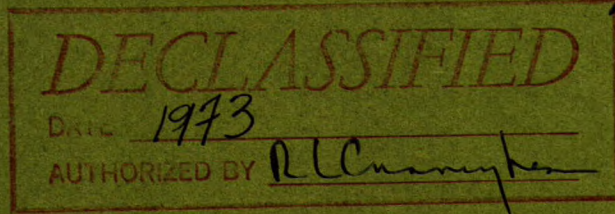


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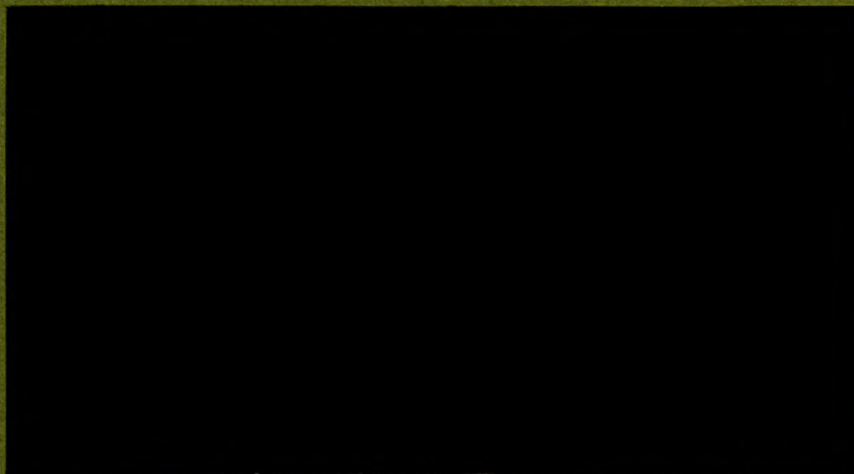
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FACTORS AFFECTING BONDING IN BASIC REFRACTORIES:  
THE SOLUTION OF CaO IN MgO AT HIGH TEMPERATURES

by

M. Palfreyman  
Mineral Processing Division

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FACTORS AFFECTING BONDING IN BASIC REFRACTORIES:  
THE SOLUTION OF CaO IN MgO AT HIGH TEMPERATURES

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M. Palfreyman\*

- - -

SUMMARY OF RESULTS

The effects of ferric oxide,  $\text{Fe}_2\text{O}_3$ , upon the solution of lime, CaO, in magnesia, MgO, at  $1700^\circ\text{C}$  ( $3092^\circ\text{F}$ ) have been studied. The source of lime was dicalcium silicate,  $2\text{CaO} \cdot \text{SiO}_2$ , which was prepared separately. Mixtures of this compound, together with high-purity magnesia and ferric oxide, were intimately blended, pelletized, and fired to  $1700^\circ\text{C}$  ( $3092^\circ\text{F}$ ), from which temperature they were quenched in an oil bath. The extent of solid solution of lime and iron oxide ( $\text{FeO}$ ) in the magnesia was determined by measuring changes in the dimensions of the magnesia crystal unit cell using X-ray diffraction techniques. The same techniques were used to identify the phases present in the quenched pellets.

The results indicate that lime tends to inhibit the solid solution of iron oxide in magnesia, which would normally be unrestricted. Dicalcium ferrite appears in some quenched specimens and is most likely the result of ferric oxide reacting with merwinite.

