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RAPID ESTIMATION OF FREE MAGNESIA IN OPC CLINKER AND $3CaO:1SiO_2$ SYSTEM BY COMPLEXOMETRY

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ABSTRACT

A simple, accurate, and rapid method of estimation of periclase in cement clinker and tricalcium silicate has been developed using chemical extraction followed by complexometric determination. The data obtained has been compared with the results of XRD. A good agreement was found between the two methods. The proposed method will be suitable for the estimation of free MgO in clinkers. It was also found that of the total MgO present in tricalcium silicate (C_3S), about 1.5% gets into the C_3S mineral and the rest crystallises out in the mineral form, as periclase. © *1998 Elsevier Science Ltd*

Introduction

Magnesia is an associated mineral occurring in varying amounts in the raw materials for the manufacture of ordinary Portland cement (OPC). During the pyroprocessing of the raw materials, a part of MgO is stabilized as a solid solution in C_3S, C_2S, and clinker liquid phase. Excess MgO crystallizes out as magnesia (i.e., periclase) during the cooling of clinker. The crystallized MgO has an adverse effect on the performance of OPC, in that it has a slower rate of hydration than the other cement minerals and results in delayed expansion, leading to durability problems. Its estimation in cement is a relatively difficult process.

Paluch et al. (1) evaluated the Bogue-Taylor (BT) method (2) and Toropow-Kacenielenbogen (TK) method (3) for the determination of periclase content of Portland cement clinker. BT method is based on leaching the periclase out of the clinker by treatment with a mixture of glycerine and anhydrous ethanol or methanol in the presence of ammonium nitrate. TK method is based on dissolving the periclase in a mixture of glacial acetic acid and methanol in the presence of ammonium chloride. Paluch et al (1) reported that neither of these methods is reliable. In the BT method, the magnesium oxide is derived mainly from the decomposition of the silicate phases by the leaching reagent, and in the TK method it is approximately the sum of the periclase content and magnesium oxide content which have passed into solution

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during the decomposition of the silicates. Arjunan et al. (4) developed the ammonium nitrate method (ANM), and after comparing it with the BT method found refluxing time to be almost one-fourth of the BT method.

In light of the above, present work has been taken up to develop a method to determine free magnesia (periclase) in cement clinker and calcium silicate and to investigate the solubility of MgO in C_3S phase. The method presented here is a modified BT method and has been found rapid, accurate, and simple.

Experimental

The method developed was applied to two sets of samples. The first set was composed of a clinker from a large dry process cement plant, to which magnesia (periclase), was added in different proportions, viz. 1, 2 and 4% by mass of clinker. The chemical composition of the plant clinker is presented below:

Chemical analysis of the clinker.

Element:	LOI	SiO_2	Fe_2O_3	Al_2O_3	CaO	MgO	Na_2O	K_2O	$*CaO_f$
Wt.%:	2.55	21.84	3.65	5.09	64.20	0.90	0.35	0.58	2.60

*By ethylene glycol method.

The entire MgO of 0.9% was present in combined form. The second set of samples were comprised of tricalcium silicate doped with 0.5, 1.0, 1.5, 2.0 and 5.0% MgO, and were prepared by sintering analytical-grade calcium carbonate and quartz in the molar ratio of 3:1 and 0.5% to 5.0% MgO by mass of C_3S (5). Along with these, pure C_3S was also prepared similarly. Specimens were fired repeatedly till free lime reduced to less than 0.2% in pure C_3S.

The following reagents were used (all were analytical grade):

1. Ammonium nitrate dried in vacuum desiccator for 7 days using P_2O_5 as desicant to remove complete moisture.
2. Ethanol dried (water $< 0.2\%$).
3. Glycerol, anhydrous 99.8% purity.
4. Patten & Reeder's reagent (P & R).
5. Thymol phthalexone indicator.
6. Ethylene diamine tetra acetic-acid disodium salt (EDTA).
7. Sodium hydroxide pellets.
8. Buffer solution pH 10.

Optimisation of Digestion Period

One gram of the clinker was mixed with 4% MgO and taken in separate conical flasks. To these was added 4 g ammonium nitrate, followed by 60 mL of 5:1 mixture of ethanol and glycerol in each flask. Flasks fitted with air condensers were kept on water bath and refluxed for 0.5, 1, 2, and 3 h, respectively. Intermittent shaking was done after every 3 min. After digestion, solutions were filtered and washed with ethanol and made up to 250 mL with distilled water. Calcium was titrated at pH 12, maintained by sodium hydroxide solution,

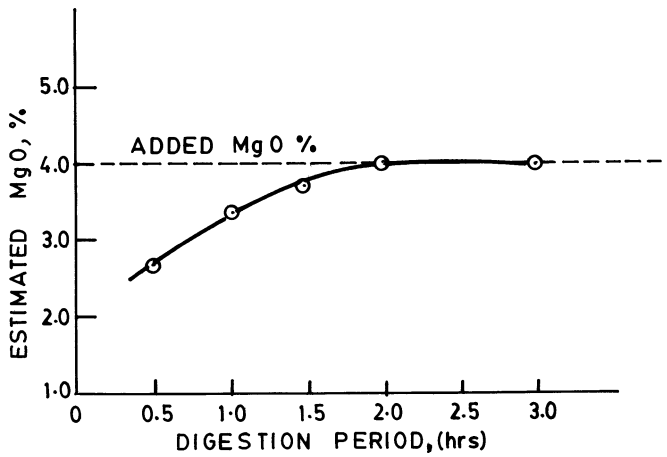

FIG. 1.
Optimisation of digestion period.

with 0.01 M EDTA using P & R indicator. Calcium and magnesium were cotitrated at pH 10, using thymolphthalaxone indicator until the colour changed from blue to violet and cloud formation disappeared. Percent MgO was obtained by difference. Results are presented in Figure 1.

