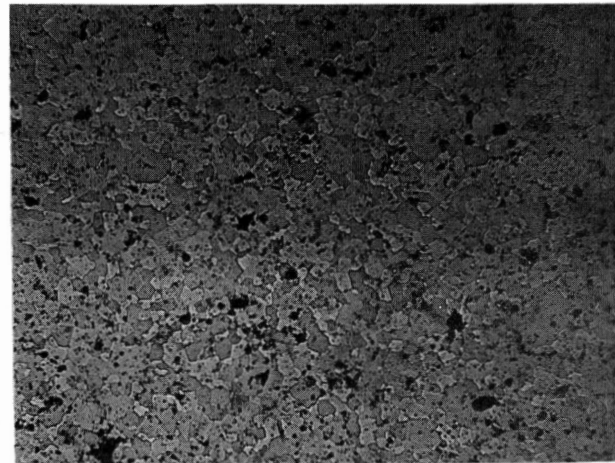
(a)



(b)



(c)



(d)

Figure 3. Microstructures of Fired Pellets x 62.5.

(a) Uncalcined, fired 1650°C, 3 hr.

(b) Calcined 2 hr at 1900°C, fired 3 hr at 1650°C.

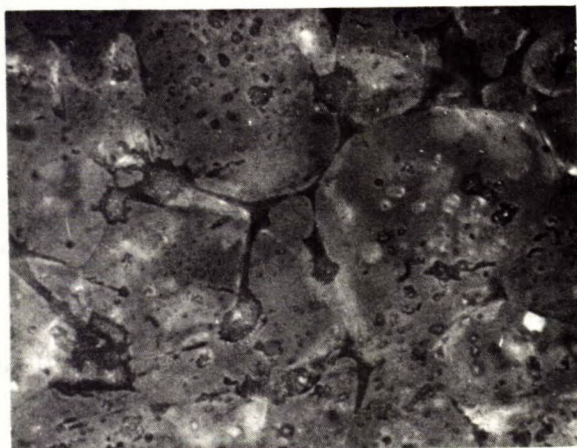
(c) Calcined 3 hr at 1000°C, fired 3 hr at 1650°C.

(d) Calcined 3 hr at 1100°C, fired 3 hr at 1650°C.

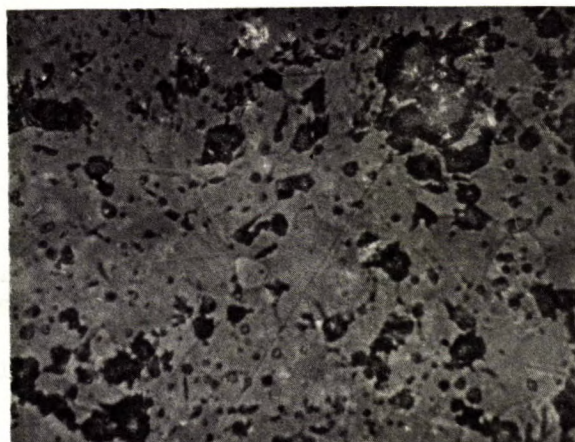
Grey Areas - Periclase.

Black Areas - Large Pores or Pullouts.

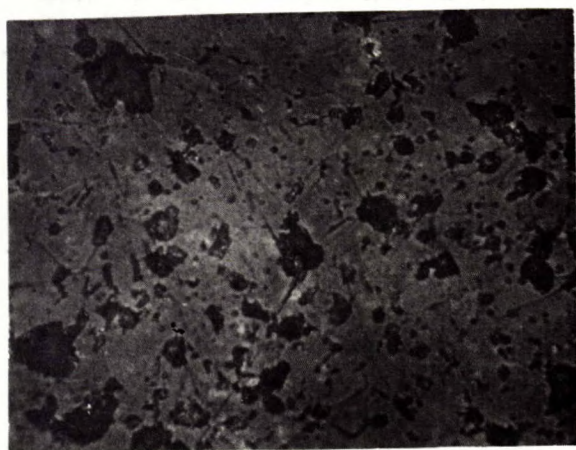
Small Circular Areas (Dark Grey) - Micropores.



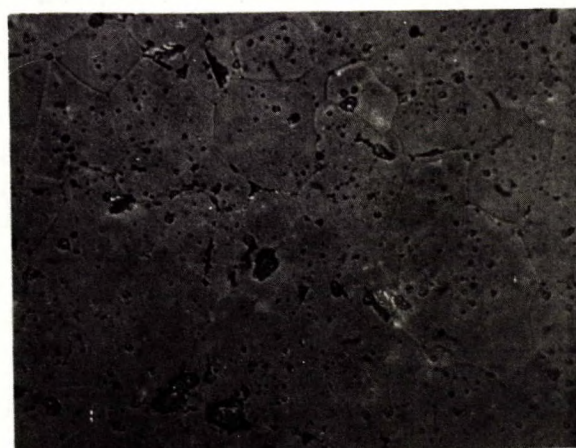
(a)



(b)



(c)



(d)

Figure 4. Microstructures of Fired Pellets x 500.

