CEMENT
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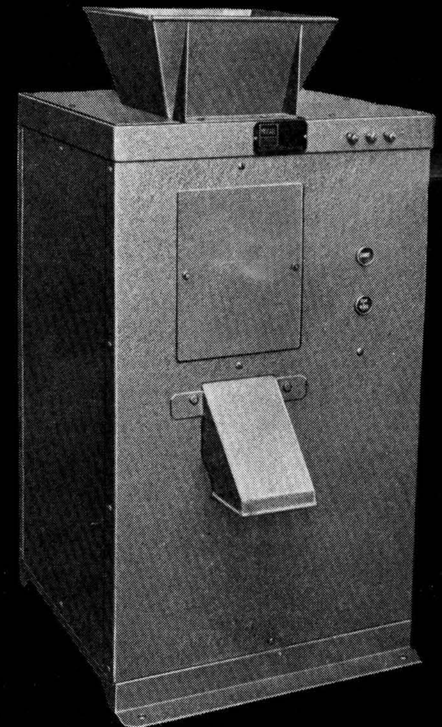

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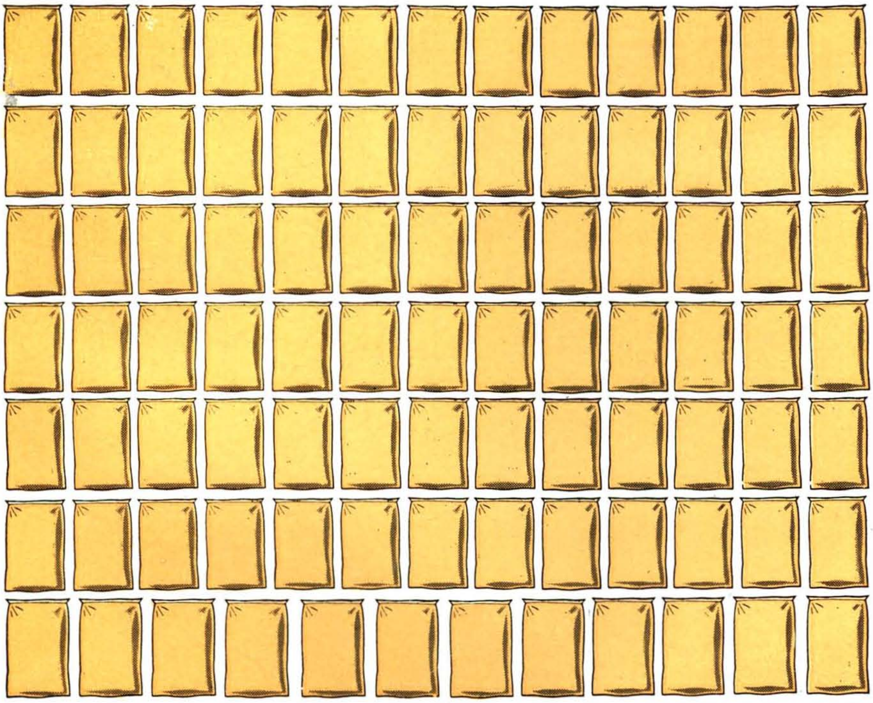

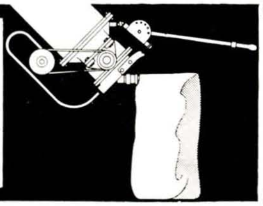

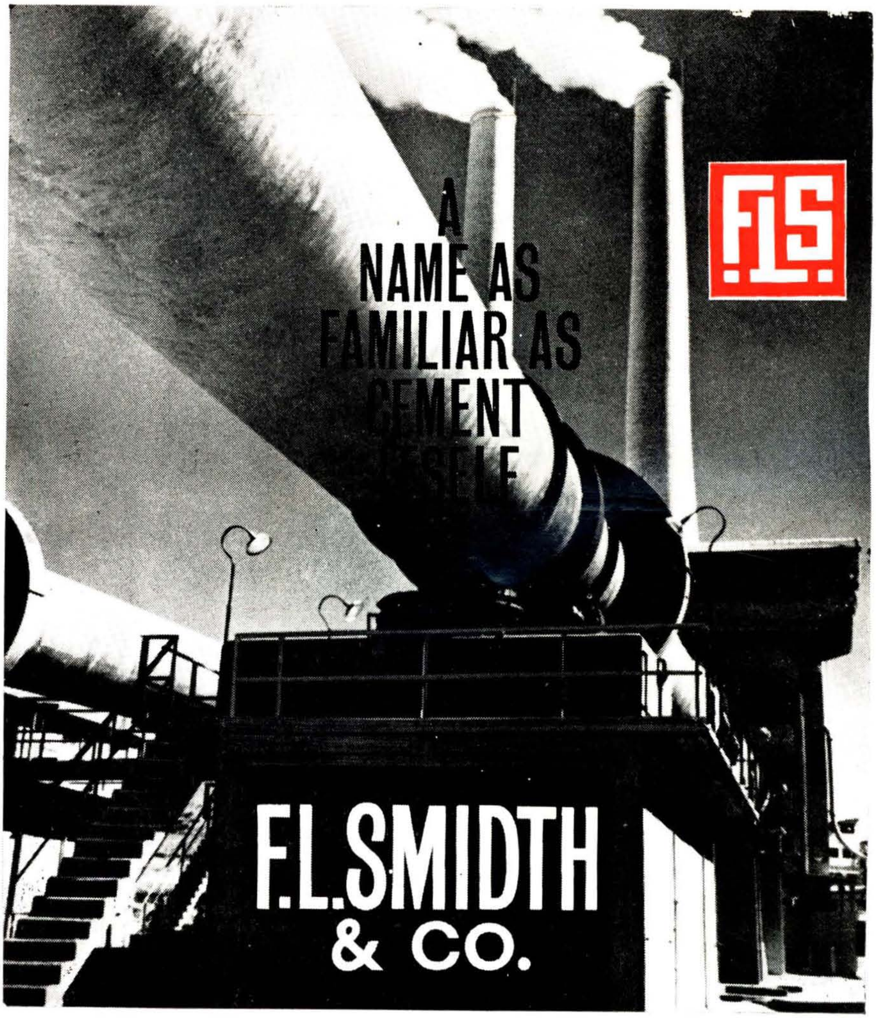
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PUBLISHER'S ANNOUNCEMENT

The publishing assets of Concrete Publications Limited, a wholly-owned subsidiary of The Associated Portland Cement Manufacturers Limited, have been transferred to the Cement & Concrete Association. Concrete Publications Ltd., is to be wound up in due course. This journal, "Cement & Lime Manufacture", and the "Concrete Year Book" and other books and periodicals published by Concrete Publications Ltd., will henceforth be published by the Cement & Concrete Association.

