

CEMENTS RESEARCH PROGRESS 1981

A survey of the literature on the science of cements published during 1981

DIE
HYDRAULISCHEN MÖRTEL
INSBESONDERE DER
PORTLAND-CEMENT

IN CHEMISCH-TECHNISCHER BEZIEHUNG
FÜR
FABRIKANTEN, BAUTECHNIKER, INGENIEURE UND CHEMIKER

VON
Dr. W. MICHAËLIS
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MIT 62 ABBILDUNGEN IM TEXT.

LEIPZIG
VERLAG VON QUANDT & HÄNDEL.

CEMENTS DIVISION
AMERICAN CERAMIC SOCIETY



CEMENTS RESEARCH PROGRESS

1981

A survey of the scientific literature
on cements, published during 1981
prepared by members of the Cements Division
of the American Ceramic Society

Coordinating Editor:

J. Francis Young

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INTRODUCTION

1981 saw the publication of the fourth and final volume of the Proceedings of the Seventh International Congress on the Chemistry of Cement held in Paris in 1980. This is referenced as *Proc. Paris Congress* (or *Congrès de Paris*); the full bibliographic reference is:

*Proceedings, Seventh International Conference on
the Chemistry of Cement, Paris 1980, Vol. IV
(Editions Septima, Paris, France, 1981)*

The format of CRP has now reached a standard structure. In these chapters where excessive patents literature is cited, the patents are separated from the rest of the references. The large volume of literature reviewed in Chapter 6 necessitated the omission of patents on admixtures entirely.

The special chapter this year reviews research in France covering the period since the last review published in 1977, while the special review looks at the characterization of cement clinkers.

I welcome Dr. Regourd, who has taken charge of Chapter 8, Durability, to the ranks of CRP contributors.

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Thanks are due to Drs. Menétriér, Professor Barret and Dr. Gartner for their special contribution to this year's volume. Professor Winslow took charge of Chapter 7 this year at short notice and we thank him for his assistance. As usual we are indebted to our typists, Barbara Wonneberg and Melody Simeone, and to Don Snyder of the American Ceramic Society. Mr. Wally Klemm provided some biographical background about Wilhelm Michaelis and the portrait on page ii.

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ABBREVIATIONS AND NOMENCLATURE

Cement chemists shorthand notation is used throughout this volume:

C = CaO	\bar{C} = CO ₂	M = MgO
S = SiO ₂	\bar{S} = SO ₃	N = Na ₂ O
A = Al ₂ O ₃	F = Fe ₂ O ₃	K = K ₂ O
H = H ₂ O	P = P ₂ O ₅	

Other abbreviations used routinely are:

C/S ratio	= CaO/SiO ₂ molar ratio;	H/S ratio	= H ₂ O/SiO ₂ molar ratio
w/c ratio	= water:cement ratio;	w/s ratio	= water:solids ratio
XRD	= x-ray diffraction;	XRF	= x-ray fluorescence
QXDA	= quantitative x-ray diffraction analysis		
DSC	= differential scanning calorimetry		
DTA	= differential thermal analysis		
TGA	= thermogravimetric analysis (or TG = thermogravimetry)		
IR	= infra-red spectroscopy		
EM	= electron microscopy;	OM	= optical microscopy
SEM	= scanning electron microscopy		
TEM	= transmission electron microscopy		
ESCA	= electron spectroscopy for chemical analysis		

Abbreviations used for convenience only in specific chapters are defined in those chapters.

Nomenclature and classification of cement compounds are not yet standardized. Reference should be made to "Guide to Compounds of Interest in Cement and Concrete Research" Highway (not Transportation) Research Board Special Report 127 (1972). In the text ettringite (C₆A \bar{S} ₃H₃₂) and monosulfoaluminate (C₄A \bar{S} H₁₂) are commonly used for calcium sulfoaluminate hydrates while Aft and AFm are more general designations for these classes of compounds.

Units are given in the form used in the original paper with SI units given in parentheses, where necessary.

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W. Michaelis sen.