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## INTRODUCTION

As far as refractories are concerned, the use of oxygen in steel-making in the basic oxygen furnace (BOF) has created new problems with respect to high-temperature strength and erodibility. This is particularly so in the case of magnesia refractories, where the high-temperature strength depends largely upon the nature of the siliceous bond<sup>(1)</sup>. With raw materials such as American sea-water magnesia or Greek natural magnesite, which contain a high proportion of direct MgO-MgO bonding, only part of the strength is lost when the siliceous bond softens at high temperatures. However, where the stress is borne entirely by the siliceous bond which envelops each magnesia crystal, catastrophic failure results when the bond softens. It has been shown<sup>(2)</sup> that natural Greek magnesite contains a high proportion of direct MgO-MgO bonding and, furthermore, contains a high calcium content in the MgO which discourages the migration of lime from the siliceous bond to the MgO. Recent work<sup>(3,4,5)</sup> has shown that at high temperatures lime may diffuse from the siliceous bond to form a solid solution with the magnesia in amounts up to 2 per cent by weight. In magnesia refractories, the silicate bond consists essentially of dicalcium silicate,  $2\text{CaO} \cdot \text{SiO}_2$ , though some tricalcium silicate,  $3\text{CaO} \cdot \text{SiO}_2$ , may exist at temperatures above about  $1250^\circ\text{C}$  ( $2282^\circ\text{F}$ ) if free lime is present at room temperature. In practice, free lime is avoided as it leads to hydration problems in storage. At high temperatures, when lime diffuses into the surrounding magnesia, the lime:silica ratio in the bond decreases so that lower melting phases such as merwinite,  $3\text{CaO} \cdot \text{MgO} \cdot 2\text{SiO}_2$ , or monticellite,  $\text{CaO} \cdot \text{MgO} \cdot \text{SiO}_2$ , may be formed. This effect becomes more detrimental as the silica content of the magnesia decreases. It has been demonstrated<sup>(6)</sup> that with a normally acceptable lime:silica mole



ratio of 2.0:1, the silica content should be not less than 0.85 per cent by weight if the maximum hot strength of the refractory is to be maintained.

The above observations have been made on systems containing pure components of magnesia, lime, and silica. In actual practice, a magnesitic raw material may contain other impurities such as iron compounds, alumina, and titania. The immediate object of the present work is to determine the effects of these impurities on the migration of lime into the magnesia, beginning with iron oxide.

Ferrous oxide,  $\text{FeO}$  (wustite), forms a continuous series of solid solutions with magnesia<sup>(7)</sup> and considerable quantities may be added before the refractoriness is lowered to the steel-making temperature range. However, in the presence of other impurities, notably lime and silica, it can be very detrimental due to the formation of lower melting phases such as calcium ferrites and fayalite,  $2\text{FeO} \cdot \text{SiO}_2$ .

Iron in one form or another is the most common impurity in magnesitic raw materials, and, furthermore, in steelmaking processes, magnesia refractories are in almost constant contact with iron oxide bearing materials.

#### MATERIALS USED

The magnesia used was Johnson Matthey Grade 1  $\text{MgO}$  having less than 9 ppm total impurities. This material had previously been characterized by Cimino et al<sup>(8)</sup>.

The iron oxide used was reagent grade material having an assay of not less than 99 per cent  $\text{Fe}_2\text{O}_3$ .

Dicalcium silicate was prepared by heating pure calcium formate with the calculated quantity of Johnson Matthey Grade 1  $\text{SiO}_2$ , which contained less



than 5 ppm total impurities. The mixture was heated for 2 hours at  $1450^{\circ}\text{C}$  ( $2642^{\circ}\text{F}$ ), after which it was ground, compacted, and reheated under the same conditions. X-ray diffraction analysis of the product showed it to be pure dicalcium silicate in both  $\beta$  and  $\gamma$  forms. The absence of free lime was confirmed by White's test<sup>(9)</sup>.

#### EXPERIMENTAL TECHNIQUE

In view of the fact that dicalcium silicate is the common silicate bond in magnesia refractories, it was decided to use this material as the source of lime rather than pure lime itself. From an academic point of view, it would have been more logical to have started with the pure components  $\text{MgO}$ ,  $\text{CaO}$ , and  $\text{Fe}_2\text{O}_3$ .

The extent of solid solution of lime in the magnesia was determined by measuring the increase in dimensions of the magnesia unit cell using X-ray diffraction techniques and comparing the results with those obtained by Henney and Jones<sup>(3)</sup>.

At high temperatures,  $\text{Fe}_2\text{O}_3$  converts to  $\text{FeO}$  which would pass into solid solution in any magnesia present. Hence, the increase in the unit cell dimensions of the  $\text{MgO}$  resulting from heating mixtures of  $\text{MgO}$  and  $\text{Fe}_2\text{O}_3$  could be related to the initial amount of  $\text{Fe}_2\text{O}_3$  in the mixture.