The change of ownership will not affect the reader of, or the advertiser in, this journal. All communications regarding subscriptions or advertisements should be addressed to the Cement & Concrete Association at 52, Grosvenor Gardens, London, S.W.1.

Forty Years of Progress

THE OCCASION of the change of proprietorship of this journal, as announced at the top of this page, prompted perusal of the earliest numbers of this journal, namely, those in the first two volumes, and the following comments, based on such a perusal, have been contributed by MR. K. C. BARRELL, F.I.Mech.E.

THE FIRST number of the predecessor of this journal appeared just forty-one years ago, in September, 1928, as a supplement in "Concrete & Constructional Engineering"* under the sectional heading of "Cement & Cement Manufacture." This supplement subsequently started its career as a separate journal under the same title in January 1929 (Volume 2, No. 1), and later was renamed "Cement & Lime Manufacture" as at present.

The opening leading article in the initial number was entitled "Portland Cement of Today & Tomorrow." In the period from 1928 to 1969, great changes have occurred in the practice in the industry and it is not without interest to take a backward glance at some of the items that were published in what may be called "yesterday".

The descriptions of new cement works included Bevan's at Northfleet, which was reconstructed with three kilns, two 250 ft. (76·2 m.) long and one kiln 294 ft. (89·6 m.) long, thus making it at that time "the largest works in Europe" with an annual output of some 500,000 tons of cement. Today, adjacent to Bevan's works,

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* Now incorporated in "Concrete".

a new Northfleet works is in the course of construction by The Associated Portland Cement Manufacturers Ltd., and this will ultimately comprise six kilns, each 650 ft. (200 m.) long, with an annual productive capacity of 3,600,000 tons.

In these early days, Johnson's works at Greenhithe were extended to incorporate two kilns, each 317 ft. (96·6 m.) long, having a combined annual output of 400,000 tons of cement. Similar activities at Chinnor, Barnstone, Holborough, all in the U.K., were noticed, while overseas the E.N.C.I. cement works at Maastricht, the first works in Holland, and the Japla works in India were described. The latest extension to the E.N.C.I. works was described in a recent number of this journal. In relation to the Indian works, it is of interest to note that the labour force was eight hundred in the works and a thousand in the quarry, for an output of 1,500 tons per week; this is in contrast with the insistent demand in many developing countries today for the most modern labour-saving equipment, although there are vast resources of labour available.

The controversy regarding the merits of the wet and dry processes for hard raw materials looms largely in the pages of the first two volumes, the wet process being definitely favoured, probably because the industry in the U.K. had been nurtured on this process. The conversion of some works from the dry process to the wet is cited as evidence in favour of the wet process. The improved fuel consumption resulting from the filtering of water from the slurry in the wet process is discussed and the view is expressed that "It is conceivable that in the future this may have a substantial effect on the equipment of cement plants." The day for widespread adoption does not appear to have arrived. The process is very sensitive to the physical characteristics of the raw material, both in respect to resistance to filtering and stability of nodules produced after filtering. A successful application, however, for example, in Western Nigeria was described in this journal for November 1963.

Because of technical developments, the one-time trend towards the wet process is now reversed where hard raw materials are concerned. New works in recent years have adopted the semi-dry or suspended-dust processes and conversions have also been made from the wet to the dry process in existing works. The recent extension at the E.N.C.I. works, previously entirely wet process, has adopted the dry process for the new extension in which the kiln is 178 m. (584 ft.) long and has a productive capacity of 3,000 tons per day. Even where the raw material is chalk, the new trend is evident; for example, at the new works at Pitstone, albeit with a low-flint chalk, which was described briefly in the January and November 1968 numbers of this journal, dry comminution is being adopted in combination with a kiln 430 ft. (131 m.) long.

The development of equipment of improved and new types and new materials were duly recorded in these early numbers and include the Fuller-Kinyon pump, high-alumina refractories, electrically-operated excavators and air-elutriation as adopted by The Associated Portland Cement Manufacturers Ltd. to determine the flour content of cement, while the Raymond mill and the "Atritor" are featured as modern pulverisers. The advantages of bulk supply of electricity to cement works and the advantages of electric drives are also dealt with. The largest mill motors mentioned are of 750 h.p. compared with 3,000 h.p., or even 6,000 h.p. today. Many of the older illustrations show motor drives for kilns, coolers and mills with flat belts without, apparently, any guards. White Portland cement manufactured in the U.K. was noted when marketed for the first time.

In these early years, the annual production of cement in the U.K. was almost 7,000,000 tons, whereas today it is about 16,000,000 tons. It is unlikely that the cement industry has yet reached the peak of its development and it will be of interest to see what the next four decades will produce: and whether Portland cement will not have found a rival in some of the newer cementitious materials that are beginning to appear.

Sir George Earle Trophy

THE SIR GEORGE EARLE TROPHY, the award made annually by The Royal Society For The Prevention of Accidents (RoSPA) for a significant contribution to industrial accident prevention, was won in 1969 by the General Post Office. In making the award to the G.P.O., which entered for the trophy for the first time, RoSPA recognised the outstanding achievement in establishing a fully co-ordinated accident-prevention organisation extending from the workshop down to the individual postman. The project involves over 400,000 employees in diverse occupations working mainly in small groups and has resulted in a reduction of accidents over a period of five years.

A special certificate of commendation has also been presented to the Ready Mixed Concrete Group of Companies for its outstanding record in the field of industrial accident prevention.

The Sir George Earle Trophy is a magnificent silver Georgian inkstand and was presented to RoSPA in 1956 by the late Sir George Earle, one-time President of The Associated Portland Cement Manufacturers Ltd. Winners hold the trophy for a year and are presented with a plaque as a permanent record of the achievement.

National Standards for Portland Cement

ON PAGES 86 to 89 is given the fourth and last of a series of tables giving the requirements of most of the national standard specifications for Portland cement. Previous tables in this series, which were published in the March, May and July numbers of this journal, related to the chemical composition, the tensile, compressive and bending strengths, and the setting times of Portland cement. The present table gives data concerning the fineness. Some of the data are abstracted from "Cement Standards of the World 1968," but other information is in accordance with the requirements of later available Standards. As previously mentioned, other revisions may have been made since the tables were prepared for the press.

