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ANISOTROPIC LIGHT ABSORPTION OF THE CALCIUM ALUMINOFERRITE PHASE IN PORTLAND CEMENT CLINKER

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ABSTRACT

The solid solution of MgO in Ca_2FeAlO_5 and the resulting change in anisotropic absorption have been studied. The solid solution of MgO was investigated by directly determining the chemical formulas of the solid solutions of the system Ca_2FeAlO_5 - MgO by electron probe microanalysis. Mg ions replace exclusively Fe and Al ions in the octahedral sites in the structure; they neither replace Ca ions nor enter the interstitial sites. The solubility limit of MgO at 1350°C was 0.75wt%, which was half the amount hitherto reported. Similarly, incorporation of Si ions in the tetrahedral sites has been confirmed. The optic orientation of Ca_2FeAlO_5 and its solid solutions is X=*b*, Y=*c*, Z=*a*. Absorption anisotropy is weak for Ca_2FeAlO_5 with Y, Z (reddish orange) >X (yellowish orange). With incorporation of MgO, absorption becomes extremely strong for light vibrating in the YZ-plane while remains practically unchanged for light vibrating parallel to the X-axis. The strong absorption in the presence of Mg ions has been ascribed to the occurrence of tetravalent iron ions under oxidizing atmospheric conditions, which compensates the deficiency of positive charge caused by the substitution of Mg for Fe and Al.

Introduction

The anisotropic absorption of light of the calcium aluminoferrite phase influences the tone of color of portland cement, in particular, its lightness (1,2). The ferrite phase, intrinsically weak in anisotropic absorption, shows strong absorption anisotropy when contaminated with MgO in solid solution and crystallized in oxidizing atmosphere (3-6).

In the present investigation we have made clear the mode and limit of MgO incorporation in the ferrite phase by determining structural formulas for a series of solid solutions by electron probe microanalysis. The color change with incorporation of MgO has been evaluated only in reflected light so far. We measured transmission spectra of visible light in the maximum and minimum absorption directions with the polarizing microscope. A hypothesis has been put forward that the increase in absorption anisotropy comes from the occurrence of tetravalent iron ions.

Experimental

A series of MgO-solid solutions were prepared by adding up to 3% of MgO to Ca_2FeAlO_5. In addition, solid solutions containing SiO_2 as well as MgO were prepared. The mixtures, after firing at 1250°C with intermediate grinding, were kept at 1350°C for 1 to 7 days and quenched in air. Crystals as large as 200μm in diameter and 60μm in thickness were grown by Ostwald ripening in the presence of a very small amount of a liquid phase; they were flat on (010) with distinct pyramidal planes.

Quantitative analyses were made, using an electron probe microanalyzer (JCMA-733, JEOL), for more than 15 spots free from inclusions for each specimen (accelerating voltage, 15kV; specimen current 0.012μA; electron probe diameter 1μm). The correction for intensities was made by the standard ZAF routines.

Spectral transmittance was measured in the visible region between 400 and 800nm using a microscope photometer equipped with a grating monochrometer. The measurement was made in the minimum and maximum light absorption directions in plane-polarized light. The spectral distributions were compared by equalizing the transmission factors at 800nm in the minimum absorption directions.

The concentration of FeO in the silicate and the interstitial parts was determined quantitatively for 22 ordinary portland cement clinkers. Some of them were separated into the inner and outer parts of the nodules. The silicate and interstitial parts were obtained as residues by treating finely powdered clinker samples with aqueous solution of KOH and sucrose and with maleic acid in methanol, respectively (7). The quantitative analysis of FeO was made in the following way (8). Samples were decomposed with hydrofluoric and sulphuric acids in the presence of pentavalent vanadium V(V) so that divalent iron Fe(II) might be preserved as equivalent V(IV) in the solution. By adjusting the pH of the solution to *ca.* 5, Fe(II) was reproduced quantitatively from V(IV), which was determined spectrophotometrically with 1,10 - phenanthroline as a color-producing reagent.

Results

1. Solid solution of Mg in Ca_2FeAlO_5

The results of microprobe analyses were represented as chemical formulas with number of oxygen 5. Figure 1 shows the number of Ca, Mg and (Fe, Al) atoms, together with Al/Fe ratios, against the amount of MgO added to Ca_2FeAlO_5.

In the structure of Ca_2FeAlO_5 (a=0.5584, b=1.460, c=0.5374nm, Z=4, Ibm2), nearly 3/4 of the octahedral sites [4(a)] is occupied by Fe ions and the remaining 1/4 by Al ions (9). The reverse is the case with the tetrahedral sites [4(b)]. The Ca ions are all in the 8(c) site and unevenly coordinated by seven oxygens.

