JOURNAL OF MATERIALS SCIENCE 22 (1987) 4061–4066

Scanning electron microscopy of industrial low-flux dolomite refractory clinkers

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Microstructural features of the industrial low-flux dolomite refractory clinkers produced in a coal-fired rotary kiln were investigated by scanning electron microscopy combined with energy-dispersive X-ray spectroscopy. SEM micrographs of polished sections of an unhydrated clinker indicated that the impurity phase, which is located between periclase and lime grains, has a glassy appearance and occasionally contains dicalcium silicate in the form of rods; most of the silicon, aluminium and iron concentrates in the impurity phase in which CaO content is high and MgO is low. The impurity phase on the surface of the clinkers has a marked effect on the enhancement of hydration resistance. Several microstructural features are reported and discussed.

1. Introduction

Although magnesia–carbon refractories are increasingly used in basic steelmaking, dolomite refractories are generally favoured for secondary steelmaking, especially for the production of clean steel [1]. MgO and CaO are less susceptible to reaction with metallic elements in liquid steel to form inclusions [1]. Another advantage of using dolomite refractories in ladies is their lower specific gravity compared with other basic refractories. The characteristic of light weight sometimes resolves crane capacity problems [1]. They are also widely used in AOD (Argon Oxygen Decarburization) and VOD (Vacuum Oxygen Decarburization) vessels and cement rotary kilns.

The microstructural aspects of low-flux dolomite refractories were thoroughly investigated by Obst and Muenchberg [2]. According to them, the optimum content of impurity oxides is required to be maintained between 0.5 and 1.5 wt % for the economical calcination of dolomite; if the impurity content is less than 0.5 wt %, it is difficult to obtain dense clinkers unless a higher sintering temperature is provided; if the impurity content is more than 1.5 wt %, dense clinkers can be obtained at a lower temperature, but the refractoriness of the clinkers will be lowered. The scanning electron microscopy (SEM) of low-flux dolomite clinkers was scarcely reported. The present work reports the use of scanning electron microscopy combined with energy-dispersive X-ray spectroscopy to disclose what appears not to have been reported by light microscopy for unhydrated and hydrated industrial low-flux dolomite refractory clinkers.

2. Experimental details

2.1. Materials

Chemical analyses of the clinkers are given in Table I. The brick-quality dolomite clinkers were made in a coal-fired rotary kiln whose sintering zone temperature was 1800 to 2000° C.

2.2. Apparatus

An Autoscan scanning electron microscope (Etec Corp., Hayward, California) was used.

2.3. Experimental procedures

Polished sections of the clinkers were prepared using ethyl alcohol (99.5%) instead of distilled water. The fracture surfaces of the clinkers were coated with carbon. Elemental microanalyses of the clinkers were conducted using a scanning electron microscope together with energy-dispersive analysis by X-rays (EDAX). The microanalyses were carried out by a non-standard quantitative method.

3. Results and discussion

3.1. Clinker surface

The surface of a typical hydrated clinker is shown in Fig. 1. Fig. 2 exhibits the surface of the hydrated clinker; the round and dense particles are periclase; the white and rough portion with heavy cracks is lime

TABLE I Chemical analysis of materials related to dolomite clinker

Type	Composition (wt %)						
	MgO	CaO	Fe_2O_3	Al_2O_3	SiO_2	LOI*	$Fe_2O_3 + Al_2O_3 + SiO_2$
Raw dolomite	19.83	32.81	0.18	0.17	0.22	46.77	0.57
Calcined dolomite	37.25	61.63	0.34	0.32	0.41	–	1.07
Dolomite clinker	37.6	60.2	0.66	0.46	1.10	–	2.22
Coal ashes	2.7	3.5	13.5	28.5	46.1	–	

*LOI = Loss of ignition.

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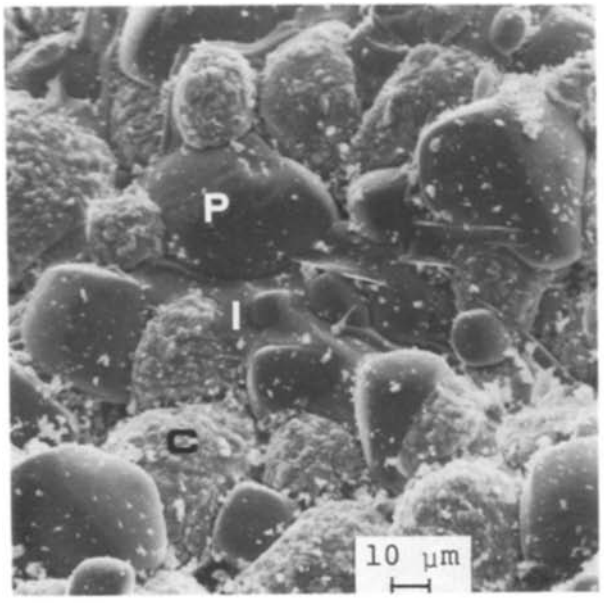

Figure 1 The surface of a typical hydrated clinker. P = periclase, C = lime, I = impurity phase.

