

CEMENT & LIME MANUFACTURE

VOL. XXXVIII. No. 1

JANUARY, 1965

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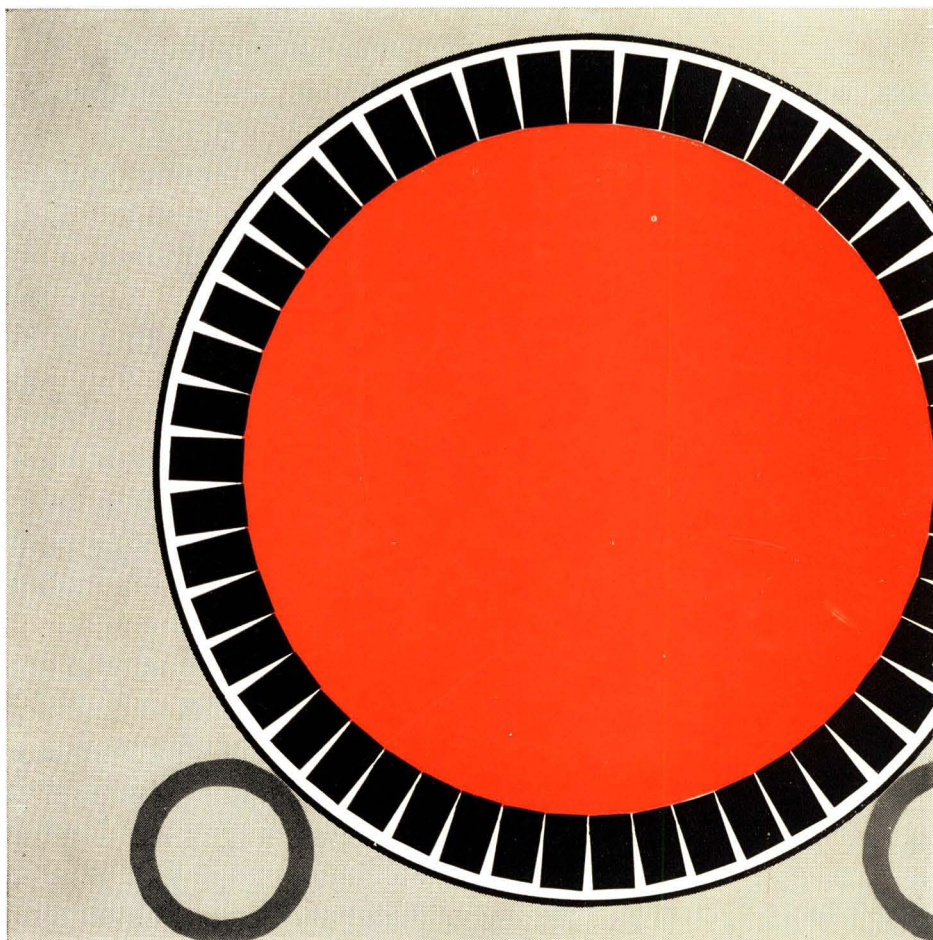
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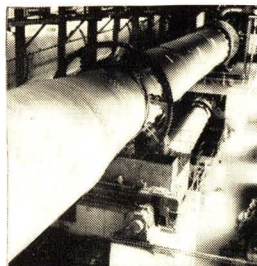
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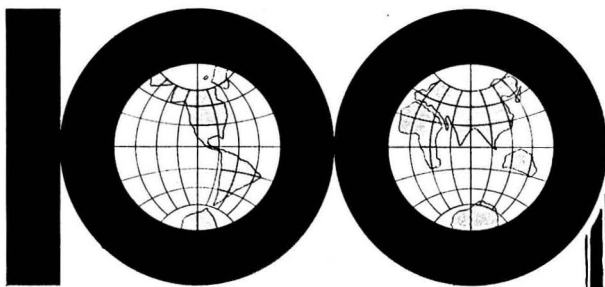
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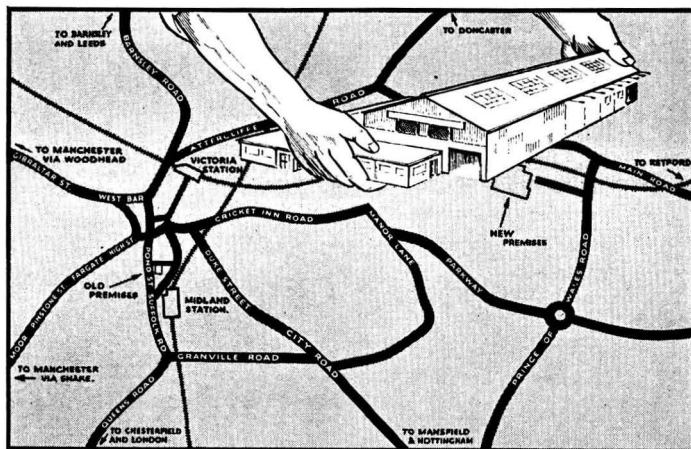
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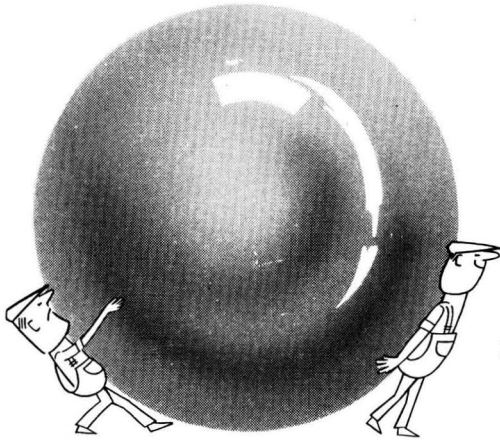
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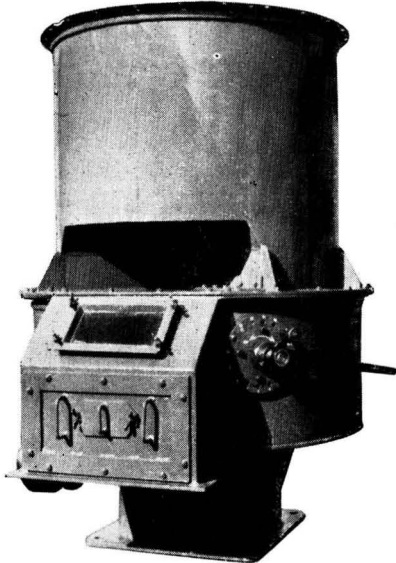
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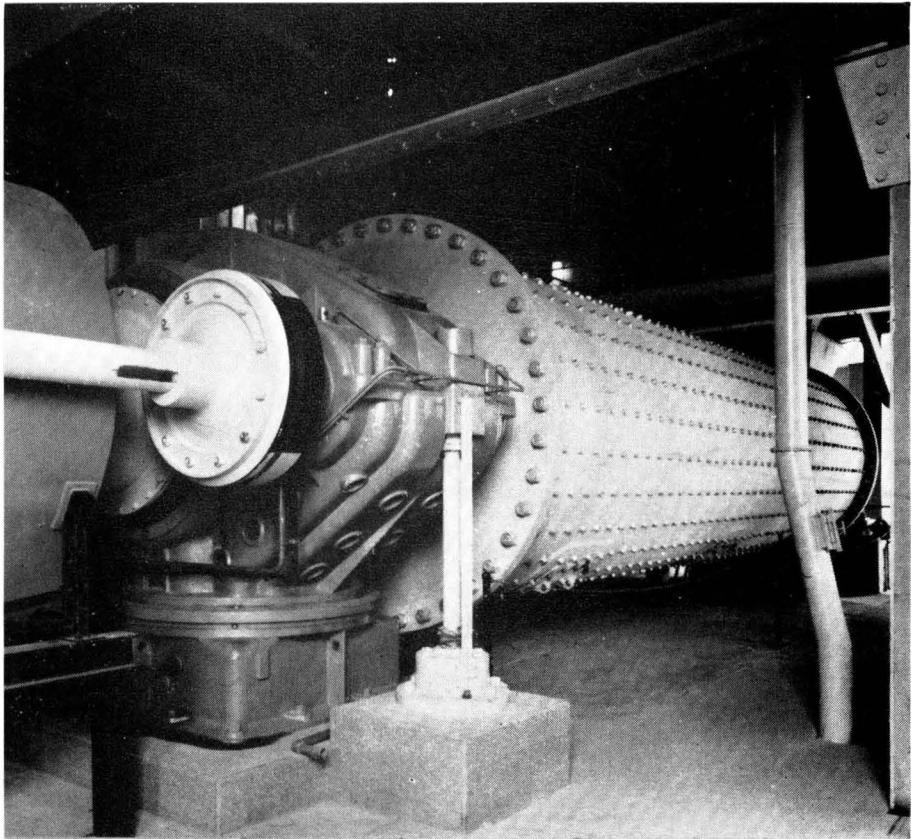
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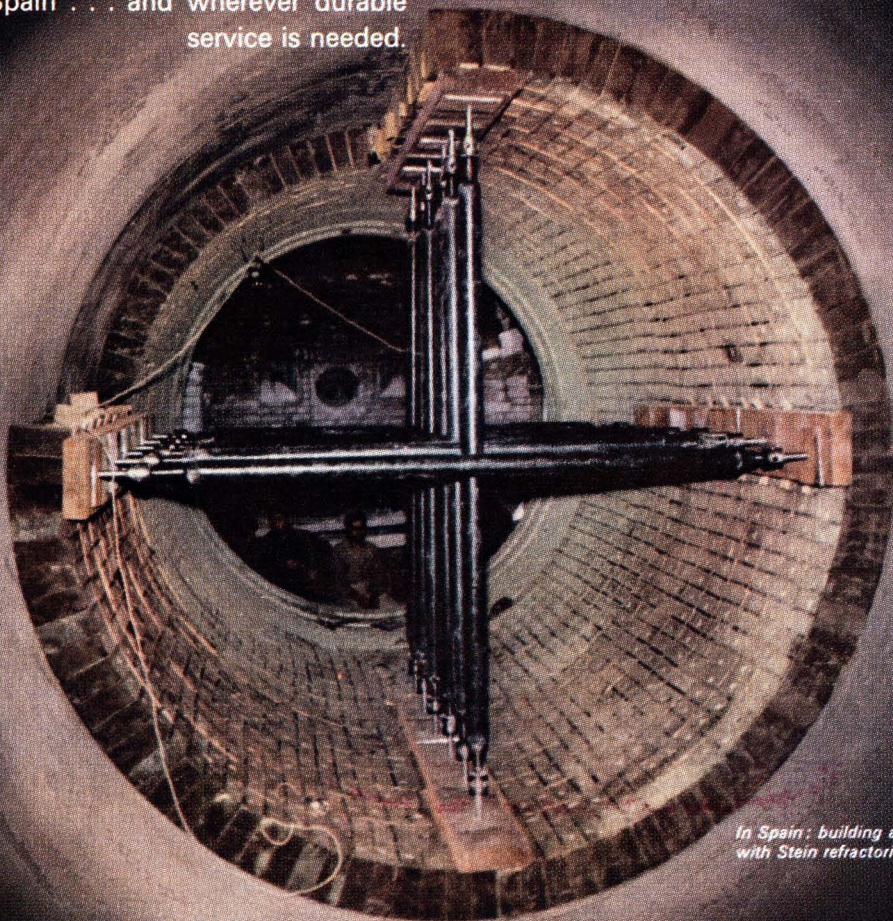
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PUBLISHED BY
CONCRETE PUBLICATIONS LIMITED
60 BUCKINGHAM GATE, LONDON, S.W.1
TELEPHONE: VICTORIA 0705/6
TELEGRAPHIC ADDRESS: CONCRETIUS, PARL, LONDON