The following abbreviations are used for the various types of Portland cement:

O—Ordinary
RH—Rapid hardening (or high early strength)
LH—Low heat
SR—Sulphate resistant
AE—Air entrained

TABLE IV.—FINENESS OF PORTLAND CEMENT

Country	Type of Cement	Sieve Analysis			Specific Surface	
		Sieves	Aperture (μ)	Maximum residue (per cent.)	Minimum (sq. cm. per gm.)	Apparatus A = Air permeability T = Turbidimeter
Argentina	O	IRAM 200	74	15	2250 individual 2500 average	A (Blaine)
	RH	IRAM 200	74	15	3700 individual 4000 average	A
Australia	LH	—	—	—	≮2800≯4200	A
Austria	O1, O2, HS	—	90	20	—	—
Belgium	O	ASTM	88	18	—	—
	RH	ASTM	88	10	—	—
	HS	ASTM	88	14	—	—
Brazil	O	—	75	15	2600	A
	RH	—	75	6	—	—
Britain	O	—	—	—	2250	A
	RH	—	—	—	3250	A
	LH	—	—	—	3200	A
	SR	—	—	—	2500	A
Bulgaria	O, HS	900 4900	200 90	2 15	— —	— —
Canada	O	200	74	18	—	—
	RH	—	—	—	—	—
	SR	200	74	18	—	—
Chile	No requirements	—	—	—	—	—
China	All types	4900	—	15	—	—
Czechoslovakia	O, RH	900 4900	200 90	1·5 15	—	—
	HS†	900 4900	200 90	6 (min)	3500	A (Blaine)

† Mostly for asbestos cement products

Denmark	O, RH	900 4900	200 90	1·5 10	— —	— —
Eire	No requirements	—	—	—	—	—
Finland	No requirements	—	—	—	—	—
France	No requirements	—	—	—	—	—
Germany (East)	O, RH1 RH2	— —	90 90	15 10	2500 3000	A (Blaine) A
Germany (West)	All types	—	—	—	2200	A (Blaine)
Greece	All types	4900	90	20	—	—
Hungary	All types	900 4900	200 90	2 20	— —	— —
Indonesia	O RH LH	— — —	90 90 90	14 7 21	— — —	— — —
Israel	O HS SR	— — —	— — —	— — —	2600 3000 { 2600 individual 2800 average	A (Blaine) A A (Blaine) A
Italy	O, HS	0·18 UNI 2331	180	2	—	—
Japan	O RH LH	— — —	88 88 88	10 10 10	2500 3000 2700	A A (Blaine) A
Mexico	All types	—	—	—	1500 individual 1600 average } 2600 individual 2800 average } If disputed T shall govern.	T (Wagner) A (Blaine)

TABLE IV.—FINENESS OF PORTLAND CEMENT (*Continued*)

Country	Type of Cement	Sieve Analysis			Specific Surface	
		Sieves	Aperture (μ)	Maximum residue (per cent.)	Minimum (sq. cm. per gm.)	Apparatus A = Air permeability T = Turbidimeter
Netherlands	O	N 480-d-0·09	90	15	—	—
	RH1	N 480-d-0·09	90	10	—	—
	RH2	N 480-d-0·09	90	5	—	—
New Zealand	O	—	—	—	2550	A
	RH	—	—	—	3250	A
	LH	—	—	—	3200	A
Norway	O	ASTM 170 or	90	10	2500	A (Blaine)
	RH	0·09 DIN 4188	90	10	3500	A
Pakistan	O	BS 170	89	10	2250	A
	RH	BS 170	89	5	3250	A
Poland	O1	—	80	20	2000	A (Blaine)
		—	200	2		
	O2	—	80	15	2500	A
		—	200	1·5		
	RH	—	—	—	3000	—
	HS1	—	80	10	2700	—
		—	200	1		
	HS2	—	—	—	3500	—
	SR/LH	—	—	—	2500	—
Portugal	O	4900	90	10	1500*	T
Rumania	O1, O2	—	90	12	2500*	A
	RH1, RH2	—	90	10	2800–4000	A
South Africa	O	BS 72	210	1·2	2250	A (Blaine)
	RH	BS 72	210	0·5	3250	A

Spain	O1, SR1 O2, O3, SR2	0·090 UNE 7050	90 90	14 14	≮2800 ≯3500 ≮3500 ≯4200	A (Blaine) A
Sweden	No requirements					
Switzerland	O HS	— —	— —	— —	2400 3500	A (Blaine) A
Taiwan	O, SR/LH	—	—	—	2600 individual 2800 average }	A
Turkey	O RH	900 4900 ·	200 90	1 15	— —	— —
Uruguay	No requirements					
U.S.A.	All types	—	—	—	1500 individual 1600 average } 2600 individual 2800 average } If disputed T shall govern.	T (Wagner) A (Blaine)
U.S.S.R.	All types	008	80	15	—	—
Venezuela	O, SR/LH	—	—	—	{ 1500 individual 1600 average	A (Blaine) A
Yugoslavia	O1, O2 RH	— —	90 90	15 15	2400 3250	A (Blaine) A

ENCI Cement Works, Maastricht

IN THE JULY number of this journal, a general report was given of the ENCI (Eerste Nederlandse Cement Industrie) cement works at Maastricht, Holland, and, in particular, the recently-installed dry-process plant was described. The following data supplements or supersedes that given in the previous article.

The consumption of cement in the Netherlands is some 400 kg. per capita per annum. The works affiliated to ENCI include ROBUR at Rozenburg and CEMI (Cement Industrie Muiden).

At the Maastricht works, the four older and smaller kilns produce Portland cement clinker. The conveyors below the central crusher pit extract up to 10,000 tons of limestone daily. The covered store for pre-blended raw materials is rectangular in plan. The drum-type dryer for the limestone is set at a 3-per cent slope.

The cement despatched by boat from the works is partly in bags and partly in bulk. There are road facilities for despatch but no facilities for despatch by rail.

Recent B.R.S. Publications

SEVERAL PAPERS on cement in the "Current Papers" series issued by the Building Research Station have been published recently. These include the following.

"The Analysis of Belite in Portland Cement Clinker by means of an Electron-probe Microanalyser." By K. E. Fletcher. (Reprinted from Magazine of Concrete Research, 1968, Vol. 20(64), September.) Current Paper 13/69.