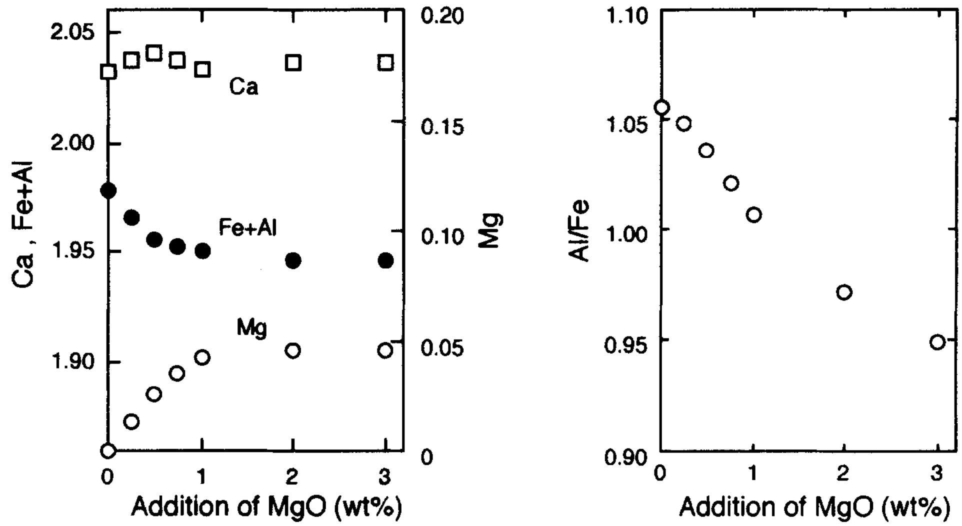

FIG. 1
Number of atoms in one chemical formula unit as a function of percent MgO added. Ca, Fe+Al, Mg (left) and Al/Fe ratio (right).

The number of Ca ions in the chemical formulas of solid solutions remains unchanged, irrespective of the amount of MgO added, with the 8(c) site occupied entirely by Ca ions, indicating that Mg ions by no means replace Ca ions in the structure of Ca_2FeAlO_5. This is quite different from the previous results that some of the Mg ions substitute for Ca ions in Ca_2FeAlO_5 (10,11,12). The number of Ca ions always exceeded 2 by 1 to 2 percent; it is not clear at present whether this is due to a systematic error of measurement or to some other significant cause. However, it is conceivable, in the light of the relevant phase equilibrium diagram, that submicroscopic crystallites of CaO occur in a small amount in the Ca_2FeAlO_5 crystals (13). Because the sum total of Fe, Al and Mg is very close to 2, Mg ions replace exclusively Fe and Al ions in the octahedral sites. There is no necessity at all, as proposed previously, for part of the Mg ions to enter the interstitial sites in the structure (12). The Al/Fe ratio of the solid solution series decreased with increasing Mg concentration in solid solution. The decrease, however, does not necessarily imply selective substitution of Mg for Al, as evidenced by the fact that the Al/Fe ratio continued to decrease even for the solid solutions from the raw mixtures with MgO added beyond its solubility limit. Presumably the liquid phase existing in small amount during crystal growth was rich in Al_2O_3 component and increased in quantity with increasing MgO added.

The solubility limit of Mg in Ca_2FeAlO_5 at 1350°C was 0.045 in one chemical formula unit, which is equivalent to 0.75wt% of MgO. This is only half the amount hitherto reported (10,11).

Table 1 gives chemical formulas for solid solutions prepared in a similar way from raw mixes containing equimolecular SiO_2 as well as MgO. The solid solution of Si in the ferrite phase, which was assumed by XRD and IR (14,15), has been confirmed directly. The coupled ion exchange as $2Fe^{3+} \rightarrow Mg^{2+} + Si^{4+}$, however, could not be concluded in this experiment. It seems that both elements go into solid solution independently. The sum of Fe, Al, Mg and Si came close to 2, indicating that Si atoms replace the tetrahedral sites [4(b)].

TABLE 1

Chemical formulas* of calcium aluminoferrite solid solutions with MgO and SiO_2

MgO (wt%)**	Ca	Fe	Al	Mg	Si	Fe+Al+Mg+Si	Al/Fe
0.50	2.016	1.061	0.907	0.016	0.007	1.991	0.855
0.75	2.021	1.095	0.867	0.019	0.008	1.989	0.792
1.00	2.014	1.121	0.843	0.021	0.010	1.995	0.752

*Number of oxygen 5; **With SiO_2 in equimolecular amount in the raw mix

2. Anisotropic light absorption of Ca_2FeAlO_5 solid solutions

The optic orientation of calcium aluminoferrite and its solid solutions close in composition to Ca_2FeAlO_5 is X=*b*, Y=*c*, Z=*a*. The crystallographic orientation was determined by the X-ray precession method. The absorption is weakest for light vibrating perpendicular to (010) (or parallel to X) and strongest for light vibrating in the (010) or YZ-plane.