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VOLUME XXXVIII. NUMBER 1.

JANUARY, 1965

A New Cement Works in Australia.

THE commissioning recently of the Waurm Ponds works of the Victoria Portland Cement Co., Pty., Ltd., a subsidiary of The Associated Portland Cement Manufacturers Ltd., marked the end of four years intensive investigation and construction. The works (*Fig. 1*) is situated seven miles from the industrial seaport of Geelong and forty miles from Melbourne. It is alongside the main-line railway from Geelong to Warrnambool and therefore there is good access by rail and road to both cities. The works, which cost £A4,000,000, is capable of producing 300,000



Fig. 1.—General View of Quarry and Works at Waurm Ponds.

tons of cement annually. Because of the characteristics of the raw materials and for economy of fuel, the Humboldt system of manufacture is employed.

Raw Materials.

The basic raw materials are located adjacent to the works, but sand and brown coal are brought by road from the Anglesea area some fourteen miles away. The limestone reserves occur beneath deposits of clay and marl. During the operation of stripping (*Fig. 2*) sufficient of the marl is left behind to provide a working face approximating to the kiln-feed in composition. The effective thickness of the stratum of usable material is 35 ft., entailing the removal of 45 ft. of overburden. Stripping is carried out by twin-power scrapers. Back-filling of the worked-out deposit is being practised to preserve the appearance of the countryside. Quarrying of the raw materials is by face-shovel and scrapers, a method of winning which eliminates variations in moisture content and chemical composition that could occur if scrapers only are used. Selective quarrying of material of high, low and medium grade is practised to facilitate feeding to the raw-mill of material approximating to the composition required in the feed to the kiln.

Raw materials are transported to the crusher, which is installed at the quarry, by 25-cu. yd. motorised dumpers. The crusher, which is a 7260 Pennsylvania Dixie hammermill operated by a 950-h.p. motor, has a maximum capacity of 700 tons per hour of product of minus $1\frac{1}{2}$ in. in size. The crusher product is carried on a belt conveyor to the raw materials storage silos (*Fig. 2*). All controls relating to the crushing operations and the filling of the silos are in the crusher control room and are operated by one man from a graphic panel.



Fig. 2.—The Quarry: Stripping in Progress.

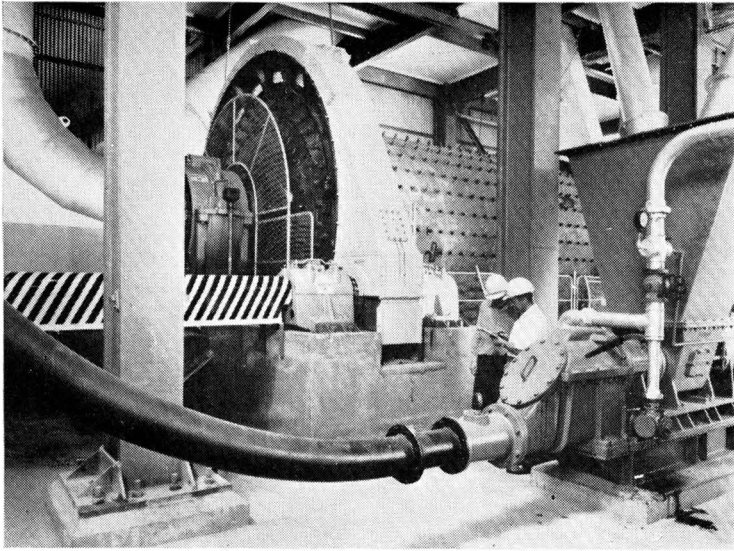


Fig. 3.—Raw Materials Mill and Pump.