"Effect of Admixtures on the Composition of the Liquid Phase and the Early Hydration Reactions in Portland Cement Pastes." By M. H. Roberts. (Paper presented at the RILEM Symposium on "Admixtures for Mortar and Concrete", Brussels, August 30–September 1, 1967.) Current Paper 61/68.

"The Composition of Alite (Tricalcium Silicate) in a Portland Cement Clinker." By H. G. Midgley. (Reprinted from Magazine of Concrete Research, 1968, Vol. 20(62), March.) Current Paper 71/68.

"The Composition and Possible Structure of the Quaternary Phase in High-alumina Cement and its Relation to other Phases in the System CaO-MgO-Al_2O_3." By H. G. Midgley. (Reprinted from Transactions of the British Ceramic Society, 1968, Vol. 67(1) January.) Current Paper 75/68.

"Studies of the Role of Calcium Sulphate in the Manufacture of Portland Cement Clinker." By W. Gutt. (Reprinted from Transactions of the British Ceramic Society, 1968, Vol. 67(10) October.) Current Paper CP89/68.

"Manufacture of Portland Cement from Phosphatic Raw Materials." By W. Gutt. (To be published in the Proceedings of the Fifth International Symposium on the Chemistry of Cement, held in Tokyo in October 1968.) Current Paper CP90/68.

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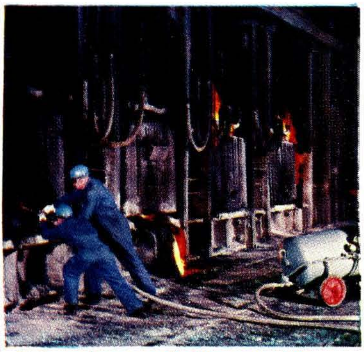

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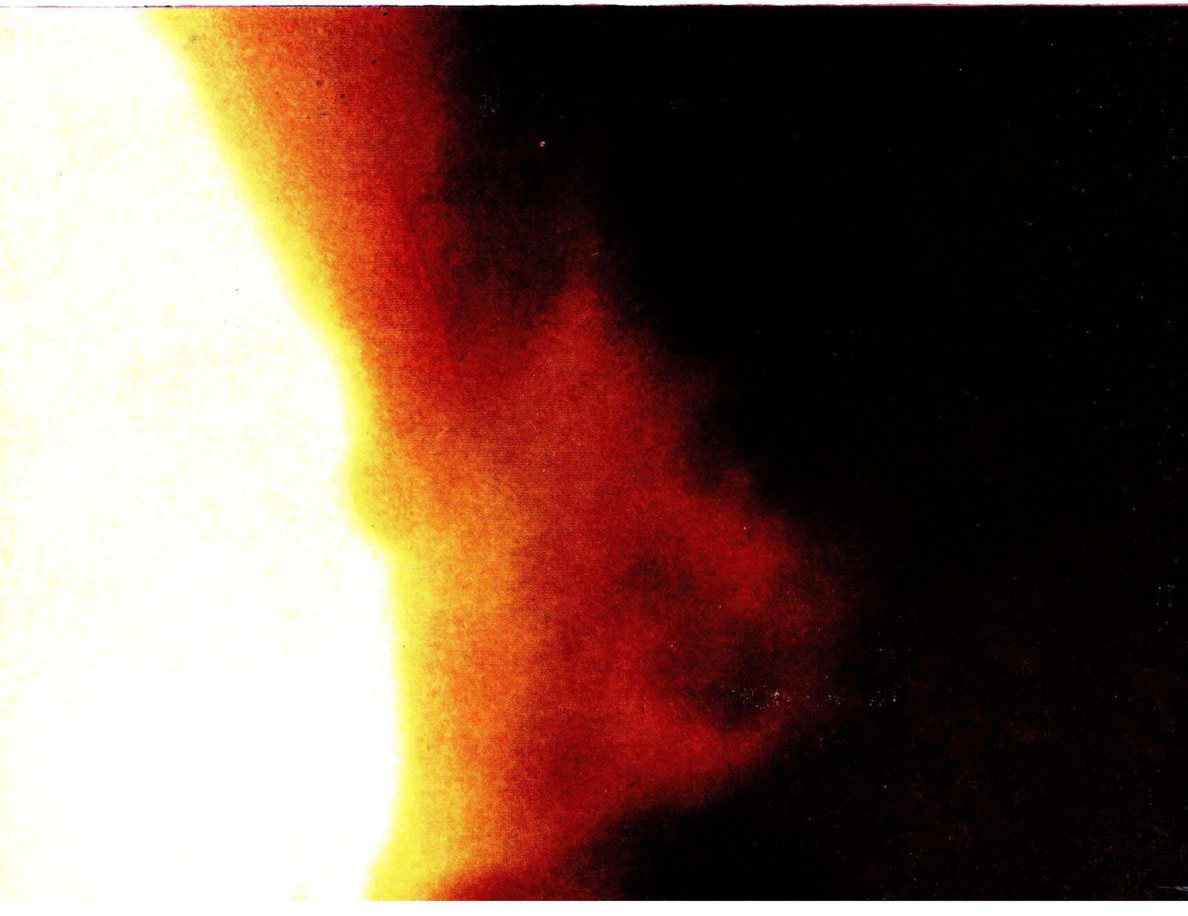

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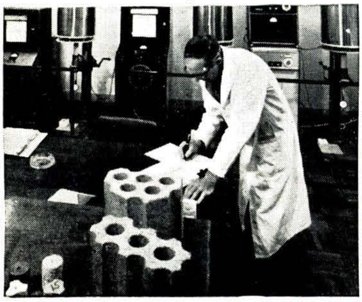

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Build-up of Rings caused by Spurrite Formation

BY F. BECKER AND W. SCHRÄMLI

TECHNICAL CENTRE HOLDERBANK (SWITZERLAND)

Synopsis

A CAREFUL investigation of the mineralogical composition of the material of a kiln ring over the whole cross-section of the ring body revealed the presence of considerable amounts of spurrite. The examination of rings in other kilns confirmed these results and led to the opinion that the formation of spurrite is typical for rings of the kind described. A special operating condition of all these kilns was insufficient decarbonisation of the feed in the calcining zone. The conditions favouring the formation of spurrite are thus considered to be at the same time those which favour the formation of rings. It is argued that the entry of incompletely dissociated material into the burning zone gives rise to a solid state reaction between calcite and siliceous material, the product of which is spurrite.

