CHAPTER II

EXPERIMENTAL PROCEDURES
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Different techniques normally used in high temperature silicate chemistry research including the use of high temperature furnaces, X-ray powder diffraction, and microscopy, in addition to the usual analytical chemistry procedures, were employed during the course of the present investigation. New test methods for measuring autoclave expansion of experimental cements and for determining quantitatively uncombined MgO with an X-ray diffractometer and uncombined Mg(OH)$_2$ by DTA were also devised. The details of different experimental procedures are described below.

(A) Preparation of Cement Clinkers

(a) Preparation of Synthetic Clinkers

The synthetic clinkers were prepared from reagent grade CaCO$_3$ (99.9% pure); crushed quartz, SiO$_2$ (99.95% pure); Al$_2$O$_3$ (99.58% pure); Fe$_2$O$_3$ (Mathey "Specpure") and MgO obtained by decarbonating MgCO$_3$ (99.9% pure) at 1300°C. The powdered materials passing a 200-mesh
sieve were accurately weighed in required proportions, mixed dry in a shaker and then decarbonated in platinum boats at 1000°C. The decarbonated mix was passed through a 100-mesh sieve, mixed in the shaker and then pelletised to form about 1 x 1-in. cylindrical pellets under a pressure of 8000 lbs. The pelletiser consisted of an assembly of a high strength steel hollow cylinder, 2.75-in. high, 1.5-in. in diameter and having 0.25-in. wall thickness and a plunger, in two pieces, fitting into it. The pressure was applied by means of an A.C.L. laboratory hydraulic press. The pellets were burnt in a platinum boat at the desired temperature for 2 hours in a 0.8 mm diameter, Pt. 80% Rh. 20% wire wound muffle furnace, fabricated in the laboratory and fitted with a motorised variac controller and a KENT multipoint temperature recorder. The control of temperature was within ± 1°C. One pellet was burnt at a time. After burning, the pellet was cooled either by leaving it out in the laboratory atmosphere (air cooled) or by submerging it under water (water quenched).

A batch of 20 g clinker was made in one run.

(b) Preparation of Clinkers Using Indian High-magnesian Limestone and Clay

The limestones and clay were first powdered
separately to pass through a 200-mesh sieve. These were then mixed together in the desired proportions to yield clinkers with MgO contents of 7.5%, 10% and 15%. Any deficiency of a particular ingredient was made up by external addition. The mix was decarbonated at 1000°C, passed through 100-mesh sieve and pelletised into 1x1-in. cylindrical pellets as described earlier. These pellets were stacked on a platinum sheet and burnt at 1450°C for 2 hours in a GLOBAR furnace, having muffle size 9" x 8" x 6" high. After burning, the pellets were air cooled. A batch of 400 g of clinker was prepared in one run.

The chemical analysis of the Indian high-magnesian limestones and clay used for producing cement clinkers are given in Table 5 below.

TABLE 5

| Chemical Analyses of Indian High-magnesian Limestones and Clay Used for Producing Cement Clinkers with 7.5, 10 and 15 per cent MgO |
|---|---|---|---|---|---|
| Material | Chemical Analysis, per cent (on ignited basis) | CaO | SiO₂ | Al₂O₃ | Fe₂O₃ | MgO | K₂O+Na₂O |
| Limestone I | 78.10 | 1.65 | 1.77 | Al₂O₃ | 18.74 | - |
| Limestone II | 82.20 | 2.69 | 1.38 | Fe₂O₃ | 13.73 | - |
| Clay | 1.53 | 67.91 | 18.41 | 7.90 | 1.23 | 3.02 |
(B) Testing of Cement Clinkers

(a) Determination of Free CaO

The free CaO in the clinker was determined by Lerch and Bogue method as recommended by Bogue (1) and Lea (2) and specified in the ASTM Designation : C 114-63 (3). A brief description of the method is given below.

(i) Preparation of Absolute Alcohol-Glycerol Neutral Solution

A solution of absolute alcohol (99.95 % pure), 5 parts and glycerol (99.55 % pure) 1 part by volume was prepared. To each litre of this solution was added 2 ml of an indicator prepared by dissolving 1 g of phenolphthalein in 100 ml of absolute alcohol. The solution was made alkaline by adding a few drops of a dilute alcoholic solution of KOH. It was neutralised by adding alcoholic solution of ammonium acetate as indicated by the disappearance of the pink colour.