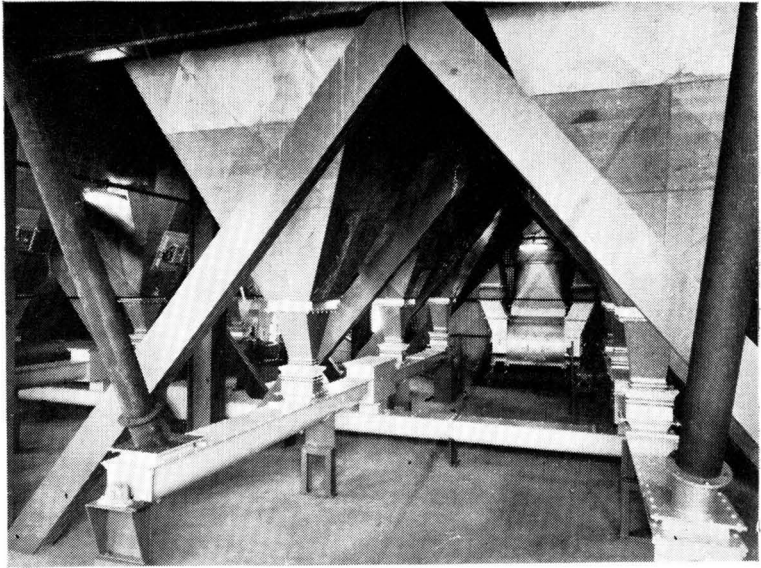
Storage for 6,000 tons of raw material is provided in three reinforced concrete silos which are 70 ft. high and 40 ft. in diameter. A separate silo, 45 ft. high and 28 ft. in diameter, is used for the storage of sand, and has a separate hopper and conveyor-belt for filling from road vehicles. Extraction from all the silos is by variable-speed belt-weighers with electronic integrating equipment to control the ratios between the various materials being drawn off from the silos. The weighers are directly controlled from the laboratory and the operator can see at a glance if there is any change in feeding conditions.

The gas-swept raw-material drying and grinding mill (*Fig. 3*) is of Humboldt design and is 11 ft. in diameter and 19 ft. long. It is a single-chamber mill driven by a 1,410-h.p. motor and has a capacity of 70 tons of dry material per hour. The drying of raw materials is achieved by utilising the exhaust gases from the first-stage preheater cyclone with an auxiliary oil-burner that is used for raw material containing moisture in excess of 8 per cent. The wet-gas exhaust to the atmosphere is by twin cyclones and electrostatic precipitators (*Fig. 4*), also of Humboldt design. Final blending is carried out by the Fuller quadrantal continuous-blending system. The kiln feed is stored in two reinforced concrete silos with a storage capacity of 3,600 tons. The raw meal is transported by means of Air-Slides and Fuller-Kinyon pumps (*Fig. 3*) throughout.

Preheater, Kiln and Cooler.

The preheater (*Fig. 5*) is of the ordinary Humboldt type. Raw meal is fed to it by a Schenk weigh-feeder and Fuller-Kinyon pump.

**Fig. 4.
Hoppers
and
Conveyors
in connection
with
Electrostatic
Precipitators.**



**Fig. 5.
The Preheater**

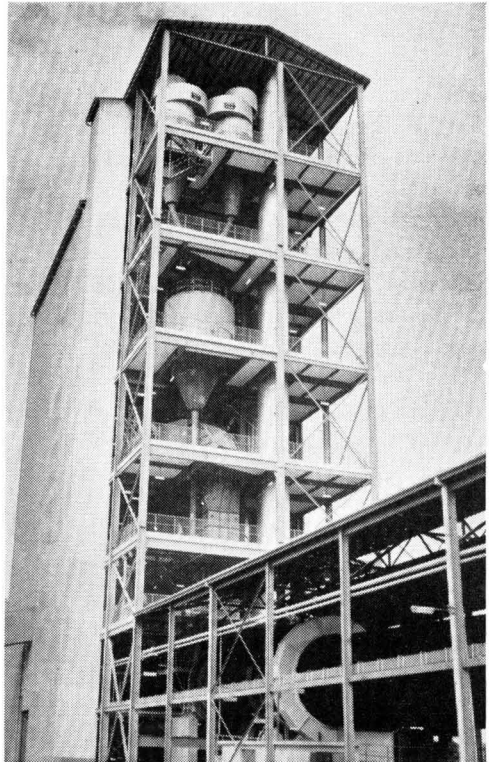




Fig. 6.—The Kiln House.

The kiln (*Figs. 6 and 7*) is also of Humboldt design and is 13 ft. in diameter and 189 ft. long. It is supported at a slope of $3\frac{1}{2}$ degrees on three tyres and has a range of speed from 0.3 to 1.3 r.p.m. It is driven by a 95-h.p. motor; there is an auxiliary diesel engine as a standby. Firing is at present with heavy fuel oil supplied from a refinery in the Geelong area. The installation of a plant for drying and

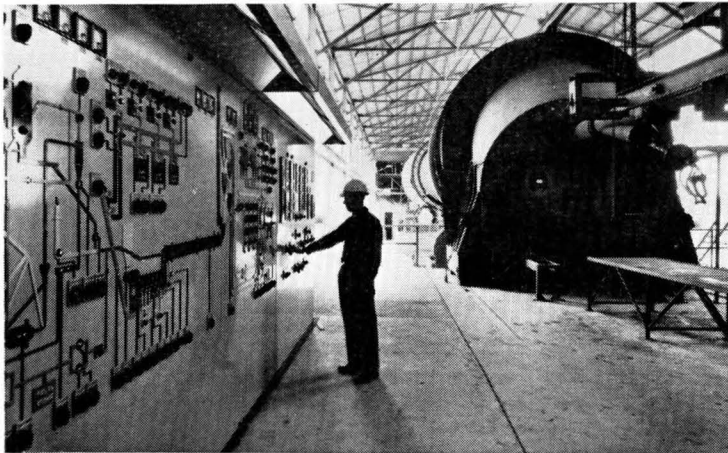


Fig. 7.—Front End of Kiln and Graphic Control Panel.



Fig. 8.—Interior & Cooler.

grinding of brown coal is to be undertaken in the near future and will permit the use of coal and oil, either separately or together.

The clinker is cooled in a No. 850 Fuller cooler (*Fig. 8*) and then conveyed by drag-chain and bucket-elevator to the clinker storage silos which have a capacity of 6,600 tons.

All controls for the kiln, cooler and fuel plant are located at the firing end of the kiln (*Fig. 7*) and are operated from the graphic control panel (*Fig. 7*).

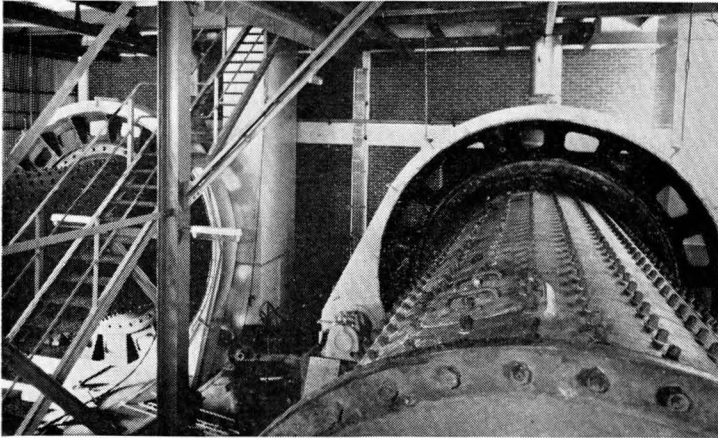


Fig. 9.—The Cement Mills.

Grinding.

Clinker and gypsum are withdrawn from the clinker storage silos using electronically controlled vibrators and are discharged onto a belt-conveyor. These controls can be interlocked as desired.