IN SOME PAPERS(1)(3) submitted to the Fifth International Symposium on the Chemistry of Cement, which was held in Tokyo in 1968, reference was made to the formation of ternary minerals consisting of dicalcium silicate and calcium or alkali carbonate or sulphate during the burning of Portland cement clinker. Earlier, Courtault(2) demonstrated in laboratory tests that spurrite C_2S. $CaCO_3$ is formed in the system CaO-SiO_2-CO_2 at temperatures as low as 850 deg. C when fluorspar is present to the extent of a small percentage. It seems to be essential that the partial pressure of CO_2 is of the order of one atmosphere. Courtault pointed out that the formation of spurrite as a consequence of the presence of fluorspar markedly favours the formation of C_3S at comparatively low temperatures. Spurrite may thus be considered as a transition phase in the transformation of belite to alite.

Amafuji and Tsumagari(3) postulated the formation of spurrite and other ternary minerals in the cement kiln as a product of reaction of CO_2 and/or SO_2 with the solid material. They advanced the idea that the spurrite and the other ternary minerals formed contribute to the formation of rings in rotary kilns due to their tendency to bind the loose material together.

Mention of the transitory occurrence of spurrite during the burning of raw mixes for cement in a laboratory furnace was also made by Herr, Hening and Scholze(4). They pointed out that the spurrite is formed even under low partial pressure of CO_2 in the presence of chlorides, which act as mineralisers.

In an attempt to clarify the conditions under which rings in a rotary kiln can be formed, the authors investigated in some detail the mineralogical composition of ring material through the entire cross-section of the ring. For this purpose, the ring body was carefully cut into pieces parallel to the kiln lining, and each piece was examined separately. The ring was located at the upper end of the burning zone, about 20m. (66 ft.) from the discharge end of the kiln. The internal diameter of the kiln investigator was 2·6 m. (8 ft. 8 in.) and its length was 103 m. (340 ft.). The maximum thickness of the ring was about 0·8 m. (2 ft. 8 in.).

The method of investigation used was semi-quantitative X-ray diffractometry. The results of this examination are summarised in *Figure* 1. Supplementary

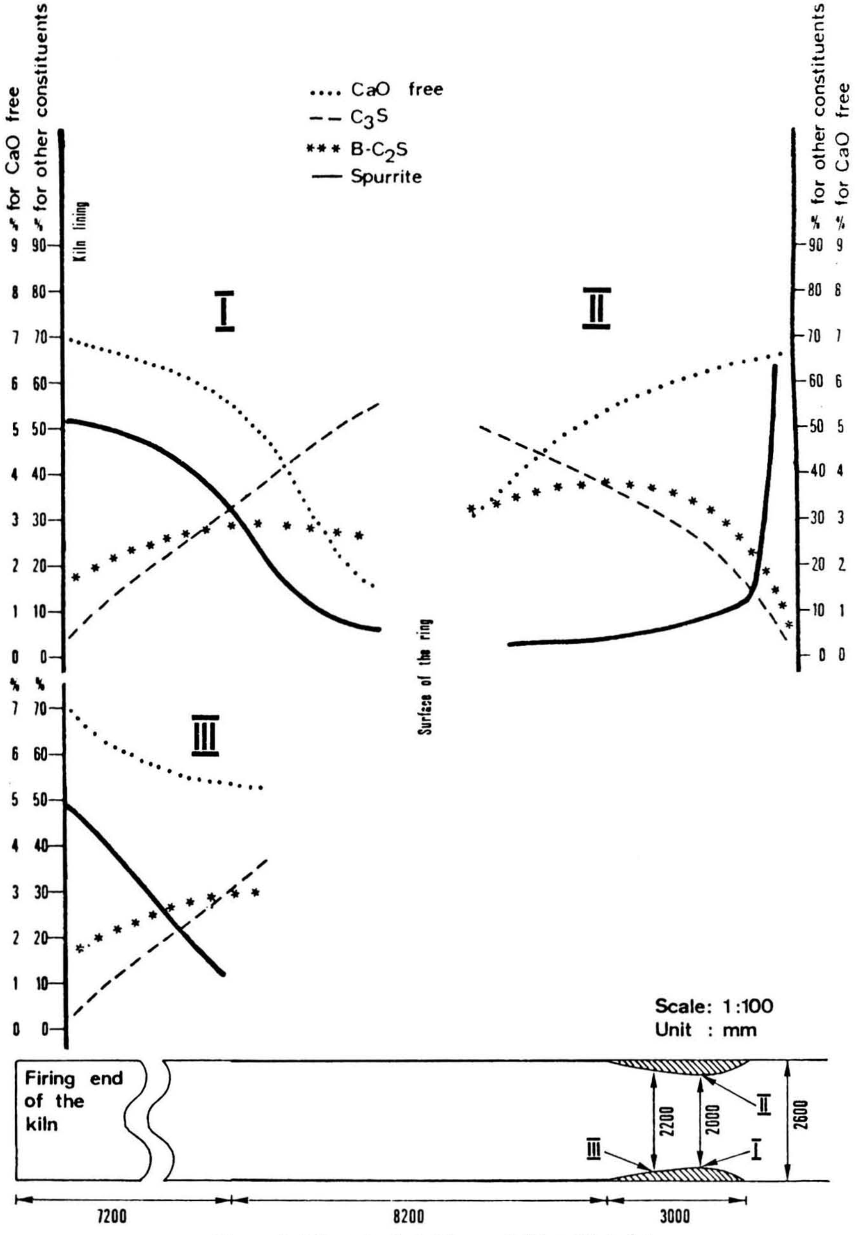

Figure 1. Mineralogical Map and Ring Material

information was obtained by chemical analysis of all pieces. The chemical composition of two pieces in extreme positions are given in *Table I*. *Figure* 1 shows that at the surface of the ring body only a small percentage of spurrite can be observed. Towards the interior of the ring the amount increases more or less steadily to reach 50 per cent or even more in the layer directly adjacent to the kiln lining. The shape of the curve indicating the alite content in the ring shows the reverse tendency for this mineral.