Figure 2 shows transmission spectra in the visible region in the minimum and maximum absorption directions for Ca_2FeAlO_5 and its solid solution with MgO. The absorption anisotropy inherent in Ca_2FeAlO_5 is weak with a pleochroic formula X - yellowish orange, Y, Z - reddish orange. The spectra for both vibration directions differ most noticeably at around 590nm. With a solid solution with MgO, the spectrum in the minimum absorption direction was nearly the same as that for Ca_2FeAlO_5. By contrast, in the maximum direction extremely strong absorption occurred over the whole spectral region and the crystals appeared almost opaque; the absorption was especially strong toward the near infra-red region. Despite this, no appreciable change in the tone of color was recognized in the spectrum in the maximum absorption direction. The above spectral change with the solid solution of MgO corresponds to the decrease in L and b values in the Lab color system in reflected light.

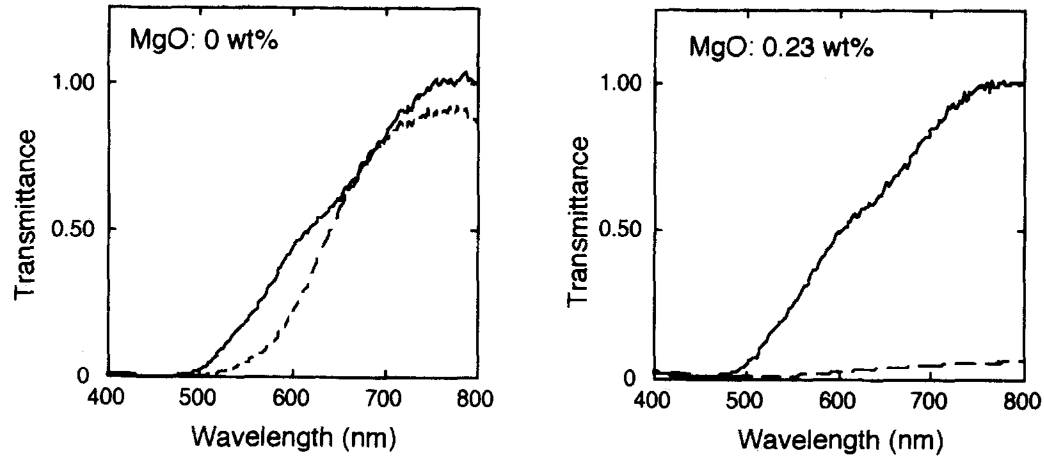

FIG. 2
Transmission spectra in minimum and maximum absorption directions.
Ca_2FeAlO_5 (left) and solid solution with MgO (right).

3. Distribution of FeO in portland cement clinker

The average FeO concentration for all the 22 clinker samples examined is given in Table 2. An exact correlation exists concerning FeO between the clinkers and their silicate parts (Fig. 3(a)). FeO/(Fe_2O_3+FeO) in the silicate part is as high as 23% on average, suggesting that Fe^{2+} preferentially replaces Ca^{2+}. A similar relation is also recognized between the clinkers and their interstitial parts (Fig. 3(b)); the lower correlation presumably came, as described later, from varying atmospheric conditions during cooling with regard to the redox equilibrium of iron ions.

The inner and outer parts of portland cement clinker nodules produced in the rotary kiln usually differ in color, bulk density, chemical composition and textures according to their difference in clinkering and nodulization processes in the kiln (16). The color is yellowish or reddish brown in the core and dark grey in the periphery. Table 3 compares the FeO concentration in the inner and outer parts of clinker nodules; the difference in color between the two parts is much larger in sample 1 than in sample 2. Accordingly, the FeO concentration in the ferrite phase, as well as in the interstitial materials, is apparently higher in the core of nodules than in the periphery, in particular, for sample 1. Reheating in air, at 950°C for 10min for example, reduced the FeO concentration of the ferrite phase in the core to as low a level as that in the periphery with darkening in color.

TABLE 2

Distribution of FeO (%)

	clinker	silicates	int. mater.
Fe_2O_3 + FeO	3.3(0.3)	1.3(0.2)	13.8(1.5)
FeO	0.3(0.1)	0.3(0.1)	0.2(0.1)
FeO/(Fe_2O_3 + FeO)	8.3(3.6)	23.2(9.7)	1.7(1.0)

Figures in parentheses indicate s.d.