There are two air-swept cement mills (*Fig. 9*), each of which produce 25 tons per hour of a product with a specific surface of 3,400 sq. cm. per gramme. The mills, which are 10 ft. 6 in. in diameter and 28 ft. long, are driven through girth gears and trunnions and gearboxes by 1,575-h.p. synchronous motors. Closed-circuit grinding using air separation ensures a cool and consistent product. The exhaust air is cleaned by bag filters.

The finished cement is conveyed from the mills by an inclined belt-conveyor and distributed to one or other of the storage silos by Air-Slides.

Packing.

Packing and dispatch facilities are provided for delivery in bulk or in bags by road and rail. Bagging is carried out by a Haver & Boecker four-spout machine having a capacity of 60 tons per hour. Bulk cement can be loaded at the rate of 120 tons per hour.

An interesting feature of this work is a lighted reinforced concrete service tunnel about 10 ft. square extending the full length of the works and from which other tunnels connect to the main electrical control and distribution points. This arrangement avoids to a great extent the necessity to provide cable trenches and overhead mains and telephone lines. Other structures at the works include the usual workshops, stores, offices and laboratory.

Electricity is supplied by the State Electricity Commission of Victoria at a voltage of 22 kv. and is transformed to 6.6 kv. for the larger motors and to 415 v. for the other motors.

The works, the cement made at which is "High Mark" brand, was designed by Klockner-Humboldt-Deutz of West Germany and Australasian Civil Engineering Pty., Ltd., these firms being the principal contractors. The works were officially opened in April last.

Conference of the Silicate Industry

THE eighth Conference of the Silicate Industry is to be held in Budapest from June 7 to 12, 1965. The subjects to be discussed include the structure of hydrated cement, transportation and homogenisation in the cement industry, modern kilns, refractories, and several other topics of indirect interest to the cement industry. The official languages of the Conference are Hungarian, English, French, Russian and German. Particulars of the Conference are obtainable from SILICONF, House of Engineering, Budapest, V. Szabadsag ter 17, Hungary.

New Foreign Publications.

“Die oxydischen Kristallphasen der anorganischen Industrieprodukte.” By Felix Trojer. (Stuttgart: E. Schweizerbart'sche Verlagsbuchhandlung. 1963. Price 94 D.M.)

THIS book, in the German language, deals only with crystal phases of an oxide nature, free from water and OH, as they occur in materials such as refractories, clay-ware, ceramic ware, ore sinter, slag and cement clinker, that is, especially in products which have either been subjected to a temperature of red heat or more, or which are intended to be used at such a temperature. Intentionally, the author does not deal with the minerals of raw materials since much literature is available in this field. In a special section of this book, some natural crystal phases are included, but the reason for this is that they also may be developed in artificial products. Natural minerals, which so far have not yet been found in artificial products but which might occur, are likewise included in the special section.

The description of crystal phases is, so far as data are available, subdivided into chemical composition, crystal structure, powder diagram (d -values in Å), physical properties, optics, etching properties, structure, crystal associations and occurrence. Good illustrations are included since such are particularly necessary in this relatively new field of microscopy of technical products; many of the micro-photographs of crystal phases are from the author's experience as a microscopist. Other subjects dealt with include the preparation of samples, the diagnosis of crystals and the origin of crystals and crystal groups, the forms of crystallisation and changes in the crystal phases. The book is a mine of information which so far was only to be found dispersed in the vast literature on the subject and as such should be of interest to works, laboratories and research bodies associated with the cement industry.

“Fabrication et Utilisation des Liants Hydrauliques.” By M. Papadakis and M. Venuat. (Obtainable from M. Venaut, 23 Rue de Croustadt, Paris XV^e. Price 65 francs.)

THIS book of 340 pages is addressed to manufacturers of cement and similar materials. Modern methods of making cement are reviewed in sufficient detail to be of value to all those interested in the processes. In the second part of the book, the properties and uses of cement and similar materials are dealt with. The text is developed from a course of lectures given by the authors at the Ecole Spéciale du Bâtiment et des Travaux Publics.

“Handbuch für das Zement Labor.” By Kurt Seidel. (Wiesbaden; Bau Verlag, 1964, 54DM.)

THIS manual for cement laboratories comprises some 400 pages of data and information required for all the physical and chemical tests normally made at a cement works. Laboratory equipment for such tests of cement, the raw materials, concrete and ancillary products and the testing procedures are dealt with in great detail. A chapter on concrete gives consideration to dealing with complaints of defective material. Although the book is mainly in the German language, much of the data would be understandable by most technicians.

The Rheology of Cement Grout.

By A. G. B. RITCHIE, B.Sc., Ph.D. A.R.C.S.T., A.M.I.C.E., A.M.I.Strut.E.*

In this report, the rheology of cement paste is discussed and the term fluidity is expressed in terms of viscosity. The report describes an investigation into the viscosity of cement pastes and shows how this property can be used to express fluidity in fundamental units.

In the design of suitable cement-water mixtures for grouting, one of the main considerations is the fluidity of the cement paste. Fluidity has been defined as the ability of a mix to flow in constricted passages. The stiffness of the cement paste is taken as the inverse of its fluidity. Unfortunately there is no recognised test, as yet, for this property. As a result it is only defined by personal judgment, which of course varies with the individual. This unsatisfactory position combined with an apparent lack of basic study regarding this important flow property prompted the author to conduct the investigation detailed in this report. From a consideration of the flow problem the author concluded that the fluidity characteristic under consideration is typified by the property of the viscosity of the mix.

The Basic Concept of Fluidity (Viscosity).

The Newtonian model of flow is shown in *Fig. 1*. It comprises two parallel plates A and B an exact distance apart, the intervening space being filled with the substance under test. Viscosity is defined by the force P which is required to induce a unit rate of shear in the substance. Suppose that the plates A and B are 1 cm. square and the substance in between is 1 cm. in depth. If a tangential force P of 1 dyne is required to move plate A with a constant speed of 1 cm. per second, then the viscosity of this substance is said to be 1 poise. When plate A is moved to the right, the layer next to the stationary plate B remains without moving, being held by adhesion. The layers above it travel, depending upon the distance from plate A, with an increasing speed to the right. Each single layer of the substance therefore passes the one below it and remains a little behind the one above it. Because the layers adhere to each other a force is encountered which opposes this movement sideways. This tenacity is called the viscosity U or internal friction of a system which, per unit area, is the same on each layer. The resistance of a substance to motion is therefore proportional to its viscosity. Therefore the force required to cause motion is given by

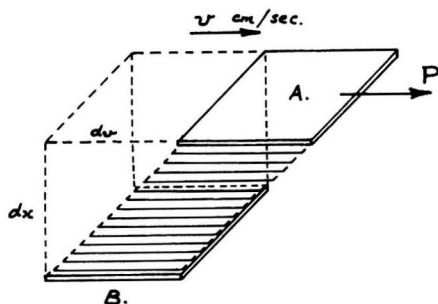


Fig. 1.—Newtonian Model of Flow.

*The University of Strathclyde, Glasgow.