The opinion advanced by Courtault(2) that spurrite is a transition phase in the formation of alite thus seems to be supported. However, it seems at least doubtful that the presence of fluorspar or of other mineralisers are indispensable prerequisites for the formation of spurrite. This was not confirmed by the author's investigations. Chemical analyses of the raw mix and the ring material revealed only traces of fluorine (0·03 per cent) and an SO_3 and alkali content of the order of magnitude found in the clinker produced in this kiln. The curve showing the content of β-C_2S reaches a slight maximum in the centre of the ring body, whereas the amount of free lime increases more or less steadily from the surface of the ring to the kiln lining.

TABLE I.—TYPICAL CHEMICAL COMPOSITION OF RING MATERIALS

	Adjacent to the kiln lining per cent	At the surface of the ring body per cent
Loss on ignition	5·6	0·7
SiO_2	19·3	21·2
Al_2O_3	7·0	6·8
Fe_2O_3	3·1	3·2
CaO	61·5	65·4
MgO	2·0	2·0
SO_3	0·7	0·2
K_2O	0·5	0·6
Na_2O	0·2	0·2
CaO free	6·9	1·7
Insoluble	0·4	0·6
CO_2	4·8	0·4

An analogous examination of the mineralogical composition of the same ring at another point along the axis of the kiln indicated the same pattern. Examinations of ring material formed in kilns of similar size and shape and also operated in a similar way, but fed with considerably different raw mixes with respect to their mineralogical and chemical composition, led to the same results.

The fact that the structure of the ring seems to be typical for many kilns leads to the conclusion that there must be peculiar conditions in these kilns causing ring formation.

The authors considered as one of the only common features of these kilns the temperature distribution throughout the kiln. They are characterised by an incomplete calcination of the carbonates in the calcining zone so that material containing a considerable amount of carbonate enters the burning zone. Bearing in mind the almost complete absence of mineralisers, the authors suggest that spurrite may be formed by a direct solid-state reaction between calcite and the siliceous components present.

The authors found an indirect proof for our reasoning in the fact that, after the installation of a denser chain curtain in the kiln on which the detailed study was made giving rise to a better heat exchange and thus to a more complete dissociation of the carbonates, spurrite was not formed any longer, and as a consequence, the ring disappeared.

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Asbestos-cement Products

THE FOLLOWING is abstracted from a brochure entitled "The Mineral Asbestos" published recently by Turner Brothers Asbestos Co. Ltd.

There is an ever-growing demand for asbestos-cement in the building trade and in industry in general. This material is used for a variety of structural purposes, such as roof and wall cladding, huts, partitions and ceilings. In addition, moulded asbestos-cement products are available as rain-water and drainage goods, flue pipes, cisterns, cable conduits and troughs. Other uses include fire protection, thermal insulation and sound-absorption treatment.

The manufacture of asbestos-cement is far removed from the simple admixture of Portland cement with an aggregate, and requires specialised knowledge and efficient supervision. The asbestos fibre is a reinforcement and must be correctly located to resist the stresses to which the finished product will be subjected. The degree of fibre separation has a most important bearing on the matured product and considerable knowledge and skill are required in the initial treatment, together with an ability to select the correct grade and blend of asbestos. Constant sampling and testing are essential features throughout production and great care is exercised to ensure a homogeneous fabric.

In the mixing of fibre with cement, a considerable excess of water is introduced. This may appear to jeopardise the setting properties of the cement, but is a purely temporary phase employed primarily for the proper positioning of the fibre. Excess water is rapidly drained off, leaving a very thin film or lamina of cement with embedded fibre on an endless belt which is eventually carried to a revolving forming bowl or mandrel. This forming bowl picks up film after film in a continuous operation, superimposing one on the other to a predetermined thickness.

Determination of Sulphate in Cement and Gypsum

The following is a translation by MR. R. KEEN of an article by N. N. BASARGIN and T. G. AKIMOVA in the Russian journal 'Tsement' (No. 6, 1968), describing a new indicator which can be used for the rapid volumetric determination of sulphate in cement and gypsum.

THE QUALITY of some building materials such as cement and gypsum is controlled by analysis of the sulphate content. There are well-known methods for determining sulphate based on ion exchange (1, 4) as well as infra-red spectroscopy(5). Of these, the ion exchange method with alkimetric titration of the sulphate merits particular attention(1).

A new rapid method has been developed which is different in principle from the foregoing. This is based on a volumetric determination of sulphate using a new indicator, nitchromazo (6, 7) which allows both the rapid and accurate determination of sulphate in cement or gypsum without the need for complicated apparatus. The method involves the suppression of calcium and magnesium by fluoride ions (from the addition of HF or NH_4F) and the direct titration of sulphates by standard barium chloride solution at a pH of 1·7 to 2·0 using the barium salt of nitchromazo as indicator. Tests have shown that a high concentration of boric acid did not interfere with the titration. The properties of nitchromazo and its synthesis are described in earlier publications(7, 8).

Determination of Sulphate in Cement

A sample of cement (0·800 g.) and water (90 ml.) are placed in a covered beaker and heated on a water bath for 15 to 20 minutes. The mixture is cooled and filtered into a 100 ml. volumetric flask. The residue is washed twice with water, keeping the total volume below the mark on the flask. The solution is acidified with a few drops of 6N.HCl to give a pH value of 4 to 5 (using indicator paper as a check) and made up to the mark.

An aliquot (5 ml.) is transferred to a 50-ml. beaker and treated with HCl (2 ml., 0·1N), water (2 ml.), NH_4F solution (1 ml., 0·1N), aqueous solution of nitchromazo (one drop, 0·2%) and ethyl alcohol (8 ml.). The solution is then titrated against standard 0·02N.$BaCl_2$ solution. The titration is carried out slowly with 15 to 20 seconds stirring after every two or three drops of solution have been added until the colour changes to a persistent blue. Hydrofluoric acid (5 ml.) can be substituted for both the NH_4F and the HCl solutions. The strength of the HF solution is 0·02N.

A blank test is carried out as follows. HCl (1 ml., 0·1N) is introduced into a 50-ml. beaker and treated with water (8 ml.), NH_4F (1 ml., 0·1N), aqueous solution of nitchromazo (one drop, 0·2%) and ethyl alcohol or acetone (8 ml.). One or more drops of the standard barium chloride solution are then added to produce a blue colour.

The sulphate content is calculated from the formula

$$SO_3 \text{ (per cent)} = \frac{(a - c)K}{W} \times 100,$$

where a = amount of standard $BaCl_2$ solution used in the titration.
c = amount of standard $BaCl_2$ solution used in the blank determination.
W = weight of sample in the aliquot portion (milligrams).
$K = K_1 \times f_1$.
K_1 = difference in normality of the $BaCl_2$ solution from 0·02 (that is the the factor on the solution).
f_1 = amount of SO_3 equal to 1 ml. of 0·02N.$BaCl_2$ solution (= 0·80).