(ii) Preparation of Alcoholic Ammonium Acetate Standard Solution

An alcoholic solution of ammonium acetate was prepared by dissolving 16 g of AnalyR grade crystalline ammonium acetate in 1 litre of absolute alcohol. It was
standardised by titrating against CaO freshly prepared by igniting CaCO₃ (99.9 % pure) in a platinum crucible at 1000°C to a constant weight. 0.1 g of this CaO was taken in a 250 ml Erlenmeyer flask containing 60 ml of the neutralised alcohol glycerol solution and 10 drops of the phenolphthalein indicator. The mixture was shaken and heated at the same time to boiling under an air reflux condenser inserted in the neck of the flask for about 20 minutes. The flask was detached from the condenser and the solution titrated immediately, while near boiling, with the ammonium acetate solution. The condenser was replaced and the boiling continued for another 20 minutes. The titration and boiling were repeated at successive 20 minutes intervals until no further colour appeared in the solution during continuous boiling for 1 hour.

The value of the solution was calculated in terms of CaO equivalent to each ml of ammonium acetate solution by dividing the weight of the CaO used by the volume of the solution required.

(iii) Determination of Free CaO in Clinkers

The clinker to be tested was powdered to pass a 300-mesh sieve. 1 g sample was weighed into the
Erlenmeyer flask containing 60 ml of the neutralised alcohol-glycerol solution and 10 drops of phenolphthalein indicator. The same procedure as used in standardising ammonium acetate solution was repeated. The free CaO content of the clinker was calculated from the known CaO value of the ammonium acetate solution as follows:

\[
\% \text{ Free CaO} = 100 \frac{v \times s}{w}
\]

where

- \( v \) = ml standard ammonium acetate solution required
- \( s \) = CaO value of standard solution in g CaO per ml
- \( w \) = weight of the sample taken.

(b) Determination of Uncombined MgO

(i) Chemical Method

In this method, the determination of uncombined MgO in clinkers was made by following the procedures recommended by Taylor and Bogue (4) and Lea (5).

0.5 g clinker freshly ground to pass a 300-mesh sieve was taken in a 250 ml Erlenmeyer flask to which 50 ml of absolute alcohol, 10 ml of glycerol and 4 g of AnalaR grade ammonium nitrate were added. The
mixture was stirred and boiled at the same time under an air reflux condenser inserted in the neck of the flask, until ammonia ceased to be expelled. The absence of ammonia was detected by holding a piece of moist red litmus paper to the mouth of the flask. When the paper no longer turned blue, the solution of MgO was considered to be complete. The solution was separated from the solid residue by filtering through Whatman No. 40 filter paper. The residue was washed upon the paper 3 times with hot absolute alcohol. The alcohol in the solution was evaporated off, about 100 ml of distilled water added, and the solution heated to boiling. It was made alkaline with NH₄OH. Silica gel formed at this stage was filtered out. The calcium in the filtrate was precipitated as calcium oxalate by adding warm ammonium oxalate solution (50 g per litre) and NH₄OH (1:1). The precipitate of calcium oxalate was separated, dissolved in hot HCl (1:4) and then reprecipitated from the solution by adding ammonium oxalate solution and NH₄OH. This was done to free any magnesium salts which may have been occluded. The precipitate was filtered out and washed several times with ammonium oxalate solution (1 g per litre). The combined filtrate was acidified with HCl and concentrated to about 250 ml. To this
solution 20 ml of \((\text{NH}_4)_2\text{HPO}_4\) (250 g per litre) was added. The solution was cooled. After cooling, \(\text{NH}_4\text{OH}\) was added, drop by drop, while stirring constantly, until the crystalline magnesium ammonium phosphate began to form, and then in moderate excess (about 10% of the volume of the solution). The stirring was continued for several minutes and then the solution was set aside overnight before filtering. The precipitate was dissolved in hot HCl (1:4) and the volume made to about 100 ml. From this solution, magnesium ammonium phosphate was reprecipitated by adding 1 ml of \((\text{NH}_4)_2\text{HPO}_4\) (250 g per litre), and then \(\text{NH}_4\text{OH}\) was described earlier. The precipitate was filtered out, washed several times with \(\text{NH}_4\text{NO}_3\) wash solution (100 g of \(\text{NH}_4\text{NO}_3\) dissolved in distilled water, 200 ml of \(\text{NH}_4\text{OH}\) added and diluted to 1 litre), and ignited in a platinum crucible at 1100°C to constant weight.