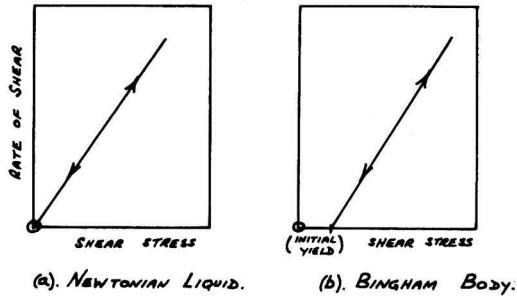
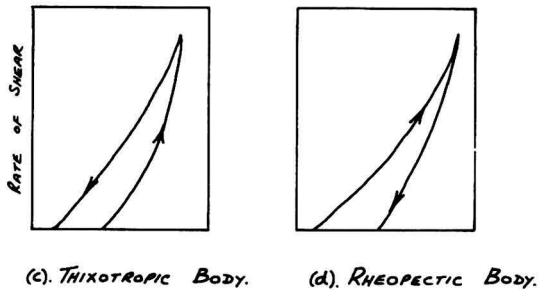


Fig. 2.—Typical Rheograms.



$$P = UA \left(\frac{dv}{dx} \right) \text{ or } U = \frac{P/A}{\frac{dv}{dx}} = \frac{\bar{\tau}}{\dot{\gamma}}$$

that is $\text{viscosity} = \frac{\text{shearing stress (dynes per sq. cm.)}}{\text{rate of shear (sec}^{-1}\text{)}}$
(poise)

The units of viscosity are therefore dynes per sq. cm. per sec⁻¹.

A true, or Newtonian, liquid is one in which the rate of shear is directly proportional to the tangential stress applied to it. For any such stress, however small, there will be a corresponding rate of shear. The flow property of such a liquid is expressed by a single constant, the coefficient of viscosity (poise). A typical rheogram for a Newtonian liquid is shown in *Fig. 2a*.

Plastic (Bingham) substances do not show any flow under normal conditions and act as if they were solid. A characteristic of these substances is that they always need a minimum shearing force in order to start the flow. Once the flow-point or yield value is reached these substances act the same way as Newtonian liquids (*Fig. 2b*). A Bingham body therefore cannot be defined by a single measurement of viscosity. A number of measurements must be made at various rates of shear. The equation for the flow curve of a plastic Bingham body is

$$(\bar{\tau} - f) = U\dot{\gamma}$$

where f is the yield stress.

Three types of rheological behaviour are found in Bingham bodies as follows.

(i) *Thixotropic*.—A paste exhibiting this characteristic will show a marked increase in shearing strength when left undisturbed. This will be lost at once if the paste is agitated but will be regained again if allowed to stand. Thixotropic flow can be recognised when periodic tests at identical ascending and descending angular velocities do not coincide. Such a substance does not immediately recover its original rigidity but rather requires time. It is typical for thixotropic substances to form curves or so-called hysteresis loops because of their time dependence (*Fig. 2c*). The descending branch of the flow curve is to the left of the up-curve.

(ii) *Reversible*.—This condition is obtained when the flow curve for increasing and decreasing angular velocities coincides exactly (*Fig. 2b*).

(iii) *Rheoplectic or antithixotropic*.—This behaviour is the reverse of thixotropic flow. The substance shows an increase in viscosity with a constant shearing force. The descending branch of the flow curve is to the right of the up-curve (*Fig. 2d*). Hence, to determine the flow category of cement paste a rheogram of shearing stress versus rate of strain must be obtained.

Previous Research.

There has been very little previous research into the viscosity of cement paste, particularly with reference to its relationship to fluidity. Lobanov (1950)¹ (translated summary by Mason²) made use of a rotational viscometer to obtain flow properties for lime and cement pastes and mortars. He discovered that above a certain rate of revolution, characteristic of each system, the curve of shear rate against shear stress became approximately linear. The flow characteristics were recorded in terms of yield value and plastic viscosity based on this straight-line plot. He then related these two properties to the pressures required to pump various pastes and mortars through a pipeline.

The Building Research Section of the Department of Scientific and Industrial Research³ carried out a research programme (1954-1957) to find a relation between the physico-chemical properties of lime pastes and their observed flow properties. By comparing laboratory results with the craftsman's judgment of a particular mix it was hoped to express subjective criteria such as workability in terms of measurable properties that had more physical significance than those defined by the ad-hoc tests then in use. A special form of rotational viscometer was developed based on the Couette type in which the paste was subjected to shear in the annular space between two concentric cylinders. Static yield values were measured very accurately by running mercury at equal rates into two vessels suspended from threads hung over pulleys and wound round a drum attached to the spindle of the inner cylinder. Unfortunately there appears to have been no corresponding measurement of viscosity. The research reports terminated in 1957 with the following brief comment. "Measurements of yield values of quicklime putty and dry hydrated lime at various concentrations, using a concentric cylinder viscometer, have so far failed to disclose any clear relationship between yield value and spread of the paste on the British Standard flow table."

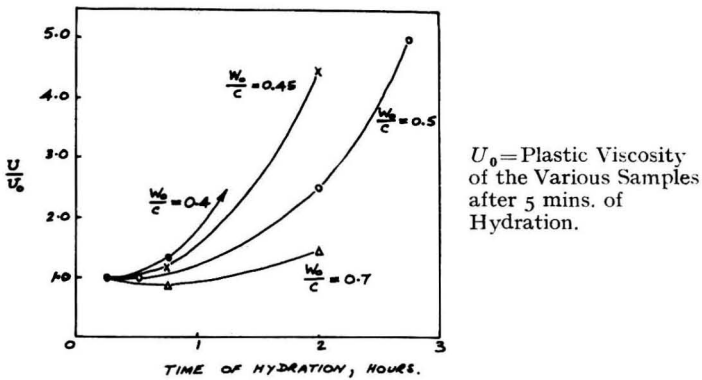


Fig. 3.—Plotting of Plastic Viscosity against Time Hydration for various Water-cement Ratios.

A considerable amount of specialised research has been carried out more recently by Shalom and Greenberg⁴ (1960) on the flow behaviour of fresh cement pastes. The main interest here was to try to correlate the flow properties with the physicochemical nature of the pastes. Rheological measurements were performed with a coaxial cylinder viscometer. Flow curves of r.p.m.-torque were determined as a function of such variables as chemical composition, mixing conditions and temperature of hydration. The section of their work which was most relevant to the present investigation dealt with the effect of time of hydration on yield value and plastic viscosity. Figs. 3 and 4 show summary plots of both these values for various water-cement ratios at increasing periods of hydration. These normalised plots illustrate the gradual increase in the viscosity characteristics with time. It is interesting to note, however, that during the period

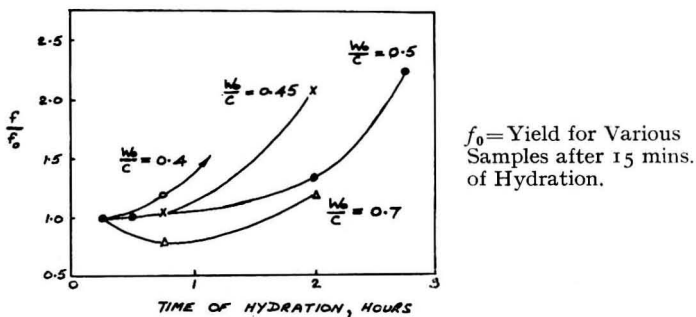


Fig. 4.—Plotting of Yield against Time of Hydration for Various Water-cement Ratios.

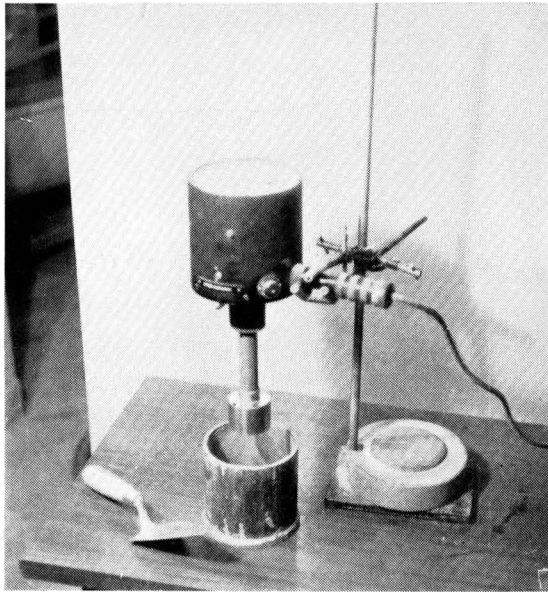


Fig. 5.—Apparatus for Viscosity Test.

between 15 minutes (the time of the first reading) and 30 minutes from the start of the test there was little or no increase in the viscosity characteristics. After 45 minutes the percentage increase in viscosity even with the richest mix is still relatively small. It would appear, therefore, that during the normal mixing, pumping and grouting-up period the time element after the first 15 minutes is not significant for viscosity considerations.

