

CEMENTS RESEARCH PROGRESS 1986

A survey of the literature on the science of cements published during 1986

**CEMENTS DIVISION
AMERICAN CERAMIC SOCIETY**



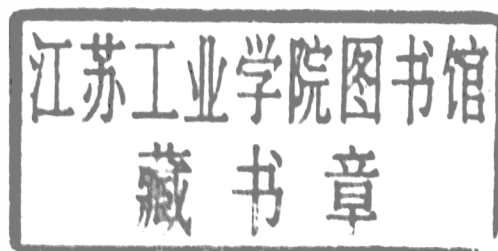
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1986

A survey of the scientific literature on cements,
published during 1986
prepared by members of the Cements Division
of the American Ceramic Society.

Coordinating Editor:

Paul Wencil Brown



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Cements Research Progress 1986

DEDICATED TO
STEPHEN BRUNAUER (1903 - 1986)

Scientist, educator, friend -- that is how most people will remember Stephen Brunauer.

Dr. Brunauer came to the United States in 1921 from Hungary. He studied at the City College of New York, at Columbia, George Washington, and Johns Hopkins Universities. He had a distinguished career at the Fixed Nitrogen Research Laboratory of the Department of Agriculture, in the U.S. Navy, at the Portland Cement Association, and at Clarkson University of Technology.

The B in his name made history. It was joined by the E and T to become known as BET, the acronym for the Brunauer-Emmett-Teller method of measuring surface areas of finely divided and porous solids. The 1938 BET-paper: "Adsorption of Gases in Multimolecular Layers" is believed to be the most widely quoted work in the chemical literature.

It is more than appropriate to dedicate this volume of CRP to Dr. Stephen Brunauer. By introducing surface chemistry into the field of cement and concrete research, he triggered a significant scientific advancement of the basic understanding of cement hydration reactions.

Many thanks Steve.

Jan P. Skalny

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INTRODUCTION

Several important conferences were held in 1986. Most notable among these was the 8th International Congress on the Chemistry of Cement in Rio de Janeiro. As a consequence, the volume of literature of interest to the cement community has been unusually large. This places an additional burden on the chapter contributors and I would like to acknowledge their efforts.

Three of the chapters in CRP-86 have been written by new contributors. I welcome these new authors and thank Peter Hawkins and Sharon DeHayes, Hal Taylor, Micheline Regourd, and Lew Cartz for their contributions.

This volume of CPR contains a special chapter surveying the chemistry of calcium phosphates while discussing the properties of a new calcium phosphate cement.

It is with a sense of loss that this volume of CRP is dedicated to Stephen Brunauer.

Paul Wencil Brown
Gaithersburg, MD

Cements Research Progress 1986

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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/SiO₂ molar ratio; H/S ratio = H₂O/SiO₂ 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

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 A \bar{F} t and A \bar{F} m are more general designations for these classes of compounds.

Due to the nature of the printer used in preparing this issue, the greek letter gamma tends to look like the greek letter tau, e.g. τ . Thus, gamma C₂S appears as τ -C₂S.

TABLE OF CONTENTS

Chapter	Page
INTRODUCTION	iii
LIST OF CHAPTER CONTRIBUTORS	iv
TABLE OF CONTENTS	vii
ABBREVIATIONS AND NOMENCLATURE	ix
1 MANUFACTURE OF STRUCTURAL CEMENTS	1
2 COMPOSITION OF CEMENT MATERIALS	21
3 HYDRATION OF PORTLAND CEMENT	37
4 HYDROTHERMAL REACTIONS OF PORTLAND CEMENT (AND OTHER SPECIAL CURING CONDITIONS)	89
5 PROPERTIES OF HYDRATION PRODUCTS	117
6 ADMIXTURES	139
7 PROPERTIES OF FRESH AND HARDENED CEMENT PASTES	187
8 BLENDED AND MODIFIED PORTLAND CEMENTS, AND HIGH ALUMINA CEMENT	217
9 GYPSUM AND PLASTERS	267
10 FIBER-REINFORCED AND POLYMER MODIFIED CEMENTS	285
11 DURABILITY	297
A NEW CALCIUM PHOSPHATE CEMENT	351
SUBJECT INDEX	381
AUTHOR INDEX	391