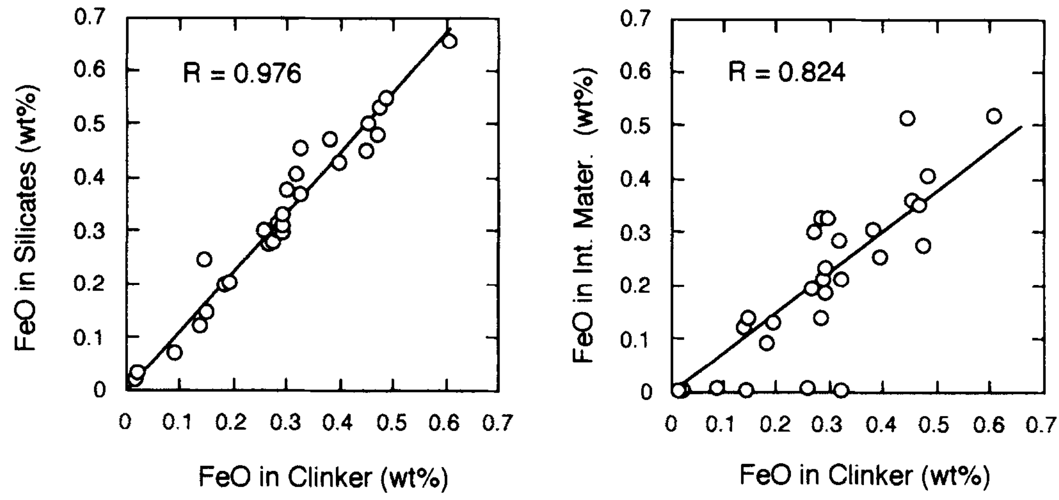

FIG. 3
Distribution of FeO in (a) silicates and (b) interstitial materials in clinker.

TABLE 3
FeO concentration in ferrite (wt%)

specimen	clinker	int. mater.	ferrite
1 core	0.53(0.02)	0.84(0.04)	0.39(0.03)
1 periphery	0.10(0.02)	0.04(0.04)	0.05(0.04)
2 core	0.11(0.02)	0.24(0.01)	0.10(0.01)
2 periphery	0.09(0.02)	0.21(0.04)	0.05(0.04)

Figures in parentheses indicate FeO percent after reheating at 950°C for 10 min.

Discussion

Because Mg^{2+} replaces exclusively Fe^{3+} and Al^{3+} in the octahedral sites in the Ca_2FeAlO_5 structure, deficiency of positive charge results with incorporation of Mg ions. Under oxidizing atmospheric conditions, the deficiency, which otherwise produces oxygen defects, may be compensated by the occurrence of extrinsic tetravalent iron ions; and these ions are considered to absorb visible light strongly. The structure of the calcium aluminoferrite phase is strongly anisotropic, consisting of perovskite-like layers perpendicular to the *b*-axis alternating with tetrahedral chains running parallel to the *c*-axis. Accordingly, the existence of tetravalent iron ions in quantity gives rise to strong absorption for plane-polarized light vibrating parallel to the layers; whereas absorption is weak for light vibrating along the *b*-axis.

This hypothesis is in accordance with the decrease of light absorption in the coexistence of tetravalent Si^{4+} ions in the ferrite phase. The absorption of the ferrite phase in portland cement clinker varied according to its SiO_2/MgO ratio (17,18). A super high strength cement containing CaF_2 as an essential constituent was less dependent in light absorption on the amount of MgO and the atmospheric conditions during cooling than normal portland cement clinkers (19). This may be ascribed to the reduction of Fe^{4+} concentration in the ferrite phase with the replacement of O^{2-} by F^-. With yttrium iron garnet ($Y_3Fe_5O_{12}$) it has been confirmed that substitution of Ca^{2+} for Y^{3+} markedly increases light absorption by producing Fe^{4+} ions (20-24).

The atmospheric conditions in which the ferrite phase is crystallized from the interstitial liquid during cooling are widely different between the core and the periphery of clinker nodules. In the periphery, high in porosity, the ferrite phase is crystallized under high partial pressure of oxygen and gives strong absorption anisotropy. By contrast, in the dense core the ferrite phase is crystallized out of contact with the atmosphere and shows only weak absorption. The latter, when pulverized and reheated in air, increases in absorption with a remarkable decrease in Fe^{2+} concentration. The occurrence of Fe^{4+} may be favored at the expense of Fe^{2+}. When the ferrite phase of large absorption anisotropy was reduced by treating with saturated aqueous solution of $FeCl_2$ at 100°C, the absorption became weak with increase in lightness. This also supports the existence of Fe^{4+} in the ferrite phase.

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