The percentage of uncombined MgO was calculated as follows:

\[
\% \text{ Uncombined MgO} = \frac{W \times 72.4}{100}
\]

where,

- \(W\) = grams of \(\text{Mg}_2\text{P}_2\text{O}_7\), and
- 72.4 = molecular ratio of 2MgO to \(\text{Mg}_2\text{P}_2\text{O}_7\) (0.362) divided by weight of sample used (0.5 g) and multiplied by 100.
(ii) X-ray Diffractometric Method

This method was developed during the course of the present investigation and is based on the determination of uncombined MgO in high-magnesia cement clinkers by X-ray diffractometry using corundum (α-Al₂O₃) as an external standard. The details of the method are as follows:

A Phillips high angle X-ray diffractometer (pw 1010) with ancillary recording instruments was used. Nickel filtered CuKα radiation was used throughout and for quantitative work a goniometer speed of 1/8° 2θ per minute was chosen. The diffractograms were recorded employing a chart speed of 53 mm per degree 2θ. Other instrumental variables such as slit sizes, rate meter setting and time constant were selected to provide the optimum resolution and intensity and these were kept unchanged throughout the series.

The strongest X-ray diffraction maximum from MgO, due to the 200 reflection occurs at d = 2.106 Å and corresponding to a 2θ value of 42.9° for CuKα radiation, was chosen for the quantitative analysis and the external standard method, the suitability of which for examining cements has been discussed by Smolczyk (6),
was preferred to the more commonly used internal standard method. Corundum (α-Al₂O₃) was selected as the external standard since one of its strong diffraction maxima lies close to the 200 reflection of MgO, thus reducing the uncertainty in the relative values of the integrated intensities used in the analysis.

A standard calibration graph was prepared relating the integrated intensity of the MgO peak and the percentage of 'free' MgO in cements. To serve as a suitable matrix, a synthetic clinker having no MgO in its composition was prepared from reagent grade CaCO₃ (99.9 % pure), crushed quartz (SiO₂ 99.95 %), Al₂O₃ (99.58 %) and 'Specpure' Fe₂O₃. The oxide composition of the clinker was CaO 66.473 %, SiO₂ 24.102 %, Al₂O₃ 4.824 % and Fe₂O₃ 4.601 %, to give a computed phase analysis (7) of 3CaO·SiO₂·(C₃S) 48.5 %, 2CaO·SiO₂·(C₂S) 32.5 %, 3CaO·Al₂O₃·(C₃A) 5 %, 4CaO·Al₂O₃·Fe₂O₃·(C₄AF) 14.0 per cent. The clinker was ground in an agate mortar to pass a 300-mesh B.S. sieve. 'Specpure' MgO was freshly ignited at 1000°C to constant weight, lightly ground in an agate mortar and mixed with the clinker powder to provide samples containing 1 to 15 per cent by weight of uncombined MgO. These powder mixtures were further ground to less than
approximately 5 \mu m in a small vibratory hammer mill using pyrex glass rods and isopropyl alcohol as the grinding medium. After grinding, the slurry was dried at 50^\circ C, passed through a 300-mesh sieve and examined under a microscope provided with a graticule eye-piece. If the particle size distribution was reasonably uniform with the majority of particles measuring less than 5 \mu m, the sample was thought to be suitable for quantitative X-ray diffractometry. It is well known (8) that unless the powder is ground to this level of fineness, X-ray intensities are not very reproducible.

The loose powder was packed densely into an aluminium sample holder by pressing a glass slide over the powder. The flatness of the sample was examined with a microscope. A standard sample of corundum was prepared in a similar fashion. The region of the diffraction spectrum recorded corresponded to 42 to 44^\circ 2\theta for both the sample and the standard. In the case of experimental samples with varying amounts of 'free' MgO, each sample was run six times, starting with a loose powder each time. This gave some idea of the variation in the packing of the sample. The instrumental variations were monitored by running the standard specimen of \( \alpha-Al_2O_3 \) before and
after each run of the experimental sample. The areas under the diffraction maxima due to MgO were measured for different specimens of the same sample with a planimeter and the average taken.