DEDICATED TO

Wilhelm Michaelis (1840-1911). A chemist by training, Michaelis was an early pioneer in scientific investigations on the constitution of cement, and of its hydration. Although his views on the phase composition of cement were incorrect, he is well-known for his colloidal theory of cement hydration, in contrast to the ideas of Le Chatelier. The debate has continued through the years.

Chapter 1

MANUFACTURE OF STRUCTURAL CEMENTS

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1. INTRODUCTION

This chapter reviews the published literature and patents on the various stages of cement manufacturing--composition and burnability of raw materials, preparation and properties of kiln feed, pyroprocessing, clinker grinding and cement storage. Much has been published, particularly in the form of patents, concerning equipment and processing modifications. Where such publications constitute significant advances to the cement manufacturing process, in the sense of energy conservation or improved clinker and cement quality, they have also been included in this review.

Several publications were of general interest. For instance, Volume IV of the Proceedings of the Seventh International Congress on the Chemistry of Cement¹ was issued in 1981. It contains General Reports, Posters, and Seminars, including coverage of Theme I, "Influence of raw materials, fuels and manufacturing processes on clinker structure and properties." Wächtler *et al.*² reviewed and discussed new ways of drastically decreasing the specific energy consumption during the clinker burning process. The formation of cement-clinker minerals under natural conditions by geological processes was reviewed by Kolodny.³

2. BURNABILITY OF RAW MATERIALS

Christensen⁴ proposed a model of the clinkering reaction based upon the principles of diffusion control and local equilibrium. The most important parameters were identified as the macroscopic and microscopic distribution of lime and silica during C_3S formation, their diffusivity through the melt, and the driving force for the reaction. Burnability can, therefore, be expressed as a function of fineness, mineralogy, composition and temperature. Mchedlov-Petrosyan *et al.*⁵ studied the relationships between the thermal decomposition kinetics of limestone and clinker formation reactions, including the mathematical modeling of C_2S and C_3S formation reactions in the presence of kaolin, gehlenite, and pseudowollastonite. The volatilization of alkali, sulfur, and chloride compounds was described by Petersen⁶ using a simple model for controlled diffusion of gases through the pore system of a clinker nodule.

Ludwig⁷ investigated the clinkering of raw meals by isothermal and isochronal burning of static or moving pellets. From the proportion of heterogeneous coarse particles, the lime saturation factor, and the potential melt content, it was possible to predict the burnability of various raw mix compositions at given clinkering temperatures. The fundamentals and kinetics of the clinkering process were reviewed by Glasser,⁸ and the influence of clinker liquid on burnability was discussed by Klemm.⁹ Fundal¹⁰ and Musikas *et al.*¹¹ related the burnability of raw mixes to the raw fineness, with particular attention to the size of quartz and calcite particles, while Humpola¹² and Kieser *et al.*¹³ studied the factors which influence the reactivity of cement raw materials. Raw mix burnability was enhanced by the use of basalt as a raw material,¹⁴ due to a reduction of melt formation by 150°C. The effects of raw mix microhomogeneity and burnability on the mechanical properties of the resulting clinker modules were determined by Egelev and Petersen.¹⁵

3. COMPOSITION OF MATERIALS

3.1 Minor Oxides

Bucchi^{16,17} has reviewed in detail the role of minor oxides in the production of portland cement clinker. The geochemical behavior of minor oxides in the sedimentary cycle was used to explain which of the rocks utilized in the cement manufacturing process are the main carriers of the minor oxides. He examined the changes in the physico-chemical properties of the clinker melt phase, due to the presence of minor oxides, and the influence of these changes on clinkering kinetics. Finally, it was shown how volatile minor oxides contributed to cycles in the burning process and influenced the formation of coatings and rings in the kilns. [The effects of adding barium compounds to cement raw mixes have been studied by several investigators (BaO ,^{18,19} BaSO_4 ,²⁰ and complex Ba-containing components (P1, P2)). After clinkering, most of the Ba is located in the C_2S , with only a limited amount in the C_3S , and the C_2S content increases with increasing Ba content. Compressive strength and sulfate resistance also improved.]

Teoreanu *et al.*²¹ found that additions of 2% FeSO_4 to cement raw mixes decreased the clinkering temperature by 40-100°C and improved the compressive strength of the cement.