The barium chloride solution is standardized against standard sulphuric-acid solution of the same strength without the addition of NH_4F or HF solution. NH_4F or HF is added to react with the calcium which, in the uncombined form, tends to affect the colour of the indicator.

When titrating in the presence of HF, the indicator changes colour more markedly from violet to blue and the aliquot portion can be increased to 10 ml. still using 5 ml. of 0·2N.HF solution.

Determination of Sulphate in Gypsum

A sample of gypsum (0·20 g.) and water (150 ml.) are heated in a 250-ml. beaker on a water bath for 15 to 20 minutes. The solution is cooled and filtered, and the residue is washed with 20 to 30 ml. of water. The volume is then adjusted to 250 ml. in a volumetric flask.

An aliquot portion (5 ml.) is transferred to a 50-ml. beaker and treated with HCl (1 ml., 0·1N), NH_4F (1 ml., 0·1N), water (3 ml.), aqueous solution of nitchromazo (one drop, 0·2%) and ethyl alcohol or acetone (8 ml.).

The sample is slowly titrated against standard 0·02N barium-chloride solution from a microburette until the colour changes from a bluish-violet to persistent blue.

A blank determination is carried out, and the SO_3 content calculated from the formula given in the foregoing.

A titration takes 5 to 7 minutes and the whole determination about 30 minutes.

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The Effect of Alkalis on the Behaviour of Cement

ACCORDING TO I. A. KRYZHANOVSKAYA and her colleagues, in an article in the Soviet journal "Tsement" (April, 1969), and translated by R. KEEN, there is a connection between the alkali content of cement and its activity in concrete. A translation of the article by R. KEEN is given in the following.

TO DETERMINE the effect of the amount and the composition of the alkali compounds on the strength of cement, cements were made up from pure synthetic minerals ground to a given fineness. The amount of alkalis in these cements ranged from 0·6 to 1·5%. The SO_3-content was varied so that there was either just alkali sulphates or a mixture of alkali sulphates and alkali calcium silicate or aluminate ($KC_{23}S_{12}$ or NC_8A_3) present in the cements. These latter compounds are formed, according to most research workers, after the sulphuric anhydride has entered into combination during the firing.

The investigations on the effect of alkalis on the hardening process were carried out with alkali-free cements (Series I) and four series of alkali-containing cements with (i) K_2O in the form of potassium sulphate only; (ii) the same but with $KC_{23}S_{12}$ present; (iii) Na_2O in the form of sodium sulphate only; and (iv) the same but with NC_8A_3 present. The compositions of the cements and the strengths obtained (from small test specimens) are presented in *Table* I.

The data show that with a K_2O-content of from 0·6 to 1·5% at K_2SO_4 (cements Nos. 3, 4 and 5), the strengths start to decrease at between three and twenty-eight days when compared to those from alkali-free cements (cements Nos. 1 and 2). Only at one day are they higher. With both K_2SO_4 and $KC_{23}S_{12}$ present, the strengths are lower still.

Introducing 0·6, 1·0 and 1·5% of alkali as sodium sulphate (cements Nos. 9, 10 and 11) brings about a more marked reduction in strength. All the 3-day strengths are lower when sodium sulphate is present. When both Na_2SO_4 and NC_8A_3 are incorporated, the drop in strength is particularly pronounced especially at later ages.

The strength is also reduced when both alkalis are introduced, the sodium compounds having a more marked effect than the potassium compounds.

The strength of potassium-containing cements increases at early ages as the SO_3-content rises. Sodium-containing cements, on the other hand, have the highest strength when the SO_3-content is minimal. So, when raw material containing sodium, such as nepheline slurry, is employed for making cement, it is particularly important to reduce the percentage of SO_3.

During hydration the alkali oxides are transferred to the liquid phase. If the K_2O and Na_2O are combined as sulphates, this transfer takes place immediately after gauging. Analyses of the liquid phase show that in only two minutes after adding the water, the amount of alkalis in solution approximates to the total amount in the cement. The alkalis are also readily transferred to the solution when the cement contains NC_8A_3. The compound $KC_{23}S_{12}$ hydrates more slowly and, when this is present, the alkalis are not fully water-soluble even after a year's hydration.

TABLE I.—COMPOSITIONS OF CEMENTS AND COMPRESSIVE STRENGTHS (USING SMALL SPECIMENS)

Series	Cement No.	Content per cent			Mineralogical composition (per cent)									Compressive strength kg. per sq. cm.						
		K_2O	Na_2O	SO_3	C_3S	C_2S	C_3A	C_4AF	K_2SO_4	$KC_{23}S_{12}$	Na_2SO_4	NC_8A_3	$CaSO_4$	days				months		
														1	3	7	28	3	6	12
I	1	—	—	—	57	22	7	14	—	—	—	—	—	12·0	25·1	37·6	53·0	130·0	132·8	139·6
	2	—	—	1·2	56	22	7	14	—	—	—	—	2·0	10·6	29·6	—	65·0	—	—	—
II	3	0·6	—	0·5	57	21	7	14	1·1	—	—	—	—	16·6	19·2	28·7	43·8	76·1	119·5	124·0
	4	1·0	—	0·8	57	20	7	14	1·8	—	—	—	—	14·6	17·6	28·8	39·7	86·7	117·8	114·0
	5	1·5	—	1·3	57	19	7	14	2·8	—	—	—	—	21·1	21·5	25·4	37·6	70·8	115·1	112·9
III	6	0·6	—	0·4	57	18	7	14	0·9	2·6	—	—	—	13·0	13·1	20·8	37·0	86·7	112·0	109·6
	7	1·0	—	0·6	57	15	7	14	1·4	5·2	—	—	—	10·6	16·0	16·4	28·0	73·4	92·8	85·2
	8	1·5	—	1·0	57	12	7	14	2·2	7·2	—	—	—	16·0	18·4	25·5	38·0	83·1	83·8	107·7
IV	9	—	0·6	0·8	57	22	6	14	—	—	1·4	—	—	15·3	12·7	16·5	33·0	63·8	96·2	101·1
	10	—	1·0	1·3	57	22	5	14	—	—	2·3	—	—	14·2	5·5	15·5	29·4	57·2	70·0	91·1
	11	—	1·5	1·9	57	22	4	14	—	—	3·4	—	—	9·7	6·7	12·5	31·5	47·8	49·3	74·1
V	12	—	0·6	0·4	57	22	3	14	—	—	0·8	3·4	—	8·1	7·3	11·1	18·7	35·1	49·4	43·2
	13	—	1·0	0·6	57	22	—	14	—	—	1·1	7·0	—	8·8	13·0	15·8	27·2	4·08	43·8	30·9
	14	—	1·5	1·0	55	20	—	13	—	—	1·8	9·5	—	14·5	19·2	23·7	47·0	70·1	71·5	47·5

If the strengths of cements containing potassium oxide and sodium oxide are compared, the higher values of the former can clearly be seen. These higher strengths are found despite the fact that $KC_{23}S_{12}$ is a compound with low activity while NC_8A_3 gives a reasonably high strength especially at early ages. The amount of chemically-bound water is approximately the same for all cements at any one age.