The Measurement of Viscosity.

It was decided to use a Ferranti portable viscometer to evaluate the rheological properties of the cement pastes. A general view of the instrument, which is of the Couette coaxial cylinder type, is shown in *Fig. 5*. It consists of a rotating outer cylinder driven by a small motor with a second cylinder located coaxially within it. The inner cylinder is free to rotate against a calibrated spring with a pointer to show the angular deflection. When a test is made the resulting rotation of the sample exerts a viscous drag on the inner cylinder causing a deflection proportional to the viscosity. For the determination of the anomalous behaviour of non-Newtonians such as the cement paste grout under investigation, a range of shear rates are available by means of a three-speed gear box and a set of changeable inner cylinders. The viscometer used for this investigation was a V.H. model and is shown in *Fig. 6* with a complete set of cylinders.

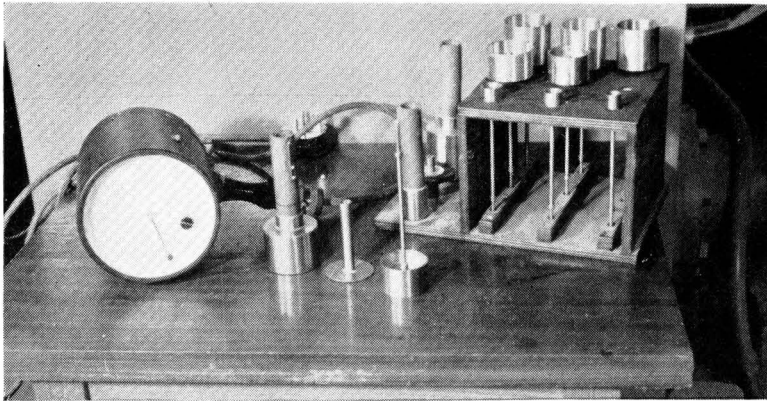


Fig. 6.—Viscometer with Complete Set of Cylinders.

Test Procedure.

A weighed quantity of cement was added gradually with a small amount of stirring to an appropriate amount of water contained in a mild steel jar. The paste was mixed vigorously by hand for two minutes, allowed to stand for one minute at rest and then remixed for two more minutes. The total mixing time was four minutes. It was found necessary to use this interrupted mixing sequence in order to eliminate false set tendencies and hence obtain reproducible results. For convenience the viscometer was mounted on a bench stand as shown in Fig. 5. As soon as mixing was completed the sample was brought up under the viscometer so that the top of the outer cylinder was just covered by the paste. Care was taken to ensure that with the viscometer in this position the bottom of the cylinder was at least half an inch clear of the base of the container. The instrument was then started in gear one, which gave the lowest speed of rotation. The pointer was given time to reach a steady condition (about one minute) and the gauge reading noted. This procedure was repeated in gears two and three. The instrument was then switched off for one minute. At the end of this interval it was restarted and a similar set of readings were taken using decreasing speeds. To obtain intermediate readings the inner cylinder was changed and the experiment was repeated using a freshly prepared sample of the same water-cement ratio. The start of each test was fixed at 5 minutes after the start of mixing. The shearing stress in dynes per sq. cm. at a given rate of shear was obtained by multiplying the instrument dial gauge reading by the appropriate factor. This gave a value in poise which was then multiplied by the shear rate (sec.^{-1}) to give the stress.

Experimental Programme.

The complete range of cement pastes which were used to investigate viscosity characteristics is given in Table I. To determine the effect of time on the flow of the cement pastes measurements were made on selected mixes after a period

TABLE I.—RELATIONSHIP BETWEEN WATER-CEMENT RATIO AND VISCOSITY CHARACTERISTICS OF CEMENT PASTES

$\frac{W}{C}$	Yield Stress (dynes per sq. cm.)	Viscosity (poise)
0.60	2	24
0.55	8	28
0.50	14	38
0.45	20	71
0.40	50	87
0.35	170	74

of 10 minutes and also after 20 minutes from the completion of mixing. In all of these tests fresh samples of cement paste were prepared and covered over with a damp cloth until the time of test was reached.

Analysis of Results.

Fig. 7 shows a typical flow curve or rheogram obtained from viscometer readings taken at increasing and decreasing rates of strain on a cement paste. This paste, of water-cement ratio 0.35, exhibited thixotropic flow with the down curve to the left of the upcurve. With the next two values of water-cement ratio namely 0.4 and 0.45 the flow changed over to rheopectic. After this the higher water-cement ratio pastes were all reversible with the upcurve and downcurve coinciding. Thus the cement paste can be classified generally as a Bingham body but exhibiting various forms of plastic flow. This change in the type of flow was also observed

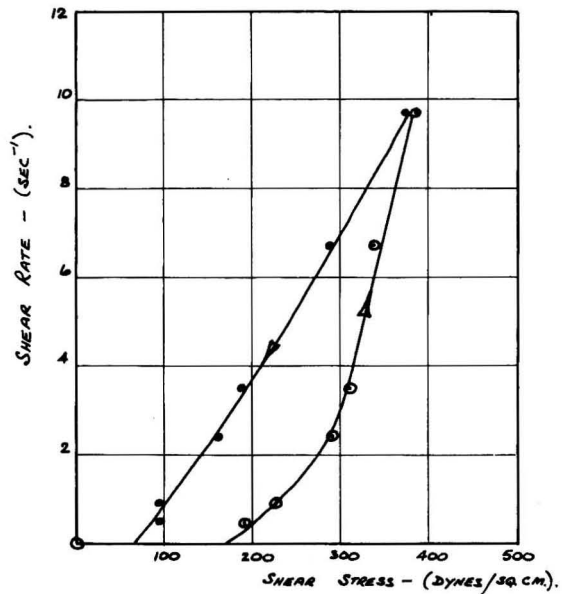


Fig. 7.—Flow Curve for Cement Paste (Water-cement Ratio = 0.35)

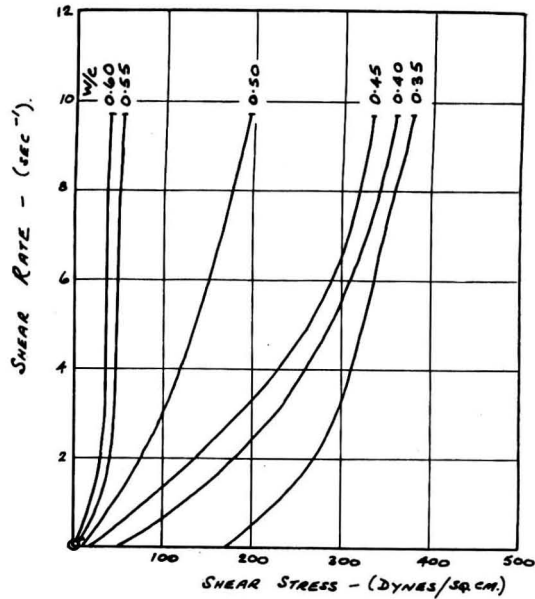


Fig. 8.—Summary of Increasing Portion of Flow Curves for Various Cement Pastes.

in the work of Shalom and Greenberg⁴. They measured the area of the hysteresis loops formed as one of the rheological parameters of the pastes. This measurement was then used to indicate the extent of the breakdown in the thixotropic structure. The areas were measured as + or - depending on the deviation from reversible flow.