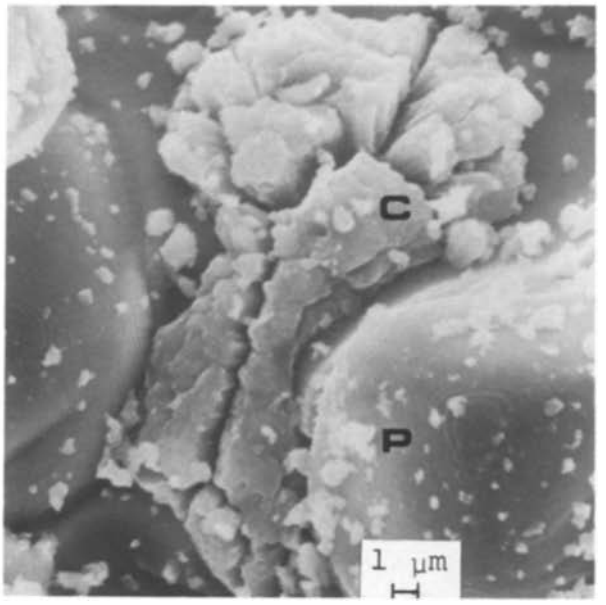

Figure 3 The surface of a hydrated clinker at higher magnification. P = periclase, C = lime.

and the cracks were formed by hydration; the light grey portion is the impurity phase, which appears to be highly hydration-resistant. According to Obst and Muenchberg [2] the impurities in raw dolomite are mainly SiO_2, Al_2O_3 and Fe_2O_3, which are from quartz, clay and iron minerals. These impurities react mainly with CaO to form the impurity phase, which has no distinct morphology (Fig. 2). In addition, Fig. 3 also demonstrates that the particles with rough surface and cracks are lime and those with round and smooth surface are periclase where the crystal growth steps are clearly visible.

The stick-like substance attaching to the periclase particles was identified as dicalcium silicate (Fig. 4).

3.2. Fracture surface

An SEM fractograph of an unhydrated clinker is shown in Fig. 5; as can be seen, the surface is very rough and dense and it is very difficult to differentiate periclase and lime from the physical appearance of the fracture surface; the well-grown crystals inside the caves are clearly visible. Fig. 6 is a fractograph of a clinker which was stored in the air for 7 days; the grey particles are periclase and the white particles with cracks are the hydrated lime which was separated from periclase since volume expansion occurred during hydration.

Fig. 7 is a fractograph of the clinker surface; the substance shown in the square is the impurity phase. EDAX revealed that the impurity phase contained 17.4% MgO, 53.7% CaO, 22.3% SiO_2, 6.2% Al_2O_3 and 0.4% Fe_2O_3. The impurity phase on the surface of a clinker appears to have the effect of protecting the clinkers from hydration attack since the lime on the right and left sides of the impurity phase cracked and expanded (Fig. 7). The impurity phase located on the clinker surface was formed mostly from the reaction in

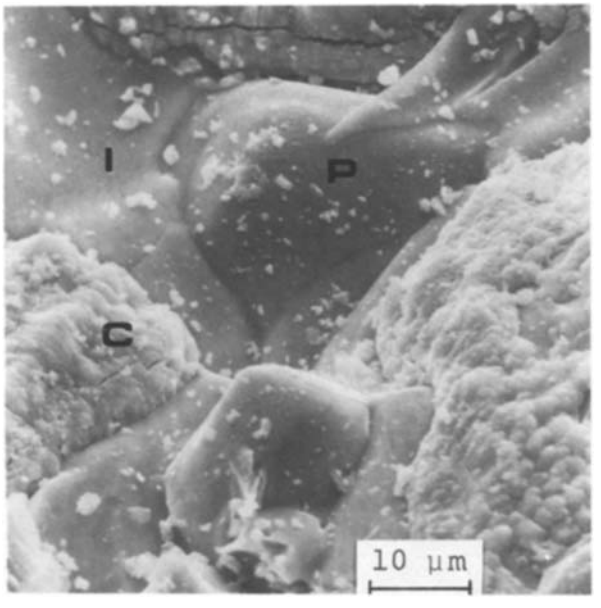

Figure 2 The surface of a hydrated clinker showing the impurity phase having no distinct morphology. P = periclase, C = lime, I = impurity phase.