The compositions of the liquid phases with alkali-free and alkali-containing cements differ with respect to the amount of hydrated calcium oxide (lime) present. In the absence of alkali, the solution is supersaturated at early ages but later becomes normally saturated with lime. The amount of lime in solution falls as the alkali-content increases. This was found with all cements at all ages between two minutes and one year.

TABLE II.—DATA ON THE COMPOSITION OF THE LIQUID PHASE AFTER 28 DAYS' HARDENING

Cement No.	Chemically bound H_2O (per cent)	Content (per cent)			Content CaO as percentage of saturation value
		K_2O	Na_2O	CaO	
1	17·37	None	—	1·50	121·9
2	—	None	—	—	—
3	12·41	0·61	—	1·26	102·9
4	12·31	0·91	—	1·09	88·6
5	14·09	1·46	—	0·82	66·6
6	13·74	0·61	—	1·18	96·0
7	12·59	0·70	—	1·07	87·0
8	12·26	1·06	—	1·05	85·3
9	12·52	—	0·58	1·08	87·8
10	13·00	—	0·96	0·93	75·6
11	12·36	—	1·44	0·79	64·2
12	12·81	—	0·67	1·10	89·4
13	15·67	—	1·10	0·82	66·6
14	17·13	—	1·61	0·70	56·9

In *Table* II data are presented on the composition of the liquid phases of cements after 28-days' hardening. The least saturated solution with respect to lime contains both Na_2SO_4 and NC_3A_8. This is evidence that the hydration of the clinker minerals is being suppressed.

The lowest strengths, especially at later ages, come from cements containing sodium oxide having a $Na_2O:SO_3$-ratio much higher than the equimolecular value and the drop in late strength is greater the higher the ratio.

In the liquid phases of cements Nos. 13 and 14, which contain 1 and 1·5% Na_2O as Na_2SO_4 and NC_8A_3, an unusually high percentage of Al_2O_3 was found in the early ages of hydration. Thus, after 3-hours' hardening 149 mg. per l. Al_2O_3 were present in the liquid phase with cement No. 14 as against 1 to 2 mg. per l. with normal Portland cement. It became less with time and reached the normal level after three days.

. The investigations established that, in the presence of 0·06% alkali, the activity of Portland cement is reduced irrespectively of the kind of alkali compounds present. An increase in the alkali-content reduces the activity both at early and late ages due to suppression of the hydration of the clinker minerals by the alkalis in the liquid phase.

Experience has shown that the use of alkali-containing cements for general construction work does not lead to long-term difficulties. These cements can be troublesome in hydraulic engineering work, especially with aggregates containing amorphous silica. Therefore it is reasonable to introduce a special grade of Portland cement, "low-alkali", containing less than 0·6% alkali with recommendations on the fields of application.

Computer Control at German Cement Plant

A BRITISH-MADE HONEYWELL DDP 516 real-time computer system, valued at nearly £43,000, has been exported to the German firm of Klockner Humbolt Deutz A.G. to aid in the control of an automated cement plant. The duties of this computer system include the analysis of data on the raw mix obtained from an on-line X-ray fluorescent spectrometer. In the analysis, the computer collates the characteristic values of the product and compares these with previously stored standard values. Any deviations from the standard cause the computer to modify the flow of raw materials from a series of bunkers.


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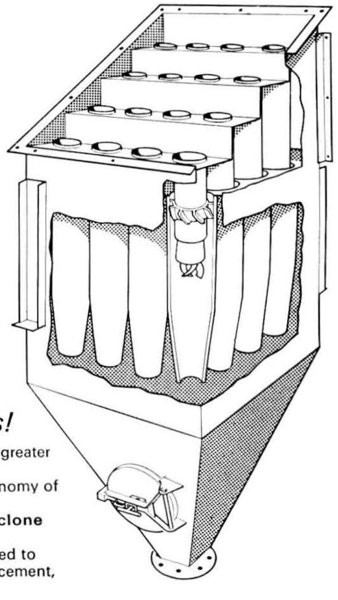
HOZ
DYCKERHOFF
pre-compacted
112 lbs
112 lbs



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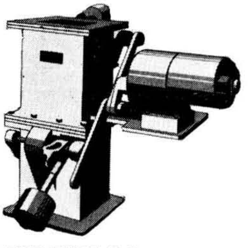

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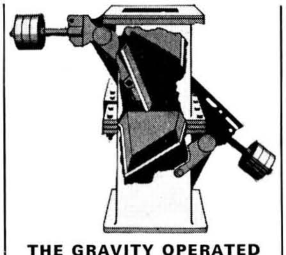

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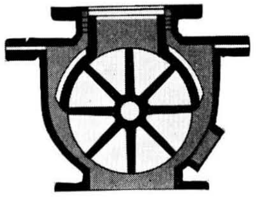

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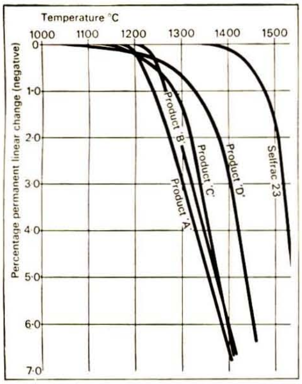

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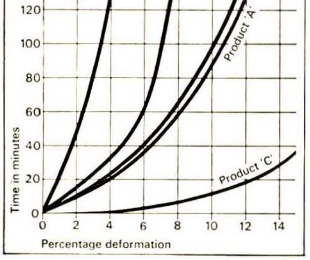

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