A series of mixtures of magnesia and dicalcium silicate, containing up to 10 per cent by weight of the latter, were prepared by grinding the components together by hand in an agate pestle and mortar. The mixes were dry pressed into cylindrical pellets  $1/2$  inch (12.7 mm) diameter and  $1/4$  inch (6.3 mm) thick under a pressure of 20,000 lbs/in.<sup>2</sup> (14.1 kg/mm<sup>2</sup>). The pellets were heated in an electric muffle furnace to  $1700^{\circ}\text{C}$  ( $3092^{\circ}\text{F}$ ) and held at



temperature for a period of 1 hour, after which they were quenched in an oil bath so as to retain the high temperature composition. Portions of each pellet were submitted for X-ray diffraction analysis to determine the phases present and the cell dimensions of the magnesia.

A second series of mixes, containing magnesia and up to 5 per cent by weight of  $\text{Fe}_2\text{O}_3$ , was subjected to the same treatment. A third series of mixes, containing magnesia and up to 10 per cent by weight of dicalcium silicate and  $\text{Fe}_2\text{O}_3$  in equal proportions, was also treated in like manner.

In order to study any variations in the unit cell size of the magnesia crystals which might occur due to the action of heat alone, samples of the pure material were heated in the temperature range 1000 to 1700°C (1852 to 3092°F) and slow-cooled to room temperature. They were subsequently subjected to XRD analyses to obtain cell edge measurements. Similar measurements were also made on samples of the magnesia which had been quenched from 1700°C (3092°F) to determine any possible variations due to straining of the crystal lattice.

A Guinier X-ray camera was used to produce the diffraction patterns on film and only the high angle reflections were used to calculate the unit cell dimensions. The radiation used was  $\text{CoK}\alpha$  with an Fe filter.

#### EXPERIMENTAL RESULTS

Variations in the cell edge of the magnesia as a function of firing temperature (slow-cooled) are given in Table 1. Because the unit cell of magnesia is cubic, only one dimension is required and is conventionally designated as  $a_0$ . The values of  $a_0$  were obtained from a least squares calculation using the high angle reflections on the diffraction pattern. Statistical calculations show that there is no significant variability between the results given in



Table 1. The mean value is 4.2118 Å with a standard deviation of  $\pm 0.0005$  Å. The value quoted by Cimino et al<sup>(8)</sup> is  $4.2115 \pm 0.0001$ . Henney and Jones<sup>(3)</sup> give the value as  $4.2115 \pm 0.0002$  Å.

After quenching the material in oil at  $1700^{\circ}\text{C}$  ( $3092^{\circ}\text{F}$ ), the value obtained for the unit cell edge was 4.2091 Å, which indicates that this treatment can, in fact, lead to changes in the unit cell size. Further work may reveal that the magnitude of the change depends upon the temperature and the severity of the quench.

The effect of iron oxide ( $\text{Fe}_2\text{O}_3$ ) additions on the unit cell edge of magnesia specimens quenched at  $1700^{\circ}\text{C}$  ( $3092^{\circ}\text{F}$ ) is shown in Figure 1. The cell edge shows a continuous increase in length with increasing additions of iron oxide up to 5 per cent by weight.

The results of quenching mixes of magnesia and dicalcium silicate at  $1700^{\circ}\text{C}$  ( $3092^{\circ}\text{F}$ ) are also shown in Figure 1. It can be seen that the cell edge of the magnesia again shows a continuous increase with increasing amounts of dicalcium silicate. However, the major increase in length occurs with an addition of 5 per cent dicalcium silicate. The further change in length which occurs on increasing the amount of dicalcium silicate to 10 per cent is only small.

When mixes of magnesia and equal quantities of iron oxide and dicalcium silicate were quenched at  $1700^{\circ}\text{C}$  ( $3092^{\circ}\text{F}$ ), the variation of the magnesia cell edge with the total addition appeared as in Figure 1. The value of the cell edge increases rapidly as the total addition is increased from zero to 2 per cent. A further small increase takes place from 2 to 4 per cent but beyond 4 per cent no further increase in the cell edge is observed.