Similarly, the areas under the corundum peaks were measured and the average taken. The average values of integrated X-ray intensities due to the known quantities of MgO relative to the corresponding values due to $\alpha$-Al$_2$O$_3$ provided sufficient data for the calibration.

The diffractograms of clinker samples having unknown quantities of uncombined MgO were recorded following the procedure described above. In this case, each sample was run three times and the average intensities relative to the corundum standard were calculated. Using these values, the amounts of 'free' MgO in the clinkers were read off from the calibration plot.

(c) Identification of Phases by X-ray Powder Diffraction

Phases present in the cement clinkers, raw materials and the additives were identified by X-ray powder diffraction. For the X-ray photographs, a focussing camera of the Guinier-Nonius type, having a diameter of 114 mm and Ni-filtered CuK$\alpha$ radiation were
used. Typical exposure time varied from 1½ to 2 hours. The powder photographs were compared with similar photographs obtained with "standard" specimens of substances expected in these samples. When such a standard specimen was not available or could not be prepared in the pure form, X-ray data published by Taylor (9) and those appearing in the ASTM powder data file (10) were used. The procedures followed for identifying an unknown substance were similar to those described by Klug and Alexander (11).

(d) Quantitative Determination of Phases by Microscopy

Quantitative determination of the phases present in the cement clinkers was carried out by microscopic point counting on clinker specimens as described by Midgley and Dharmadhikari (12). The polished section was made by placing small pieces of freshly crushed clinker at the bottom of a small plastic sample tube of about 1-in. diameter. This was filled to a height of about 1/2-in. with a mounting plastic prepared by mixing Araldite (MY 753), 10 parts, and Araldite Hardener (HY 992) 1 part by volume. The Araldite and Araldite Hardener are the proprietary products of CIBA Ltd., and were obtained from CIBA (A.R.L.) Ltd., Cambridge, England.
After evacuation for about 1 hour, the specimen was placed at 55°C overnight, when the mounting plastic was thoroughly hardened. The plastic tube was then broken away and the section was ground first with medium sized carborundum powder and water on a rotating lap and then by hand with a finer grade of carborundum powder and water on a glass plate. It was polished by using diamond paste of 6 μ, 1 μ and 1/4 μ particle size in succession on a canvas covered rotating disc. After polishing the sections were thoroughly washed with absolute alcohol, and then exposed to HF vapours, which etched C₃S yellow, C₂S blue, while leaving the interstitial comprising of C₃A and a ferrite phase belonging to the C₂F-C₂A solid solution series, unaffected.

For point counting an automatic stage designed by James Swift & Sons Ltd., England was used on a reflecting microscope (Reichert). The instrument consists of a servo operated traversing carriage which is attached to the stage of the microscope and is coupled to an electrical recording or counting unit under the control of the observer. The traverse of the specimen carriage is not continuous but is broken into a series of equally spaced steps. These are triggered electrically
in the horizontal direction by switches in the counting unit and by hand in the vertical direction. Thus any preparation can be sampled by a symmetrical grid of points. The instrument used had a horizontal interval of 1/3 mm and a vertical interval of 1 mm. The series of push buttons in the counting unit were labelled to conform to the constituents C₂S, C₃S and interstitial. As the constituent appeared under the cross wires of the microscope, it was identified and the appropriate push button on the counting unit was depressed, automatically moving the specimen on one space, for further identification of the next constituent under the cross wire.

About 1000 – 1200 counts were made on each section excluding the plastic used for impregnation. The vertical steps were adjusted so that the whole area was covered while using different sides of the clinker section. The counting method gives the percentages by volume. These were converted to weight per cent by multiplying by the densities of the phases identified and recalculating as a percentage. The densities used were C₃S = 3.13, C₂S = 3.28 and interstitial = 3.40 g per cc (12).
(a) Preparation of Cements

The clinker samples were first crushed in a percussion mortar to pass 100-mesh sieve. 4 per cent gypsum (AnalaR grade CaSO₄·2H₂O and passing 100-mesh sieve) by weight was then added and the material ground in a small steel ball mill of 50 g capacity, to a fineness in terms of specific surface of about 3500 sq.cm. per g. Ordinary Portland cements, commercially produced have been generally found to be of this fineness (13).