Clinker specimens mixed with 1 to 4% MgO and tricalcium silicate samples doped with MgO (0.5 to 5.0%) were digested for 2 h and MgO_f estimated as above. Results are presented in Tables 1 and 2.

Estimation of Periclase by X-ray Diffraction

X-ray diffraction studies were carried out on Philips X-ray Diffractometer PW 1120 using CuK radiation with Ni filter at 20 mA current and 30 KV voltage. The intensities of x-ray diffraction peaks were measured with a proportioned detector. The most intense peak of periclase (200) at 2.106 Å was selected for quantitative estimation of periclase in both, the clinker samples and doped C_3S samples. Other peaks of periclase are of weak intensities and hence are of limited use for quantitative analysis. However it may be borne in mind that some very weak lines of alite, belite, and C_3A lie in the vicinity of 2.106 A line and these produce an increased background in the region of the periclase peak chosen.

To estimate the periclase content in clinker and C_3S, two sets of standard samples for

TABLE 1
Estimation of periclase in clinker.

	Sample	Estimated % MgO_f	% MgO by XRD
1	Clinker 1% MgO	0.95, 1.10, 0.90 (A.V 0.98)	0.95
2	Clinker 1.5% MgO	1.45, 1.55, 1.50 (A.V. 1.50)	1.45
3	Clinker 2% MgO	2.10, 2.05, 1.90 (A.V. 2.01)	2.02
4	Clinker 4% MgO	3.95, 4.04, 3.90 (A.V.3.96)	4.08

TABLE 2
Estimation of periclase in doped C_3S sample.

	Sample	Estimated % MgO_f	A.V %	% MgO_f by XRD	%MgO fixed in C_3S
1	C_3S doped with 0.5% MgO	Nil	–	–	0.5
2	C_3S doped with 1% MgO	Nil	–	–	1.0
3	C_3S doped with 1.5% MgO	Nil	–	–	1.5
4	C_3S doped with 2.0% MgO	0.5, 0.49, 0.51	0.50	0.49	1.5
5	C_3S doped with 5% MgO	3.5, 3.51, 3.48	3.50	3.52	1.5

calibration were prepared by wet mixing with 1, 2, 4 and 5% MgO by weight, in clinker and pure C_3S sample. It was considered necessary to have matching matrix with unknown samples to draw two separate calibration curves for each set of samples. The peak height at 42.92 2° O was then plotted against the percent of periclase added (Fig. 2). Peak height was measured in arbitrary units. Results obtained by XRD studies on clinkers with 1 to 4% free MgO and C_3S doped with 0.5 to 5% MgO are presented in Tables 1 and 2.

Results and Discussion

MgO as determined by EDTA as a function of period of digestion (Fig. 1) indicates that a 2-h period for digestion is optimum. MgO content in specimens digested for lesser periods is found to be less than the amount added. Larger digestion period may lead to partial hydration of other phases, leading to extraction of some of the combined CaO and MgO.

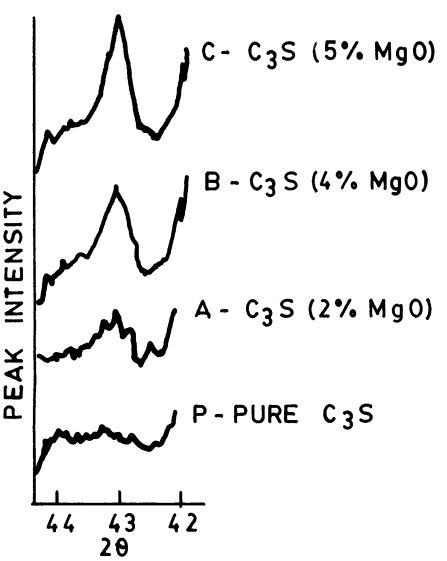

FIG. 2.
XRD showing periclase peak in doped C_3S samples.

The results presented in Table 1 indicate that the values of % MgO compare favourably by both the EDTA and XRD method, with those of MgO added.

Periclase was prepared by sintering analytical grade magnesium carbonate at 1450°C for 1 h. The crystal size of the periclase used was in the range of 10 um to 62 um. The crystal size of periclase in plant clinker remains well below this range. So, the periclase content in the commercial clinkers can be extracted reliably with in the optimized digestion period (2 h).

Arjunan et al. (4) used ethanol as solvent along with ammonium nitrate. In the present work, ethanol/glycerol solvent has been used. Ethanol/glycerol mixture, besides acting as an extraction medium also helps in accurate estimation of calcium by the EDTA method, as calcium forms calcium glycerate with glycerol, which makes the detection of end point better.

Solubility of MgO in tricalcium silicate phase has been studied by many researchers. Woerman (6), Spohn (7), and Locher (8) have reported the solubility of MgO in C_3S phase to be 1.5% at 1425°C; 1.6% at 1450°C; and 1.5% at 1420°C, respectively. However, the results obtained by the method developed indicate that 1.5% MgO goes into solid solution of C_3S at 1450°C. The results of XRD (Table 2), also indicate that the solubility of MgO in C_3S is 1.5%, as no peak for MgO could be detected in specimens doped with MgO up to 1.5% MgO. The peak was observed in the specimen with 2% and above concentration of MgO (Fig. 2).

Conclusion

The method reported here can be used to distinguish the dispersion of MgO in clinkers and magnesia doped calcium silicate samples. The method is rapid, accurate and convenient for the estimation of free MgO (periclase). The EDTA method as developed, is capable of giving accurate results and can be used as an alternative, to the well established XRD method for the determination of periclase in cement and cement minerals.

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