(a) Uncalcined, fired 1650°C, 3 hr.

(b) Calcined 2 hr at 1900°C, fired 3 hr at 1650°C.

(c) Calcined 3 hr at 1000°C, fired 3 hr at 1650°C.

(d) Calcined 3 hr at 1100°C, fired 3 hr at 1650°C.

All Surfaces Polished with Cerium Oxide on a Silk Lap Etched 1 minute in 50% HCl. (Applies also to Figure 3).

Measurements of the cell edge for the periclase showed no significant variation from the published value in the ASTM card index.

These results throw no light on the two-phase appearance of the microstructures.

Fired Grain Diameter

Measurement of mean grain diameter in the fired pellets was carried out by the method of line intersection on the photomicrographs. In the case of pellets fired for 3 hours at 1650°C, an average grain diameter of about 27 μ m was indicated. Such a value shows the material to be well burned under these conditions.

DISCUSSION OF RESULTS

The dead-burning data given in Table 1 indicate that in the single-stage process, there is no advantage to be gained by increasing the temperature from 1650 to 1700°C. Furthermore, at 1700°C no increase in density is obtained by soaking for up to 3 hours at temperature.

In the two-stage process, the fired bulk density is greatest for material calcined initially at 1100°C. There appears to be no difference in fired bulk density for material calcined initially at 900 or 1000°C. As in the single-stage process, raising the firing temperature from 1650 to 1700°C does not increase the fired bulk density. In addition to the higher densities obtained with material calcined at 1100°C, there is also a marked decrease in apparent porosity. The value of 0.04% obtained for the material fired at 1650°C in the single-stage process appears to be anomalous.

In all cases, the fired pellets were light brown in colour. After crushing it was noted that the interior of the pellets was of either white or light creamy colour. Cracks in the pellets also showed the brown coloration at the surface. This indicates the diffusion of some impurity, possibly Fe₂O₃, to the surface, or, oxidation of the same impurity where it was in contact with the atmosphere.

The densification curve, shown in Figure 2, indicates that densification takes place rapidly between 1300 and 1350°C after which, it decreases to zero on reaching the maximum density at about 1550°C. The high rate of densification at these relatively low temperatures is possibly due to the formation of calcium ferrites from the lime and iron impurities. It is known that calcium ferrites lead to an increased rate of dead-burning

and reduce the after-contraction in the final product(2). In the Alterra process(4), calcium ferrites are added to the raw material for this particular purpose.

The hydration stability data given in Table 2 show that with firing temperatures of 1500°C and above, the product is very stable. From a refractory point of view the value of 1.49% obtained at 1400°C is acceptable. The fact that such a high degree of hydration stability can be obtained at this relatively low temperature again indicates the presence of some impurity which brings about this effect. One such material is boric oxide, B_2O_3 , which Svikis(5) has demonstrated to be extremely effective in increasing hydration stability when present in amounts as low as 0.2% by weight. The effect of the boric oxide is enhanced in the presence of silica, which apparently forms a low-melting borosilicate, which, in turn, coats the grains and protects them from hydration. Such a phenomenon could also explain the rapid densification at low temperatures.

Spectrographic analysis for boron was carried out by Acres Western Ltd.(2), the results of which showed only trace quantities. The rapid attainment of hydration stability is evidently due to some other effect.

Though the microstructures of the fired pellets showed evidence of being two-phase in nature, there appears to be no reasonable explanation for the phenomenon. The microscopic examination failed to indicate any glassy phases in the grain boundaries.

From the refractory point of view, the raw material appears to be satisfactory for the production of dead-burned magnesia.

The results herein indicate that dead-burning could probably be carried out satisfactorily at a temperature of 1650°C, and moreover, possibly by a single-stage firing process.

Since the chemical analysis(2) indicates a lime: silica ratio of 3:1 it may be necessary to add silica in order to combine with the free lime during the dead-burning process. Such an addition would lower the refractoriness of the final product.

CONCLUSIONS

The magnesite sample submitted is satisfactory as a raw material for the production of refractory-grade dead-burned magnesia, as indicated by the results obtained herein, and trials at the pilot plant stage would be worthwhile on the basis of this information.

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4. A. G. Alterra, Brit. Pat., 394311, July 5, 1933.
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