(b) Determination of Fineness

The fineness in terms of specific surface of cement samples was determined by the Air Permeability Method using Lea and Nurse apparatus as specified in BS : 12-1958 (14) and IS : 269-1958 (15). A brief description of the method is given below.

The ground cement sample was taken and its density was determined in the usual manner by displacement of kerosene oil in a density bottle. At this density, the weight of the cement which when compacted in the permeability cell would give a porosity of 0.475 was selected from the data provided in the standards (14,15). The required weight of the cement was then
accurately weighed out and compacted into the permeability cell. After placing the permeability cell in its position in the apparatus, the air was turned on. The rate of air flow was adjusted until the flowmeter showed a steady difference in level of about 50 cm. The difference in level \(h_1\) of the manometer and the difference in level \(h_2\) of the flowmeter was noted. These observations were repeated to ensure that steady conditions have been obtained as shown by a constant value of \(h_1/h_2\). The specific surface was calculated from the following formula:

\[
\text{Specific surface, sq.cm per g} = \frac{K}{d} \cdot \frac{1}{h_1/h_2}
\]

where,

- \(K\) = a constant = 10830 for the apparatus used, and
- \(d\) = density of the cement.

(c) Determination of Compressive Strength

Compressive strengths of cement samples were determined by the method developed by Parker (16) and currently used at the Building Research Station, England, for testing the strengths of experimental cements. The description of the method is as follows:
1/2-in. cubes were cast using mortar prepared by mixing cement, 1 part, sand 3 parts by weight and distilled water corresponding to water/cement ratio 0.52, on a clean and dry glass plate with a small steel spatula. The mortar was filled into the brass mould in 3 stages: (i) about 1/3 of the mould was filled and the mortar tamped down 25 times using 1/4-in. square brass rod, (ii) up to 3/4 of the mould was filled and the mortar tamped down 25 times, and (iii) the mould was filled up to the top and the mortar was tamped down 6 times with a 1/2-in. square brass rod. The top surface was then smoothed by drawing the flatside of the spatula (with the leading edge slightly raised) across the surface. The specimens so cast were stored in moist air \( (17^\circ \pm 1^\circ C \text{ and above } 90\% \text{ relative humidity}) \) for 24 hours. The cubes were then removed from the moulds, taking care to avoid damage to edges etc., and subsequently stored in distilled water at \( 17^\circ \pm 1^\circ C \) until required for test. The tests were done within 20 minutes of the exact test age required. The compressive load was transmitted through a ball setting, special care being taken to obtain accurate centring, and was applied at the rate of 300 lb. per minute. Six cubes were tested at a test age and the compressive strength was calculated
by dividing the crushing load with the actual surface area over which the load was applied.

The results obtained by this method were recently correlated by Welch and Gutt (17) for several commercial Portland cements with those obtained using 2.78-in. cubes as recommended in the standards (14,15). The following correlation was established:

\[
\text{Strength (2.78-in. cube)} = 2.2 \times \text{strength (1/2-in. cube)} + 1200 \text{ lb. per sq.in.}
\]

(d) Determination of Tensile Stress

For determining tensile stress, cylindrical specimens, 1/2-in. in diameter, 1-in. in length, of neat cement or cement + fly ash and distilled water were cast. The amount of water was chosen to give a consistency corresponding to that obtained in an ordinary Portland cement with water at standard consistency determined by Vicat apparatus. After keeping in moist air (17°C ± 1°C and above 90% r.h.) for 24 hours, the specimens were removed from the moulds and autoclaved at 295 ± 10 p.s.i. for 3 hours and then cooled to ambient temperature by following the procedure described under test for "determination of soundness". The dimensions were measured and the specimens were placed with its axis
horizontal between the platens of a testing machine and loaded. The load was applied at the rate of 300 lb. per minute until failure, by splitting along the vertical diameter took place. The final load was recorded and the tensile stress was calculated by the following relationship (18):

\[
\text{Tensile stress, p.s.i.} = \frac{2P}{\pi L D}
\]

where,

- \(P\) = Compressive load on the cylinder, lbs.
- \(L\) = Length of the cylinder, inches
- \(D\) = Diameter of the cylinder, inches.