A comparison of the plastic flow characteristics of the various pastes can be obtained by a summary plot of the upcurve portions of all the flow curves.

This is shown in Fig. 8 and Table I gives details of the corresponding values obtained for yield stress and plastic viscosity. The viscosity was taken as the slope of the tangent to the flow curve at zero rate of shear. As the water content of the pastes was reduced the samples became visibly stiffer and harder to mix. This relative stiffness was recorded by a gradual increase in the initial yield stress value and also the tangent viscosity at zero rate of shear. An illustration of the effect of time on the flow characteristics is given in Fig. 9. This indicates an increase in the initial yield value and a change from reversible to antithixotropic flow. The relative shape of the upcurve remains the same so that the viscosity measurement is virtually unaltered.

Discussion.

The variation in the type of flow behaviour from reversible to the various degrees of thixotropic or rheopectic flow without any apparent pattern complicates the interpretation of the results. It is difficult to decide which portion of the flow curve should be used for defining and comparing the viscosity characteristics. The author has taken the values obtained from the initial values of the upcurve

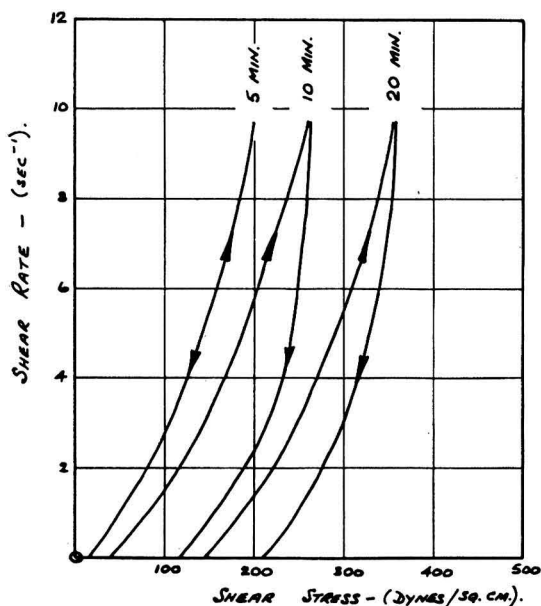


Fig. 9.—Flow Curves for Cement Paste (Water-cement Ratio = 0.5) at increasing Times of Hydration.

since this represents the sample in its original condition before too much re-moulding has taken place. Shalom and Greenberg preferred to use the straight portion of the downcurve while Lobanov used the straight curve he obtained above certain rates of shear. The Building Research Station dispensed with viscosity measurement altogether and used only the initial yield stress values. It is obvious therefore that the interpretation of viscosity measurements at present varies with the investigator. However this divergence of opinion is understandable and does not deter from the value of the rheological investigation. Any of the above methods of analysis gives a definite basis for comparing the different pastes and expressing their fluidity in absolute terms.

It is hoped that this investigation and subsequent analysis will lead to a clearer understanding of the flow of cement pastes and that the viscosity test described will assist in the expression of the properties of colloidal cement grouts in fundamental physical units.

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Hydration of Calcium Aluminoferrite.

A study of the action of water on the calcium aluminoferrites, a solid solution series normally present in Portland cement, has been completed recently at the U.S.A. National Bureau of Standards in the Building Research Division of the Institute for Applied Technology, U.S.A. Department of Commerce. Results of the study show that varying the temperature and the amount of water changes the reaction of calcium aluminoferrites with water.

The chemical reactions involved in the hydration and hardening of cements are studied to obtain information essential, not only for the proper formulation and use of cements, but also for preventing their deterioration. The reaction of water on three of the four major constituents of cement, namely, tricalcium aluminate, tricalcium silicate, and dicalcium silicate, has been studied extensively. Calcium aluminoferrite is recognised as the fourth major constituent and it is frequently assumed that its formula is $4\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{Fe}_2\text{O}_3$. However, the formula is known to represent one member of a solid-solution series in which the ratio of Al_2O_3 varies widely in either direction. The study supplies some data on the hydration of calcium aluminoferrites for various ratios of Al_2O_3 to Fe_2O_3 as the temperature and the amount of water are varied.

Six preparations of calcium aluminoferrite, with a range of compositions of Al_2O_3 and Fe_2O_3 wider than the range normally found in Portland cement, were synthesised, ground, and analysed. The amount of Al_2O_3 varied from 8 to 2 parts, and of Fe_2O_3 from 4 to 10 parts, while CaO remained constant at 24 parts.

The powdered calcium aluminoferrites were treated with water, at certain controlled temperatures, under three experimental conditions: continuous leaching with a stream of water; stirring powder into a relatively large amount of water; and hydration in "paste" form with a small amount of water, simulating actual use of cement. The products of hydration were studied by X-ray diffraction for identification of the phases. X-ray diffraction was also used to determine possible differences in the positions of the lines on the patterns, indicative of solid solution.

The results show that, when the quantity of water is large in relation to the amount of calcium aluminoferrite, the latter decomposes slowly, and the calcium and aluminium oxides go into solution, leaving a residue consisting essentially of ferric oxide. A minute amount of ferric oxide also goes into solution. If the quantity of water is decreased sufficiently, the concentration of the solution will increase to a point at which calcium aluminate hydrate will be precipitated. The precipitate will be $2\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 8\text{H}_2\text{O}$ if it is formed at room temperatures, but at 70 deg. C. it will be $3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 6\text{H}_2\text{O}$ with a small fraction of the Al_2O_3 being replaced by Fe_2O_3 . The rate of dissolution reaction increases with increases in the temperature and in the ratio of Al_2O_3 to Fe_2O_3 in the aluminoferrite.

Hydration of the aluminoferrites in paste form progresses in a different manner. The hydration products depend on the temperature and on the ratio of Al_2O_3 to Fe_2O_3 . At low temperatures, $2\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 8\text{H}_2\text{O}$ is formed from the composition highest in alumina, and a related compound, $4\text{CaO}\cdot(\text{Al}_2\text{O}_3\cdot\text{Fe}_2\text{O}_3)\cdot n\text{H}_2\text{O}$, is formed

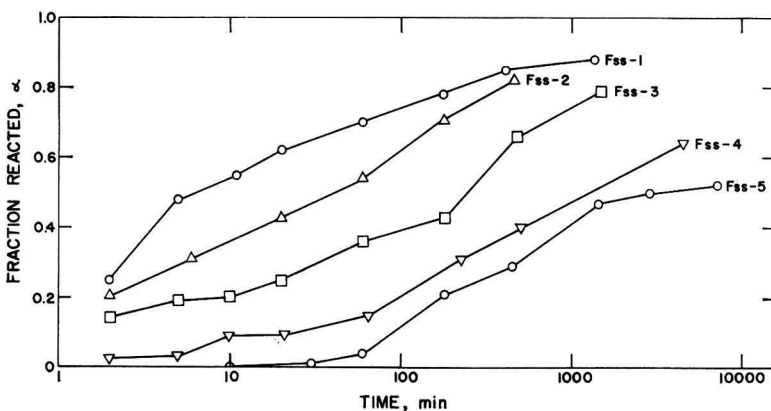


Fig. 1.

from those highest in iron oxide. Both of these hydrates crystallize in the form of hexagonal plates. The intermediate members of the series produce a hydrogarnet of the composition $3\text{CaO} \cdot (\text{Al}_2\text{O}_3, \text{Fe}_2\text{O}_3) \cdot 6\text{H}_2\text{O}$. The ratio of Al_2O_3 to Fe_2O_3 is always higher in the hydrogarnet than in the anhydrous aluminoferrite, as some of the Fe_2O_3 remains uncombined after hydration.