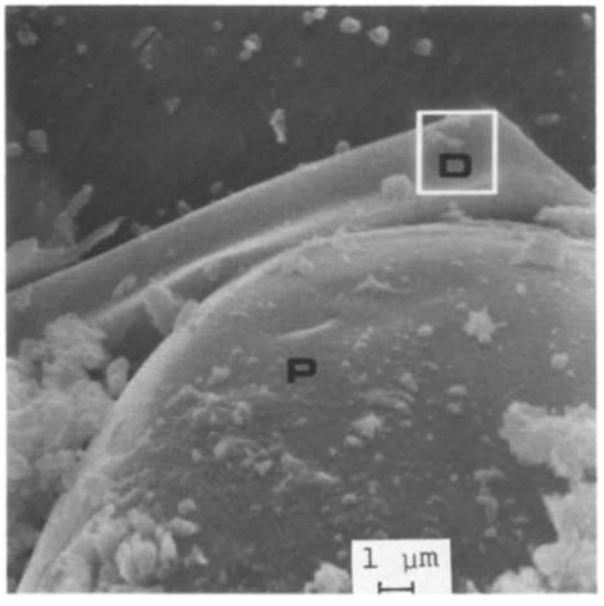

Figure 4 Dicalcium silicate (D) attached to a periclase particle (P).

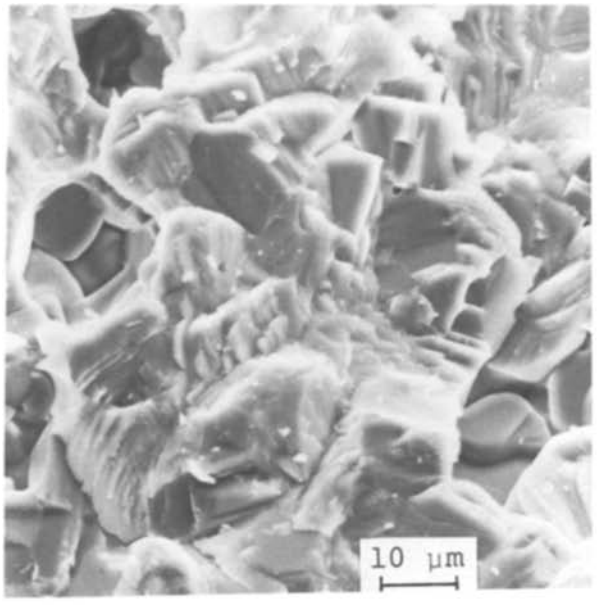

Figure 5 SEM fractograph of an unhydrated clinker.

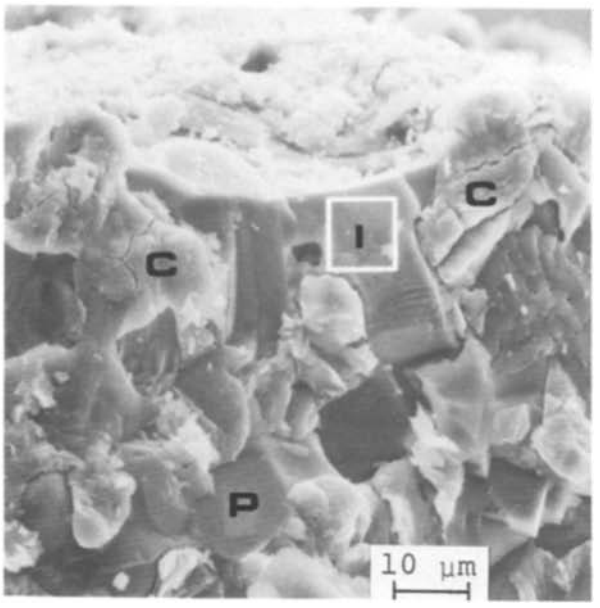

Figure 7 SEM fractograph of a clinker surface. P = periclase, C = lime, I = impurity phase.

which coal ashes reacted with calcined dolomite, since the clinkers were produced in a pulverized coal-fired rotary kiln.