3.2 Fluxing Additives

Christensen and Johansen²² reviewed the effects of CaF_2 mineralizers on clinker melt formation and clinkering reaction kinetics. A cement composition has been patented (P3) in which the CaF_2 -mineralized clinker could be ground without additives and achieve adequate set control through a SO_3 content bonded in the presence of alkalies and/or fluoride. A special mineralizer consisting of 0.5% CaF_2 + 0.5% CaSO_4 was evaluated by Kumar and Kataria,²³ who found that the quality and setting behavior of mineralized clinkers produced at 1300-1350°C were superior to normal clinkers produced at 1400-1450°C. Tanaka, Sawada and Shibaoka²⁴ studied the effects of several mineralizers, including CaF_2 , CaSO_4 , ZnO , and NiO . The addition of 0.5 - 1.5% CaF_2 and 6% CaSO_4 suppressed the formation of C_3A , enhanced the ferrite phase, and appeared to improve the sulfate-resistance of the cement, but ZnO and NiO were less effective. Other workers^{25,26} (P4) have investigated the mineralizing action of CaF_2 and CaCl_2 on silicates formation. A process is claimed (P5) in which a 1:1 mixture of fluoride and mineral phosphate is injected into the burner pipe of the rotary kiln, thereby realizing a 10% savings in fuel plus a 50°C decrease in clinkering temperature.

With additions of 0.5% F as H_2SiF_6 , clinker mineral formation was completed at 1300°C.²⁷ Mineralization with CaSiF_6 is also beneficial,²⁸ increasing the clinker melt content, lowering its temperature of formation, and allowing C_3S to form at 1200°C. The production of white cement clinker using a Na_2SiF_6 - MgSiF_6 mineralizing additive is described (P6). The effect of reduced clinkering temperatures, brought about by mineralizer additions, on specific energy consumption was studied by Gardeik.²⁹ An energy balance model showed that when the clinkering temperature was decreased by 200°C, the calculated values for energy savings were <5%, but these calculations are strongly dependent on the clinker cooling efficiency. Additional energy savings may be achieved by decreasing melt viscosity and increasing clinkering reactivity.

3.3 Waste Materials and Slags

A large number of mining, metallurgical, and industrial wastes have been suggested for use in cement production; for example, waste lime sludge derived from acetylene generation.³⁰ A waste from the production of caprolactam was used (P7) to increase the porosity and mechanical strength of clinker nodules. Other wastes considered as raw materials included siliceous minerals separated from dolomitic limestones,³¹ waste molding sand (P8), red mud,³² gold extraction sludge waste (P9), Ni and Al_2O_3 production wastes,³³ Ti-Mg production wastes,³⁴ ash from humate mining waste (P10), spent oil shale,³⁵ coal gasification waste (P11), and coal liquefaction residue (P12). Power plant wastes, as siliceous components, included fly ash^{36,37} (P13), power plant slag,³⁸ coal ash³⁹ (P14), and a mixture of belite slime and coal ash.⁴⁰

A variety of by-product slags have found use as raw mix components: P'yachev and co-workers⁴¹⁻⁴³ used oxidized Ni ore melting slags as an Fe-containing component in cement manufacture. Other slags included electrothermophosphoric slag,⁴⁴ silicomanganese slags,⁴⁵ LD slags,⁴⁶ blast furnace slag,^{47,48} pyrite cinders and blast furnace slag,⁴⁹ pig iron/steel desulfurization slag (P15), and a mixture of steel-making sludge, dust, and converter slag (P16) as an iron component (52% Fe_2O_3).

4. KILN FEED PREPARATION

Various grindability testing methods were compared by Zisselmar,⁵⁰ who showed the application of scaling up laboratory tests to large-scale raw material and clinker grinding plants. Cotea *et al.*⁵¹ considered the suitability of raw materials for crushing and grinding could be a means of reducing electrical energy consumption in the cement industry. Other workers^{52,53} discussed the effects of stockpile-storage, prehomogenization, and homogenization processes on the chemical variability of raw materials.