Examination of the X-ray diffraction patterns obtained from the various mixes for phases present other than magnesia produced the results given in Table 2.



TABLE 1

Increase in Cell Edge of Pure MgO  
As a Function of Firing Temperature  
(After Slow Cooling)

Firing Temperature °C	Cell Edge, a <sub>o</sub> Å
1000	4.2121
1100	4.2117
1200	4.2112
1300	4.2117
1400	4.2118
1500	4.2114
1600	4.2127
1700	4.2120

TABLE 2

Phases Identified in X-ray Diffraction  
Patterns of Quenched Mixes

Original Phases in Mix	Fe <sub>2</sub> O <sub>3</sub> Wt %	2CaO.SiO <sub>2</sub> Wt %	Phases Identified in Quenched Specimen
MgO 2CaO.SiO <sub>2</sub>	- - - - - -	0 1 2 5 7.5 10	MgO MgO MgO MgO, & 2CaO.SiO <sub>2</sub> MgO, & 2CaO.SiO <sub>2</sub> MgO, & 2CaO.SiO <sub>2</sub>
MgO 2CaO.SiO <sub>2</sub> Fe <sub>2</sub> O <sub>3</sub>	1 1 1 1	1 2 5 7.5	MgO MgO MgO, 2CaO.SiO <sub>2</sub> , & 3CaO.MgO.SiO <sub>2</sub> MgO, 2CaO.SiO <sub>2</sub> , & 3CaO.MgO.SiO <sub>2</sub>
MgO 2CaO.SiO <sub>2</sub> Fe <sub>2</sub> O <sub>3</sub>	2 2 2 2	1 2 5 7.5	MgO MgO, Fe <sub>2</sub> O <sub>3</sub> MgO, Fe <sub>2</sub> O <sub>3</sub> , & 2CaO.SiO <sub>2</sub> MgO, Fe <sub>2</sub> O <sub>3</sub> , & 2CaO.SiO <sub>2</sub>
MgO 2CaO.SiO <sub>2</sub> Fe <sub>2</sub> O <sub>3</sub>	5 5 5 5	1 2 5 7.5	MgO, Fe <sub>2</sub> O <sub>3</sub> , 2CaO.Fe <sub>2</sub> O <sub>3</sub> MgO, Fe <sub>2</sub> O <sub>3</sub> , 2CaO.Fe <sub>2</sub> O <sub>3</sub> , & 2CaO.SiO <sub>2</sub> MgO, Fe <sub>2</sub> O <sub>3</sub> , & 2CaO.SiO <sub>2</sub> MgO, Fe <sub>2</sub> O <sub>3</sub> , & 2CaO.SiO <sub>2</sub>