3.3. Interior surface of a closed pore

Fig. 8 reveals that the interior surface of a pore in a clinker is well packed and unhydrated. The pore is believed to be of a closed type, or the perfectly unhydrated condition cannot be maintained. As can be seen in Fig. 8, the periclase grains are readily distinguished by their dark gray colour and wave-like appearance, and the white and flat grains are lime. Since there was no contamination from coal ashes inside the pore, the crystals on the interior surface of a closed pore were well grown. Fig. 9 shows the interior surface of a closed pore after hydration. As can be seen, the degree of hydration was much more serious than at the surface of the dolomite clinker and there appears to be very little impurity phase. Fig. 9 suggests that the burnt dolomite is virtually a mixture of lime and periclase in which the impurity phase is not readily visible if the dolomite is pure enough and burnt in an environment of no contamination.

3.4. Distribution of the impurity phase

The calcination of dolomite is based on the chemical reaction $MgCO_3 \cdot CaCO_3 \rightarrow MgO + CaO + 2CO_2$. Theoretically, the weight loss after calcination is 47.75% and hence the amount of the fluxing impurities in the calcined dolomite will be doubled, compared with raw dolomite, as shown in Table I. Table I also shows that the impurities in the industrial dolomite clinkers increased to around 1%, compared with the laboratory-calcined dolomite. The clinkers were produced in a pulverized coal-fired rotary kiln in which coal ashes react with clinkers. Consequently, the clinkers had a higher impurity content. These impurities tend to react theoretically with CaO to form an impurity phase such as dicalcium ferrite,

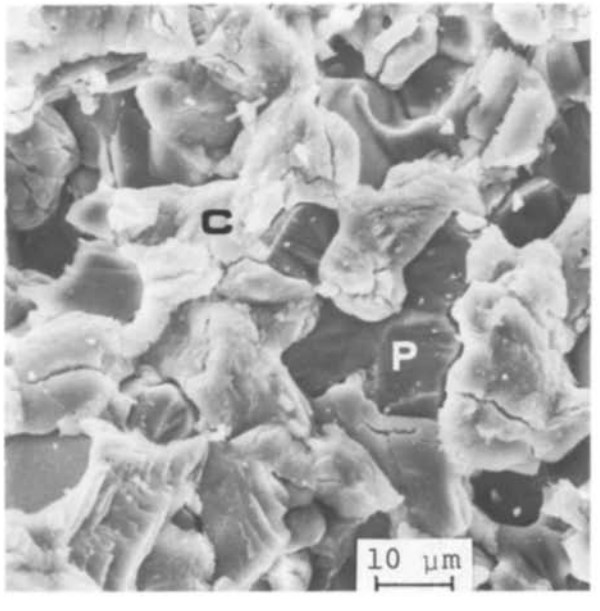

Figure 6 SEM fractograph of a hydrated clinker. P = periclase, C = lime.

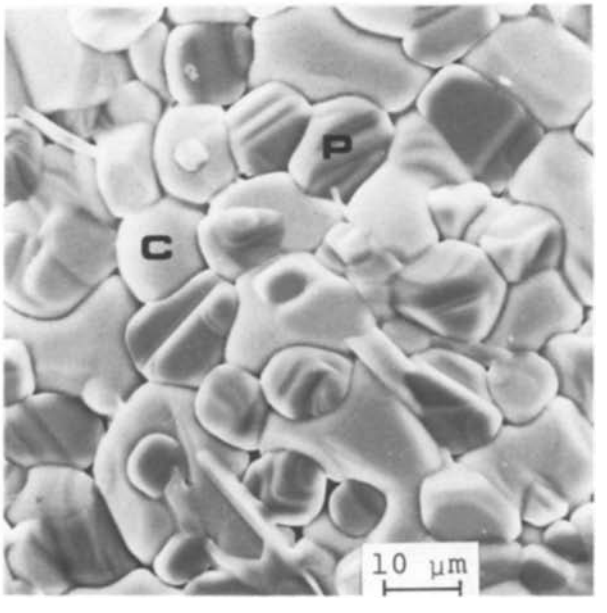

Figure 8 The interior surface of a closed pore in a clinker. P = periclase, C = lime.