In wet process manufacturing, slurry thinners are used to reduce the water content and, therefore, the energy consumption during the burning

process. Slurry thinners included lignins,⁵⁴ tannery waste water,⁵⁵ and polyol-phthalic aldehyde wastes.⁵⁶ Fluidization of raw slurries for the purpose of transporting the slurry to a pyroprocessing facility some distance away was also the subject of two patents (P17, P18). Raw slurry can be activated by waste gases containing CO_2 and SO_3 , and subsequently clinkered (P19). Other patents included processes for dewatering slurry prior to burning (P20), and introducing recovered kiln dust into the kiln as a paste (14-18% H_2O) with the raw feed (P21). This latter technique allows efficient handling of kiln dust without high fuel consumption.

The interaction of fuels with raw materials was the subject of several patents. Diesel oil was used (P22) as a grinding aid on a roller mill, which later contributes heating value during the clinkering process. Cement raw materials can also be intimately mixed with a low-grade carbonaceous fuel (P23); the fuel component provides about 60% of the heat used in the calcination zone. Solid polymer wastes has been used (P24) for the same purpose. Another patent (P25) described a process in which fly ash loaded with $(\text{NH}_4)_2\text{SO}_4$ is fed into a kiln or preheater with raw materials at 700-1100°C to decrease the NO_x content in the exhaust gases and make the fly ash a mix component. This denitration process was more efficient than that obtained through NH_3 injection. Rollin and Estaque⁵⁷ utilized acid sludge blends from acid/clay treatment of waste crankcase oils as supplemental fuel in cement kilns. Toxic elements in the oil (Pb, Zn, P and Ba) were trapped in the clinker during burning, and no increase of toxic elements in the kiln dust was observed.

5. SPECIAL CLINKERS AND MANUFACTURING PROCESSES

Talaber and Dolezsai⁵⁸ varied the clinkering temperature for high alumina cement clinkers, and the calcium to alumina ratio in the raw mix, to determine what compounds formed and the effect on cement strengths. Two improvements were described for producing white cement clinker: one method^{59,60} involved removing iron oxide from the raw material by calcination in a Cl_2 or $\text{N}_2 + \text{Cl}_2$ atmosphere, the other⁶¹ used an additive consisting of a fluorine-containing waste from the manufacture of AlF_3 . Zubar, Gulai and Men⁶²

studied a cement composed mainly of a C_4AF solid solution, and suggested that it be used for cold pelletizing of iron ore concentrates. Two patents (P26, P27) were published that dealt with belite cement, which is produced from an active, C_2S -rich clinker. Belite clinker particles, smaller than 7 mm, burned at approximately 1300° and quenched, were shown to produce a superior cement; larger-sized clinker produced an inferior cement, but could be ground in a vibratory mill and added to the previous belite cement without lowering its strength. A self-disintegrating belite clinker was described by Savel'ev and co-workers^{63,64} based on the inversion of $\beta-C_2S$ to $\gamma-C_2S$, which was promoted by added FeO. Such cements are not as hydraulic as portland cement.

The phase composition of alinite (Cl-doped) clinker was detailed by Boikova *et al.*;⁶⁵ in addition to alinite ($Ca_{11}AlSi_3O_{18}Cl$), all other clinker minerals were also found to contain Cl and other impurities. Nudel'man and co-workers⁶⁶⁻⁶⁹ investigated low temperature salt (LTS) clinker and its desalination. Crushing the clinker gave⁶⁶ a clinker size that is optimal for subsequent desalination. A thermal balance for desalination at 1100° in a shaft furnace was calculated⁶⁷ and various parameters of low temperature clinker and the $CaCl_2$ melt and their effects on desalination of the clinker described.^{68,69}

The hydraulic properties of coal and oil shale ashes have been assessed. A process for firing coal or coal plus limestone and grinding the resulting ash with anhydrite produces (P28) a hydraulic binder with strength comparable to portland cement. Ish-Shalom and co-workers^{70,71} determined that oil shale ash showed reasonable cementing properties, especially when the paste or mortar was compacted to reduce its water content. The general topic of gypsum-free portland cements is reviewed by Skvara.⁷²