Cements Research Progress 1986

Chapter 1

MANUFACTURE OF STRUCTURAL CEMENTS

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Contents

1.	Introduction	2
2.	Burnability of Raw Materials	2
3.	Composition of Materials	3
3.1	Minor Components	3
3.2	Waste Materials	4
4.	Kiln Feed and Fuels	4
4.1	Kiln Feed	4
4.2	Fuel	5
5.	Special Clinker and Manufacturing Processes	6
6.	Kiln Parameters	7
6.1	Preheaters and Precalciners	7
6.2	Burning	8
6.3	Cooling	9
7.	Clinker Grinding	9
7.1	Clinker	9
7.2	Clinker with Slag, Ash or Other Additives	10
7.3	Storage and Handling	10
8.	Environmental Protection	11
8.1	Kiln Dust	11
8.2	NO _x and SO ₂ Emission	11
9.	References	12

1. INTRODUCTION

This chapter reviews published papers and patents on production of structural cement. The emphasis is on processes, not on basic chemistry or equipment.

Of special interest to the readers of this chapter are the first part of Vol. I and also Vol. II from the 8th International Congress on the Chemistry of Cements [1]. The proceedings from the Engineering Foundation Conference entitled "Research on the Manufacture and Use of Cements" [2] should also be noted, as well as the proceedings from the 21st Rock Products Int. Cement Seminar [3].

The modernization of cement plants was discussed by both Taddei [4] and Kurdowski [5], while Steuch [6] reported on the problems involved in setting up a cement plant, the main problems being process control, material flow in the kiln riser duct, and production of low alkali clinker.

2. BURNABILITY OF RAW MATERIALS

By using the sandwich method, Chromy [7] showed that the thermal history of the lime does not affect lime reactivity or the rate of C_3S formation. Ziemer et al. [8] studied the effect of different gas atmospheres on the reaction of CaO and SiO_2 . The acceleration effect of water vapour on the reaction was increased in the presence of CaO in the status nascendi. The effect on clinker formation and clinker phases when changing from fuel oil and natural gas to brown coal dust was reported by Wächtler [9].

Masood et al. [10] have reviewed the use of mineralizers, such as fluorides, sulphates, chlorides, phosphates, and oxides. The structure and reactivity of alite produced at low temperatures using CaF_2 and ZnO as mineralizers was reported by Bürger et al. [11], and Ludwig et al. [12] showed that lowering the lime

saturation factor decreases the cement burning temperature, which may be further reduced by adding ZnO as mineralizer. Addition of ZnO reduced the burning temperature of chlorite-muscovite and kaolinite based raw meals. Tonak [13] observed that K_2CrO_4 had a similar effect. The influence of two different CaF_2 products on the linker formation at different temperatures was studied by Perez-Méndez et al. [14], and Misra et al. [15] found that 9.5% CuO when added in the form of $Cu(NO_3)_2 \cdot 6H_2O$ was the most efficient mineralizer for alite formation from rice husk ash and calcium carbonate.

3. COMPOSITION OF MATERIALS

3.1 Minor Components

Several publications dealt with the various problems concerning alkalis, sulphur and chloride. Kurdowski [16] studied the internal circulation and found that chlorine increases the volatility of alkalis, while sulphur reduces the volatility. Vogel [17], in a double paper, described the evaporation of alkalis in the kiln system with and without sulphates and reviewed the effect of raw meal bed thickness on the evaporation and condensation in the kiln system and the design of by-pass systems. The use of a by-pass to control the amount of volatiles, the proportion of gas through the by-pass, and the effect on fuel consumption were reported by Popescu et al [18]. Strunge et al. [19] published the third part of their study on the influence of alkalis and sulphur on cement properties. They found at the optimum degree of sulphatization depends on the lime standard, while the alumina ratio may vary without changing the optimum sulphatization degree. Richartz [20] found that the degree of sulphatization is only really important for clinker containing more than about 1% K_2O . The effect of alkalis on cement strength was also studied.