(e) Determination of Soundness

An autoclave test for determining soundness or volume stability of the experimental cements, using 1/2-in. cube in place of specimens measuring 1x1x1\frac{1}{2} inches with a 10-in. effective gauge length recommended by ASTM (19) and Indian (15) Standard Specifications on Portland Cement, was developed and used in these investigations. The need for such a test method arose from the fact that the experimental cements were produced in small quantities, whereas, about 500 g of cement was needed to cast only one specimen of the size 1x1x1\frac{1}{2} inches. The details of the method are as follows:
1/2-in. cubes of neat cement mortar, prepared by mixing cement and distilled water on a clean and dry glass plate, were cast using brass mould. 5 g cement was required for 1 cube. The amount of water was chosen to give a consistency corresponding to that obtained in an ordinary Portland cement with water at standard consistency determined by the Vicat apparatus by following the standard procedure (14,15). It was found that about 26 per cent water by weight of cement was sufficient for most of the cement samples. The brass moulds were filled by following the procedure described earlier under test for determining compressive strength. After keeping in moist air (17° ± 1°C and above 90% relative humidity) for 24 hours, the cubes were removed from the moulds and their dimensions measured along two directions with a precision micrometer capable of reading differences up to 0.0001 inch. These were autoclaved at 295 ± 10 p.s.i. for 3 hours according to the standard procedure (15,19). After autoclaving the cubes were put in hot water (above 90°C) and cooled slowly to ambient temperature. Their dimensions were measured along the two directions. The differences between the dimensions of the cube along the two directions before and after autoclaving was calculated
and the average taken. The autoclave expansion was calculated as follows:

\[
\text{Autoclave Expansion, per cent} = \frac{B}{A} \times 100
\]

where,

\[A = \text{average of the dimensions of the cube along two directions before autoclaving}\]

\[B = \text{average of the expansion of the cube along two directions after autoclaving.}\]

The reproducibility of the results was checked by measuring the autoclave expansion of 50 cubes cast from the same cement on different days. For comparative purposes 12 standard specimens 1\times1\times11\frac{1}{2} inches with a 10-in. effective gage length were made using the same cement and their autoclave expansions were determined by a length comparator as per standards specifications \((15,19)\).

(f) Determination of Setting Time

The initial and final setting times of the samples of cements containing fly ash were determined using Vicat apparatus as per standard method \((14,15)\). A brief description of the method is given below.
The Vicat mould was filled with cement paste prepared by gauging cement with 0.85 times the water required to give a paste of standard consistency. The temperature of the distilled water and that of the test room was \(27^\circ \pm 2^\circ\) C, as per Indian Standards Specification (15).

The initial time was recorded as the period elapsing between the time when water was added to the cement and the time at which the needle (0.039-in. square) failed to pierce the test block by about 5 mm. The cement was considered finally set when, upon applying a needle (fitted with a metal attachment hollowed out so as to leave a circular cutting edge 0.20-in. in diameter, the end of the needle projecting 0.02-in. beyond this edge) gently to the surface of the test block, the needle made an impression thereon, while the attachment failed to do so.

(g) Determination of the Effect of Gypsum Content on Compressive Strength

For determining the effect of gypsum content on the compressive strength of high-magnesia cement containing fly ash, various amounts of ground gypsum
(AnalaR grade CaSO₄·2H₂O) were mixed intimately in cements prepared by grinding clinkers having 7.5%, 10% and 15% MgO and which contained 20%, 30% and 35% fly ash by weight respectively. The gypsum was ground separately in 3 lots to specific surface equal to that of each of the cements, in order to ensure that the specific surfaces of the cement samples with different amounts of gypsum remained the same. The compressive strength was determined using 1/2-in. cubes by following the procedure described in an earlier section C,(c).

(h) Determination of Free Mg(OH)₂ by Differential Thermal Analysis

To determine free Mg(OH)₂ in autoclaved samples of high-magnesia cements stabilised with fly ash by Differential Thermal Analysis (DTA), a standard calibration plot was prepared first. For this purpose, mechanical mixes having free Mg(OH)₂ contents varying 5.0 to 15.0 per cent by weight, were prepared using Mg(OH)₂ freshly prepared by autoclaving 'specpure' MgO at 295 ± 10 p.s.i. for 3 hours and drying under vacuum, and a sample of synthetically prepared ordinary Portland cement without MgO and containing 30 per cent fly ash by
weight and autoclaved at 295 ± 10 p.s.i. for 3 hours, dried under vacuum and powdered to pass a 100-mesh sieve. DTA of these mixes were carried out by raising the temperature of the furnace at a uniform rate of 10°C per minute. The specimen block was similar to that used by Grimshaw, et al (20). The differential thermocouple made of chromel and alumel was connected to a sensitive galvanometer. The areas under Mg(OH)$_2$ endothermic peaks were measured and plotted against Mg(OH)$_2$ content to get a standard calibration plot. At each level of Mg(OH)$_2$, DTA was done 3 times, using exactly the same weight of fresh sample each time.