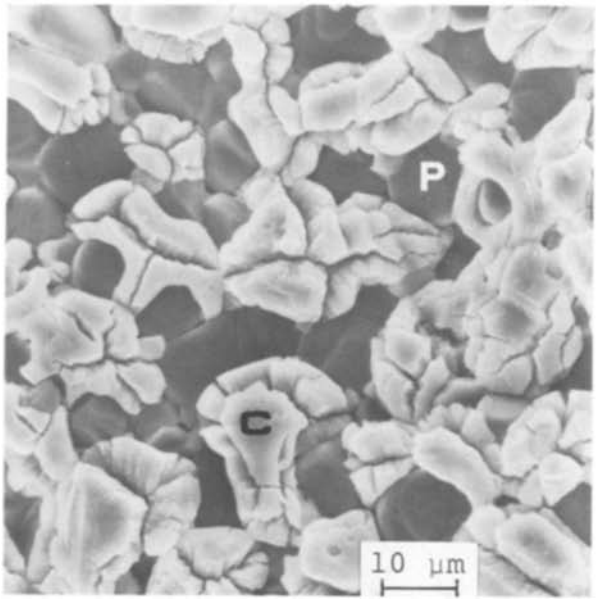

Figure 9 The interior surface of a closed pore in a clinker after hydration. P = periclase, C = lime.

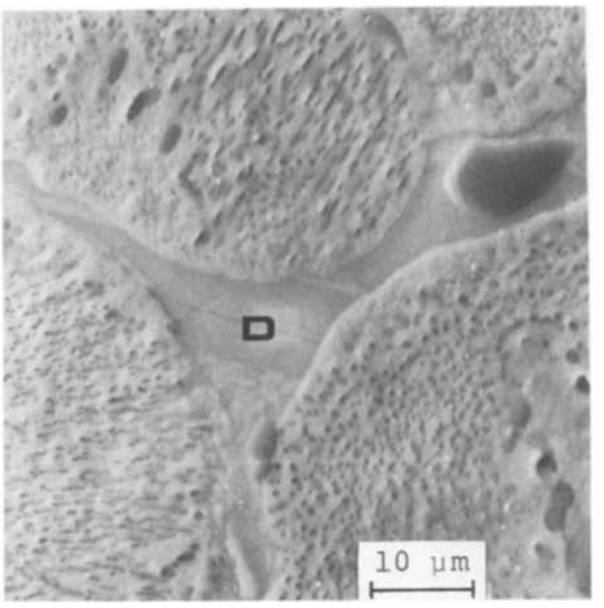

Figure 11 SEM micrograph of dolomitic lime. D = dicalcium silicate.

tricalcium aluminate, dicalcium silicate, tricalcium silicate or Brownmillerite, etc. The present calculation suggests that the amount of impurity phase in the dolomite clinkers was around 5 to 10 wt %. Moreover, the impurity phase related to coal ashes concentrates on the surface of the clinkers, while that related to the impurities in raw dolomite mostly disperses in the interior of the clinkers. This explains why the impurity phase is readily observed on the surface of a clinker, but not in the interior.

3.5. SEM of polished sections

Fig. 10 is an SEM micrograph of a polished section in which the dark grey round particles are periclase and their boundaries are very distinct; the larger light grey area is lime, which occupies most of the area with less distinct boundaries.

Fig. 11 shows dolomitic lime in which small dark grey periclase particles are dispersed in the large light grey lime; the long grey rod was identified as dicalcium silicate. Fig. 12 shows that the small grey round lime particles are dispersed in the large dark grey periclase particles.

Figs 13a to d are SEM micrographs of a polished section of a dolomite clinker. The light grey particles are lime and the dark grey particles are periclase; the remaining portion without a distinct appearance is the impurity phase. As can be seen, the boundary between lime and the impurity phase is a smooth curve and that between periclase and the impurity phase has a more or less angular nature. The shapes of the boundaries suggest that lime reacts more readily with the impurity phase than periclase does. The X-ray mapping of Fig. 13 reveals that most of the silicon, aluminium and iron concentrates in the impurity phase where the CaO content is high and the MgO content is low.