The diagram in Fig. 1 shows the progress of the reaction between calcium aluminoferrite preparations and water as a function of stirring time, when 1g. of each preparation was treated with 1 litre of water at 25 deg. C. In the study of hydration of calcium aluminoferrites, the ratios of CaO to Al_2O_3 to Fe_2O_3 in calcium aluminoferrite solid solution series Fss-1 to Fss-5 were respectively: 24-8-4, 24-7-5, 24-6-6, 24-5-7, and 24-4-8.

The Cement Industry in 1963.

STATISTICS relating to the cement industry throughout the world in 1963 are given in "The Cement Industry, 1963," an annual report published in November 1964 by the Organisation for Economic Co-operation and Development. This document also gives the trends for 1964.

Production of cement in 1963 in the O.E.C.D. countries (excluding Japan) amounted to 185,200,000 metric tons, an increase of 9,200,000 tons compared with 1962. The U.S.A. was the largest producer and produced 33½ per cent. of this total, or 16.6 per cent. of the total world production. The United Kingdom produced 14,330,000 metric tons which was 3.8 per cent. of the world total.

The growth of the industry was slightly slower in European O.E.C.D. countries in 1963 than in 1962, and production in Western European countries expanded less rapidly than overall industrial production, thus reversing the trend of the past few years.

The labour force in the cement industry increased slightly in 1963. Slightly less new productive capacity was installed than in 1962. Prices were relatively stable except in France and Switzerland.

British-made High-alumina Cement

THE physical and chemical characteristics of high-alumina cement are given in a recently published "Report on the Use of High-alumina Cement in Structural Engineering". (Published by the Institution of Structural Engineers, 11 Upper Belgrave St., London, S.W.1.; price 15s.). The following notes are abstracted by permission of the Institution.

The method of manufacture of high-alumina cement varies from country to country. In Russia, AG-cement consists of a mixture of high-alumina cement and gypsum, but it does not have the normal properties of high-alumina cement. In Germany, high-alumina cement is made in blast-furnaces and has a high sulphur content. In Great Britain, high-alumina cement is made by fusing bauxite and limestone in a reverberatory furnace under controlled conditions. The data and recommendations in the Report refer to high-alumina cement manufactured in Great Britain.

Chemical Composition.

High-alumina cement consists of combinations of lime, alumina, silica, and oxides of iron, together with other minor constituents, in amounts varying between the following limits.

CaC: 36 to 42 per cent.; Al_2O_3 : 38 to 51 per cent.; SiO_2 : 3.5 to 9 per cent.; Fe_2O_3 : 0 to 1.4 per cent.; FeO: 0 to 8 per cent.; MgO: 0.1 to 1.4 per cent.; TiO_2 : 1.5 to 2 per cent.; sulphur as sulphide: 0 to 1 per cent.; SO_3 : up to $\frac{1}{2}$ per cent.; total alkalis: 0.2 to 0.6 per cent.

The higher values for sulphur and SO_3 relate to cement made from blast-furnace slag.

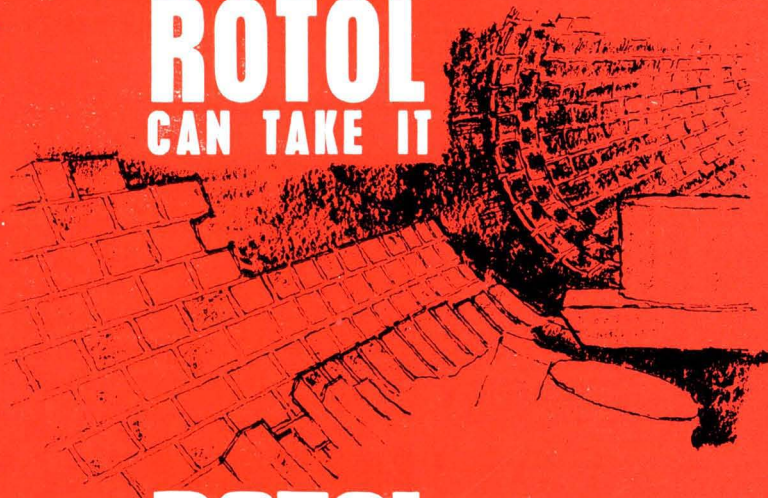
The oxides combine to form various anhydrous calcium-aluminate and silicate mineral compounds. The constitution of high-alumina cement is not as well established as that of Portland cement, but the main constituents are CA, (which is the most important), CA_2 , C_2AS and β - C_2S . Most of the properties of high-alumina cement are reproducible in a synthetic cement made of pure mono-calcium aluminate. Little is yet known of the iron compounds or of a fibrous compound which is generally believed to contain lime, alumina, silica and ferrous iron.

Physical Properties.

High-alumina cement manufactured in Great Britain is dark grey, almost black, in colour, but foreign cements vary in colour from a very light grey to black. Quality bears no relationship to colour, which is a function of the quantity and degree of oxidation of the iron compounds. The specific gravity, which varies between 3.00 and 3.25, is controlled to a large extent by the iron content. The maximum residue on a British Standard No. 170 sieve is between 2 and 6 per cent., and the specific surface, as measured by the British Standard method, varies between 2500 and 4000 sq. cm. per gramme.

There is usually a very slight expansion of high-alumina cement on setting under water, but unsound expansion, such as can occur with Portland cement, is not known.

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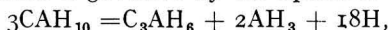
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Hydration.

The action of water on the anhydrous constituents of cement leads to the formation of hydrated compounds and consequent setting and hardening. At ordinary temperatures the most important reaction is the formation of mono-calcium-aluminate hydrate CAH_{10} . If the anhydrous cement has an excess of Al_2O_3 , some alumina gel will be formed, which in time will crystallise as gibbsite (AH_3), whereas if there is an excess of CaO , some C_2AH_8 may be expected. The SiO_2 component combines with the lime to form hydrated calcium silicate, as with Portland cement. Little is known about the reactions of the iron compounds, but they are believed to be relatively unimportant. In the presence of alkalis, which may be derived from the cement, from the aggregate or from external sources, C_2AH_8 will form at the expense of CAH_{10} . It should be noted that, in contrast to Portland cement, calcium hydroxide is not formed at normal temperatures under any circumstances, which is one reason for the resistance of high-alumina cement to attack by sulphate and dilute acid. However, if lime, either in the form of slaked lime or combined as Portland cement, is added to high-alumina cement, C_2AH_8 is rapidly formed, and this results in very quick setting and reduced strength.

The hydrated compounds CAH_{10} and C_2AH_8 crystallise in the hexagonal system and are sometimes referred to collectively as the "hexagonal aluminates". At temperatures in the neighbourhood of 20 deg. C., they are metastable in contact with water and tend to transform gradually into the stable compound C_3AH_6 and either alumina gel or gibbsite, AH_3 . The compound C_3AH_6 crystallises in the cubic system and is known as the "cubic aluminate".

Since the specific gravities of these compounds differ, it is apparent that the conversion reaction, which is governed by the equation:



produces a considerable reduction in the volume of the solid products. Since the overall dimensions of specimens remain essentially constant, the conversion of hexagonal to cubic aluminates must result in a very large increase in porosity.

A Large Rotary Kiln.

THE research institute for cement-making machinery in Togliatti, on the Volga, has prepared for production a design of a large rotary kiln and the first kiln of this type is being built there. At present the largest rotary kilns in the U.S.S.R. are 5 metres in diameter and 185 metres long and produce 75 tons of clinker per hour. The new kiln will be 7 metres in diameter and 230 metres long. Its hourly capacity will be 125 tons of clinker. A works including this kiln would turn out 1,150,000 tons of cement annually.

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