DTA of samples of high-magnesia cements containing the required amounts of fly ash and freshly autoclaved at 295 ± 10 p.s.i. for 3 hours, were carried out following the same procedure. The areas under Mg(OH)$_2$ thermal peaks were measured. The contents of free Mg(OH)$_2$ against these areas were read off from the standard calibration plot.

(i) Characterisation of Phases in Set Cements

The phases present in set high-magnesia cements with and without fly ash, obtained on curing
under distilled water at 17° ± 1°C for different periods, as well as autoclaving at 295 ± 10 p.s.i. for 3 hours, were characterised mainly by powder X-ray diffraction. The procedures for identifying the phases were similar to those described in an earlier Section A, (c).

(D) Mechanism of Stabilisation

In order to understand the mechanism by which pozzolanic materials such as fly ash stabilise high-magnesia cements, at least in the autoclave conditions, some fundamental studies were made.

(a) Substitution of MgO in Hydrothermally Synthesized Tobermorite at 215°C

In the first series of experiments, mixes of CaO and SiO₂ with CaO/SiO₂ molar ratios ranging from 0.1 to 1.5 were accurately weighed out using CaO freshly prepared by decarbonating CaCO₃ (99.9 % pure) at 1000°C to a constant weight and crushed quartz, SiO₂ (99.95 % pure); both passing 300-mesh sieve. After thorough mixing, freshly boiled distilled water was added to make their pastes, which were then autoclaved
at 295 \( \pm 10 \) p.s.i. corresponding to a temperature of 215.7° \( \pm 1.7 \)°C, for 3 hours. The autoclaved material was crushed, dried with ether and x-rayed using Guinier-Ni-filtered Cu Ka radiation as described earlier in Section B.(c).

In the second series of experiments the CaO requirements were met by using pure CaS synthesized in the laboratory. In the CaO-SiO\(_2\) mixes having CaO/SiO\(_2\) molar ratio 5/6, various molar substitution of CaO and SiO\(_2\) with MgO, Al\(_2\)O\(_3\) and Fe\(_2\)O\(_3\) were made. The pastes of these mixes were made with freshly boiled distilled water and autoclaved at 295 \( \pm 10 \) p.s.i. for 3 hours. The autoclaved material was crushed, dried with ether and x-rayed as described above.

In another experiment, well crystallised tobermorite was synthesized by keeping a paste of CaO-SiO\(_2\) mix having CaO/SiO\(_2\) molar ratio 5:6, at 175°C for 19 hours as per method used by Sidney Diamond, et al (21). The X-ray diffraction pattern so obtained served as a standard for 11 A tobermorite.

(b) Hydrothermal Synthesis in MgO-SiO\(_2\)-H\(_2\)O System

Mixes of MgO and SiO\(_2\) with MgO/SiO\(_2\) molar ratios varying from 0.25 to 1.5 were accurately weighed
out using MgO freshly prepared by decarbonating MgCO₃ (99.9% pure) at 1300°C and crushed quartz, SiO₂ (99.95% pure). After thorough mixing, freshly boiled distilled water was added to make their pastes, which were then autoclaved at 295 ± 10 p.s.i. for 3 hours. The autoclaved material was crushed, dried with ether and x-rayed as described above.

(c) Mechanical Strength of Autoclaved Fly Ash - High Magnesia Cement and Portland Cement

Both compressive strength and tensile stresses of a high-magnesia cement containing varying proportions of fly ash, autoclaved at 295 ± 10 p.s.i. for 3 hours, were measured. The high-magnesia cement was prepared by grinding clinker containing 10 per cent MgO with 4 per cent gypsum by weight. The procedures for these determinations have already been described in Section C,(c & d). These experiments were repeated with a sample of ordinary Portland cement.
REFERENCES