Several papers have dealt with new processes for clinker burning. Clinker production from coal-containing raw material pellets utilizes (P29) a fluidized bed. Fedorov *et al.*⁷³ described a very high-speed synthesis of C_2S in molten pig iron; synthesis time was reduced from 6 hours to 60 seconds by calcination in the molten metal. Bikbau *et al.*⁷⁴ developed an optical

furnace for production of portland cement clinker from solar or electric arc sources; such clinker was superior to regular portland cement clinker. Clinker production using a plasma rotary kiln to obtain temperatures of approximately 1950°C is claimed (P30) to lower energy consumption and alkali contents. An electric furnace is proposed (P31) for melting mixtures of such materials as fly ash and lime for clinker production.

The general topic of manufacturing methods for co-production of cement and some other material received increased attention, for example, methods for co-producing a potassium components for use as a fertilizer (P32, P33). Other co-production processes described produce, in addition to cement clinker, sulfuric acid⁷⁵ (P34, P35), aluminum oxide (P36), silica gel (from nepheline),⁷⁶ pig iron (from a bauxite slurry),⁷⁷ a high pressure and temperature process (P37), and magnesium or calcium from dolomite or limestone, respectively.

6. KILN PARAMETERS

6.1 Preheating and Precalcining Processes

Tiggessbaeumer⁷⁸ reviewed cement calcining plants that are based on predrying and calcining. A new process using a travelling grate was patented (P38), in which some of the raw mix is granulated and partially decarbonated in the travelling grate, while the remainder of the mix is partially decarbonated in a cyclone preheater. Pospisil *et al.*⁷⁹ measured the tensile strength of heated raw mixes to explain deposits and plugging in preheaters. They found that the tensile strength of raw mix agglomerates increased with increasing temperature and increasing calcite content. Gartner⁸⁰ reported on a study that sought more efficient ways of removing alkalies from raw materials by handling the high-alkali raw materials separately, but concluded that this was not a practical alternative to conventional precalciner technology. Several papers and patents dealt with fuel in precalciner or preheater systems. Freire⁸¹ described partial substitution of rice husk as fuel in preheating and precalcining towers. A

patent (P39) described a process of introducing the pulverization effluent gas into the transition zone of the calcination and the preheating stage, claiming several advantages for the process. Other patents (P40, P41) suggest disbursing gaseous fuel into a multi-stage suspension preheater at the duct connecting the kiln feed and the lowest cyclone of the preheater, thus improving the efficiency of the system.

6.2 Burning Process

Various computer models for kiln control have been described. Bailey and Willison⁸² reviewed the advantages of a computer control system--its instrumentation, design, and application in lime kilns. A control system developed by F. L. Smidth,⁸³ combining a high-speed infrared temperature scanner with a process computer, was designed to protect the kiln shell and prolong the life of the refractory lining. Guruz and Bac⁸⁴ describe a steady-state mathematical model of cement kilns which uses a zone method to provide temperature distribution in the gas and solid charge, and compound distribution in the solid charge.

The problems associated with heating a rotary kiln for the first time are discussed by Ludera.⁸⁵ Locher⁸⁶ and Sprung⁸⁷ have reviewed the general topic of how burning conditions affect clinker properties. Miller and Egelöv⁸⁸ related NO_x content in kiln exit gases to the kiln operating parameters. In regard to specific kiln parameters, Alimmaryi and Tamas⁸⁹ showed that rapid calcination improved the burnability of cement raw materials and enabled the use of lower calcination temperatures. A long soaking was unnecessary since the maximum temperature and lime saturation factor of the mix were the main factors controlling free lime content of the clinker. Bomas *et al.*⁹⁰ also reported that rapid heating permitted a shorter total residence time in the kiln. The effects of reducing conditions were studied by Sylla,⁹¹ who reported that reducing conditions alter the composition of the C_4AF , increase the content of C_3A , enhance the reactivity of C_3A , and decrease the stability of C_3S . Mackenzie⁹² also found that the composition of C_4AF was altered under reducing conditions, and suggested that the ferrous ions might replace aluminum in the C_3A phase.