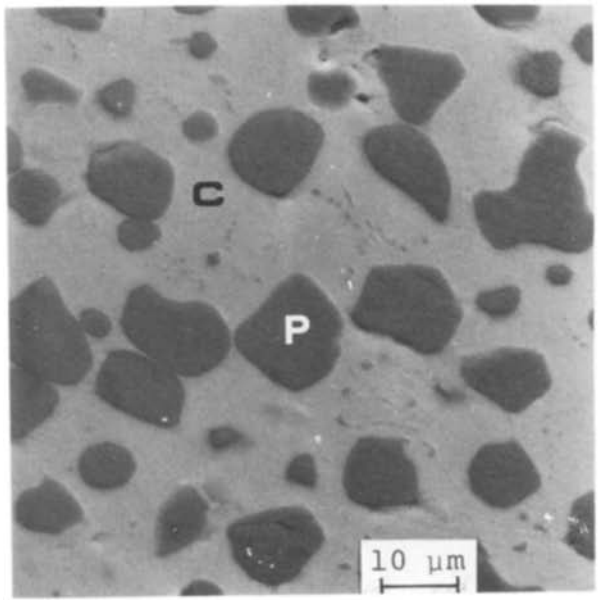

Figure 10 SEM micrograph of a typical polished section of a dolomite clinker. P = periclase, C = lime.

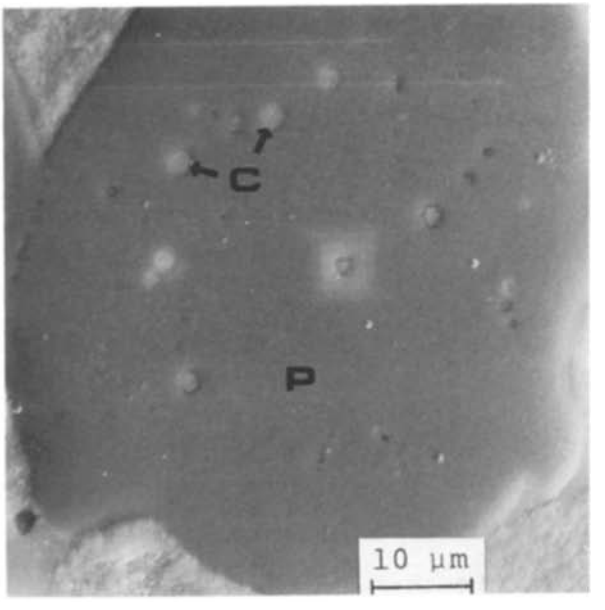

Figure 12 SEM micrograph showing lime particles (C) dispersed in a periclase grain (P).