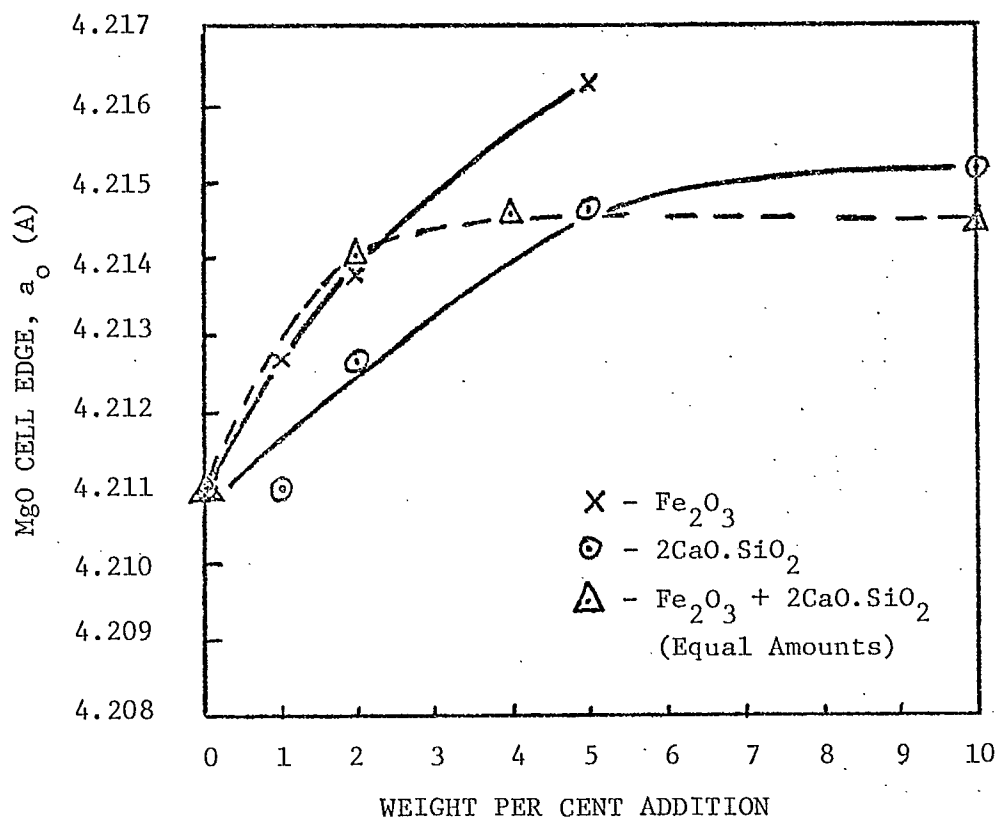


Figure 1. Mixes of MgO with  $\text{Fe}_2\text{O}_3$  and  $2\text{CaO} \cdot \text{SiO}_2$ .  
Quenched at  $1700^\circ\text{C}$  ( $3092^\circ\text{F}$ )



In mixes containing magnesia and dicalcium silicate only, the latter appears in the diffraction pattern for additions of 5 per cent or greater. With a 1 per cent addition of ferric oxide, merwinite  $3\text{CaO} \cdot \text{MgO} \cdot 2\text{SiO}_2$ , appears in the diffraction pattern for additions of 5 per cent dicalcium silicate or greater. When the ferric oxide addition is increased to 2 per cent, the identifiable phases are magnesia, ferric oxide, and the  $\beta$  and  $\gamma$  forms of dicalcium silicate. With a ferric oxide content of 5 per cent, dicalcium ferrite appears in the quenched specimens with small additions of dicalcium silicate, but disappears as the quantity of the latter is increased.

#### DISCUSSION OF RESULTS

The results obtained for variation of the magnesia unit cell edge ( $a_0$ ) after slow cooling samples from temperatures in the range 1000 to 1700°C (1832 to 3092°F) agree very closely with those obtained by Cimino et al<sup>(8)</sup>. However, these workers did not fire samples at temperatures above 1300°C (2372°F), which would explain the slight difference between their value for  $a_0$  and the one obtained in this work.

After quenching the magnesia at 1700°C (3092°F), a considerable decrease in the value of  $a_0$  was observed and this can only be explained in terms of strain in the crystal lattice. It is probable that even with FeO or CaO in solid solution, the magnesia crystals will still be under some strain when quenched at 1700°C (3092°F). This implies that the solid solution conditions existing in the quenched specimens may be somewhat different to those which existed immediately prior to quenching. The most likely effect would be for some material to be thrown out of solid solution during the quench as a result of the induced strain. Henney and Jones<sup>(3)</sup> showed that CaO is thrown out of solid solution when specimens are cooled slowly in the furnace. However, under these conditions there would be no



strain imposed upon the magnesia crystal lattice. High-temperature X-ray techniques would enable this point to be elucidated but unfortunately these facilities were not available.