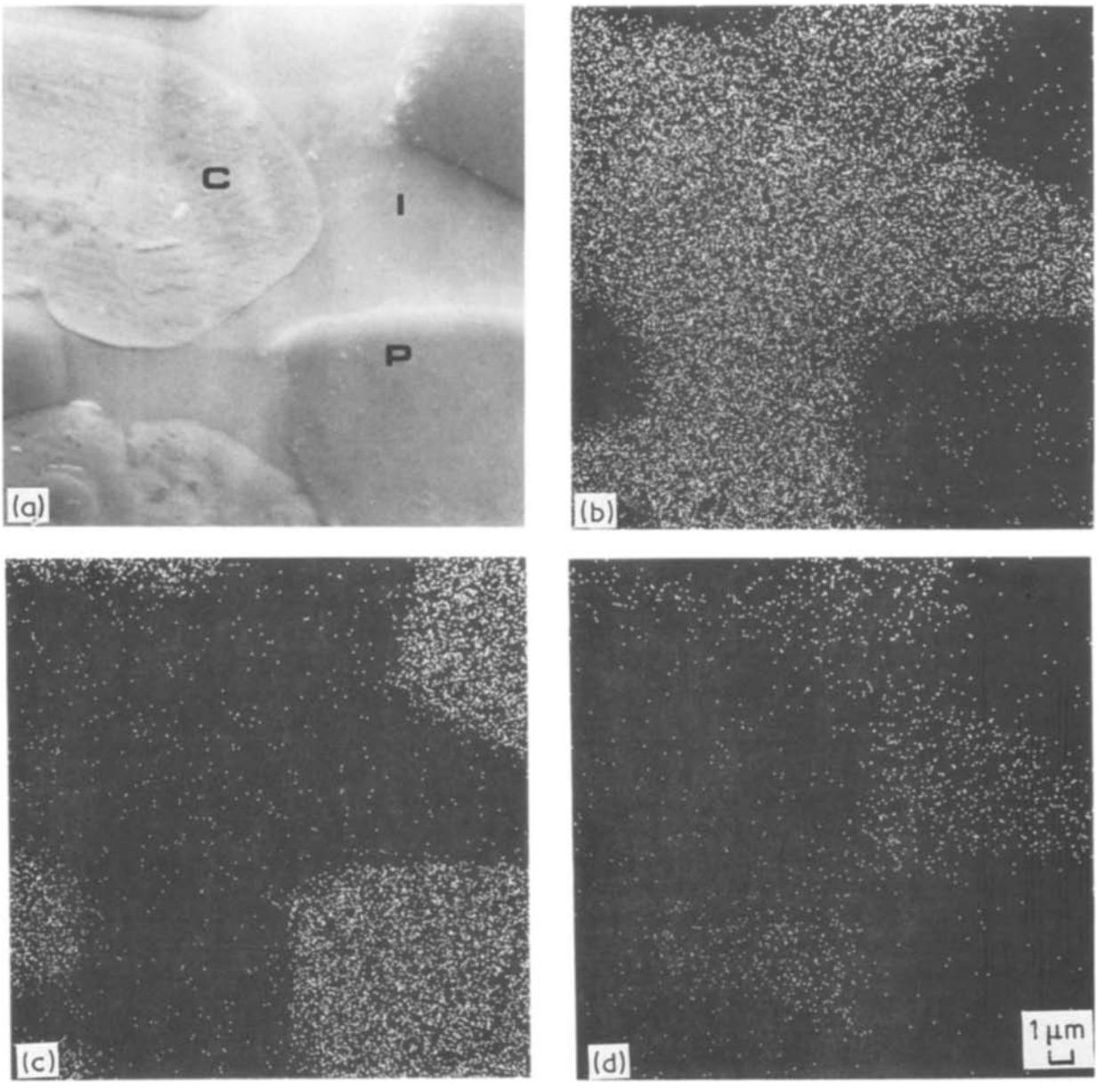

Figure 13 SEM and X-ray analysis micrographs of a polished section of a dolomite clinker at higher magnification: (a) SEM, (b) calcium, (c) magnesium and (d) silicon. P = periclase, C = lime, I = impurity phase.

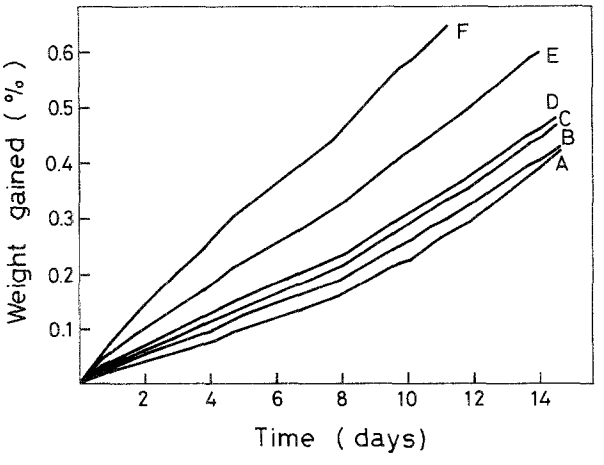

Figure 14 The time dependence of weight gain in the air for various sizes of as-received dolomite clinker: (A) > 11 mm, (B) 11 to 6.3 mm, (C) 6.3 to 4.7 mm, (D) 4.7 to 3.4 mm, (E) 3.4 to 2.4 mm, (F) 2.4 to 0.7 mm.

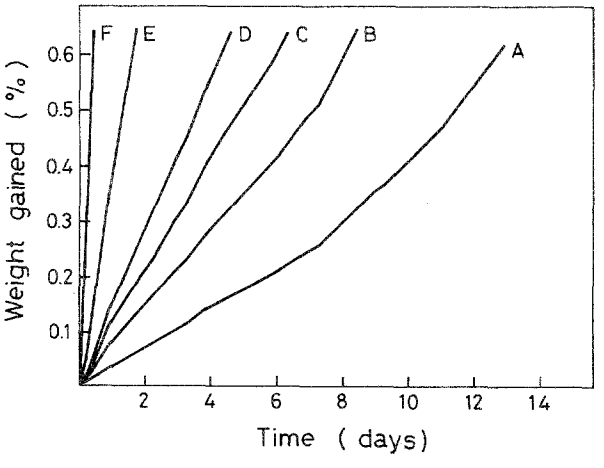

Figure 15 The time dependence of weight gain in the air for various sizes of crushed dolomite clinker: (A) 11 to 6.3 mm, (B) 6.3 to 4.7 mm, (C) 4.7 to 3.4 mm, (D) 3.4 to 2.4 mm, (E) 2.4 to 0.7 mm, (F) < 0.7 mm.

3.6. Hydration resistance of the clinkers

Figs 14 and 15 exhibit the time dependence of weight gain in the air for various sizes of as-received and crushed clinkers. As can be seen, the hydration rate is quite obviously influenced by particle size; the smaller the size, the higher the hydration rate and vice versa; for the same particle size, as-received clinkers have a much higher hydration resistance than the crushed ones. It is concluded that the impurity phase on the surface of clinkers can enhance their hydration resistance.

It was observed that a clinker split into two parts after having been exposed in the air for some time and the fracture surface was very flat. Fig. 16 shows a long straight crack on the fracture surface and Fig. 17 shows the crack at a higher magnification. It is believed that the crack was caused by the volume expansion due to hydration in which lime transforms into portlandite. The crack is probably responsible for further crack propagation to create more fresh and reactive surfaces containing CaO to accelerate hydration. Consequently, the hydration rate should increase as hydration continues. This conclusion is supported by Figs 14 and 15 in which the slope of the curves increases considerably as the test goes on, more noticeably for the larger grains.

4. Summary

The industrial low-flux dolomite refractory clinkers produced in a coal-fired rotary kiln were investigated by scanning electron microscopy combined with energy-dispersive X-ray spectroscopy. SEM micrographs of the morphology of periclase, hydrated lime and the impurity phase, the fracture surfaces of unhydrated and hydrated clinkers, the interior surfaces of a closed pore, polished sections, and the fracture surface produced by hydration have been presented. The impurity phase which is located between periclase and lime grains has a glassy appearance and occasionally contains dicalcium silicate in the form of rods; most of the silicon, aluminium and iron concentrates in the impurity phase in which the CaO content is high and the MgO content is low. The impurity phase on the surface of the clinkers has a marked effect on the enhancement of hydration resistance.

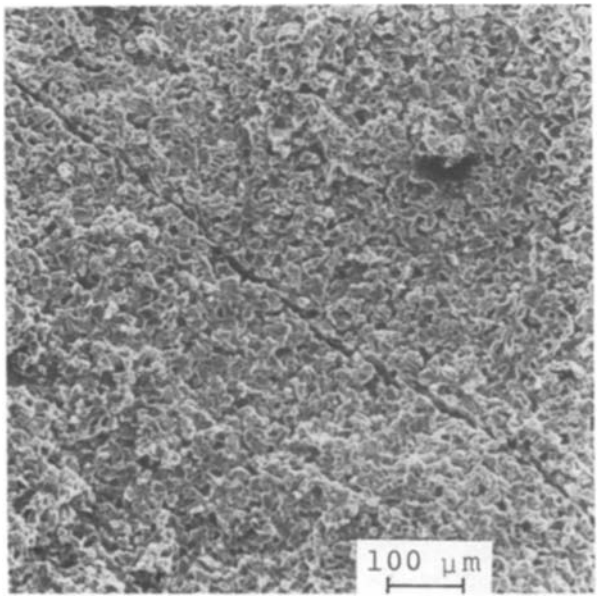

Figure 16 SEM micrograph of the fracture surface of a dolomite clinker caused by hydration.

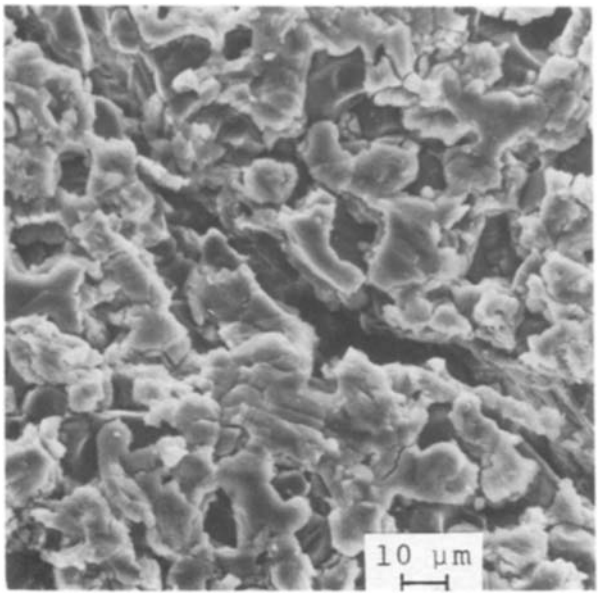

Figure 17 SEM micrograph of the fracture surface of a dolomite clinker caused by hydration at higher magnification.

Acknowledgements

The authors thank J. Y. Huang, Manager of Research and Development and I. L. Cheng, Vice-President, Technology at China Steel Corp., for their support.

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Received 7 January
and accepted 1 April 1987