The curves shown in Figure 1 indicate that on a weight for weight basis the addition of ferric oxide produces a greater increase in the magnesia cell edge than either the addition of dicalcium silicate alone or the latter in combination with ferric oxide. It should be remembered that iron oxide dissolves in the magnesia as  $\text{FeO}$  and not  $\text{Fe}_2\text{O}_3$ , and furthermore, it is the  $\text{CaO}$  from the dicalcium silicate which dissolves and not the latter as such. Even after accounting for the facts that 1 part of  $\text{Fe}_2\text{O}_3$  produces 0.9 parts of  $\text{FeO}$  and 1 part of  $2\text{CaO} \cdot \text{SiO}_2$  can produce a maximum of 0.62 parts of  $\text{CaO}$ , the above observation still holds true.

For additions up to about 2.5 per cent, equal quantities of either ferric oxide or 50:50 mixtures of ferric oxide and dicalcium silicate produce the same result. This implies that under these conditions both  $\text{FeO}$  and  $\text{CaO}$  can dissolve simultaneously in the  $\text{MgO}$  without mutual interference.

Between about 2.5 and 5.0 per cent, the values obtained for  $a_o$  with the 50:50 mixture of ferric oxide and dicalcium silicate are very little greater than would have been obtained by using just the ferric oxide contained in the mixture. At first sight, it could be concluded that the major portion of the cell expansion was due to the dissolved  $\text{FeO}$  and that very little of the  $\text{CaO}$  had dissolved. However, this point needs to be examined more closely. From the results given in Table 2, it can be seen that for an addition of 2.5 per cent of a 50:50 mixture of ferric oxide and dicalcium silicate, the only detectable phase in the quenched specimen would be  $\text{MgO}$ . For a 5 per cent addition of the 50:50 mixture, the detectable phases should be  $\text{MgO}$  and  $\text{Fe}_2\text{O}_3$ . A 5 per cent addition of ferric oxide should dissolve completely in the  $\text{MgO}$  and give a much



greater value for the cell edge than that observed for the 5 per cent addition of the 50:50 mixture. Hence, it can be concluded that, between 2.5 and 5 per cent additions of this mixture, the solution of the iron oxide in the magnesia is inhibited by the presence of the lime. The same general conclusion may be reached when the additions of the 50:50 mixture exceed 5 per cent. The curves in Figure 1 indicate that each component tends to inhibit the solution of the other in the magnesia. However, the inhibiting effect of the lime upon the iron oxide is apparently much greater than the reverse situation. This is supported by the results given in Table 2, which indicate that with the higher additions of ferric oxide the quenched specimens contain ferric oxide with or without dicalcium ferrite.

The appearance of a calcium ferrite in some of the quenched specimens is of interest because the phase equilibrium systems  $\text{CaO-FeO-SiO}_2^{(10)}$ , and  $\text{CaO-Fe}_2\text{O}_3\text{-SiO}_2^{(11)}$ , show that dicalcium silicate can exist in equilibrium with FeO or  $\text{Fe}_2\text{O}_3$  under the conditions investigated. When lime from the dicalcium silicate dissolves in the magnesia, the bond becomes richer in silica and under these conditions the reaction of the bond with FeO or  $\text{Fe}_2\text{O}_3$  should not lead to the formation of calcium ferrites, according to the equilibrium diagrams. It can only be argued that they are formed as a result of magnesia taking part in the chemical reactions. The results in Table 2 show that merwinite,  $3\text{CaO.MgO.2SiO}_2$ , was present in some of the quenched specimens, which would react with ferric oxide to form calcium ferrites<sup>(12)</sup>.



### CONCLUSIONS

The addition of ferric oxide to the system  $\text{MgO} - 2\text{CaO} \cdot \text{SiO}_2$  does not prevent lime passing from the dicalcium silicate to form a solid solution with the magnesia under the conditions set in this investigation. The presence of iron oxide in a magnesia refractory would lead to a loss in refractoriness if in sufficient quantity to form dicalcium ferrite.

### RECOMMENDATIONS

The mixes used in this work were prepared by blending  $\text{MgO}$ ,  $2\text{CaO} \cdot \text{SiO}_2$ , and ferric oxide as such. Therefore, on heating these mixes, the iron oxide and lime could be regarded as competing for solution in the magnesia. However, if one of the components, say the iron oxide, was already in solid solution in the magnesia, the results may have been somewhat different. Further work should be undertaken to investigate this aspect.



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