The circulation of alkalis, sulphur, and chloride in a rotary kiln with heat exchanger was studied by Ioganson et al.

[21]. A 1% increase in the MgO content in the raw meal caused a 9% increase in the volatility coefficient. Uchikawa et al. [22] studied variations in clay minerals and MgO in raw materials, and their effect on cement hydration.

Wächtler et al. [23] studied the effect of alkalies, sulphur, and chloride from the fuel on the aluminate reactivity, and Kihara [24] reports the effect of coal minerals on the clinker composition and quality.

The behavior of heavy metals such as Tl and Pb is discussed by Kirchner [25]. Tl is highly volatile, and thallium halides build an internal cycle in the cyclone preheater. No thallium is combined in the clinker, while substantial amounts of lead are combined.

3.2 Waste Materials

Ostrovlyanchik et al. [26] found that the use of power plant ash as raw material instead of argillaceous components was highly effective for increasing the output of a wet process kiln. Fuel savings were also obtained.

Kuznetsova et al. [27] investigated the effect of using sulphate containing wastes in clinker production. By simultaneous addition of MgO, the amount of C_3S was increased.

In a patent [P1] a limestone - slag mixture is mixed with crushed fireclay from spent furnace linings. In another patent [P2] synthetic slag and ash from natural magna melt are used as raw materials for clinker burning.

4. KILN FEED AND FUELS

4.1 Kiln Feed

A comprehensive review on size reduction and homogenization of raw materials is given by Mälzig et al. [28]. Air separation as well as grinding of clinker are also included.

Schneider [29] also reviewed dry grinding systems for raw materials and compared energy consumption, while Ostmeier et al. [30] discussed methods for controlling raw materials composition including the effect on kiln operation.

A new control system for raw mix preparation based on prompt neutron activation analysis (PGNNA), which permits elemental analysis of bulk solids in nearly real time, was reported by Weiss et al. [31], while Wang [32] described a control system for direct digital control of the flow rate of four belt weighers, control of raw mix ratios and control of the productivity optimization of the crusher. Joergensen [33] reported on practical experience with Atox mills for grinding of raw materials, and Petersen [34] described how to calculate the blending efficiency of a continuous raw meal blending silo.

4.2 Fuel

A review by Hochdal [35] covers aspects such as fuel supply, processing, storage, and control of fuels and waste fuels, combustion systems, and heat recovery. Radic [36] reviewed methods for coal drying and grinding, while energy conservation in the cement industry was reviewed by Aguanell et al. [37].

Mullinger [38] described how a kiln burner system can be designed to achieve optimum combustion and heat transfer.

The use of waste fuels was reported in a survey by Hupta [39]. Practical experience gained from using the waste was included. The reasons for variations in fuel energy consumption are discussed by Seidel [40]. It is shown that energy savings are possible, especially for fuels with low flame temperature or with low heat variation capacity. Vértessffy et al. [41] found for two different kiln systems that the total fuel consumption was strongly influenced by the silicate modulus of the clinker and the amount of secondary fuel.

Studying combustion of solid fuels, Tiggesbäumker et al. [42] found that higher oxygen concentrations and temperatures at

the inlet of the calciner promote the initiation of combustion but not the overall burn-out. Kupper et al. [43] and Schulz et al. [44] also studied combustion of solid fuels and found that alkali salts had an inhibiting effect on fuel burn-out.

The use of solid fuels with low volatile contents in precalciners was reported by Narang [45] and Nielsen [46]. The former states that the fuel must be ground to 5% +90 and requires a long retention time for complete burn-out, while Nielsen found a remarkable increase in the degree of combustion by raising the temperature level in the calciner. This was shown in a precalciner fired with semi-anthracite and pet-coke.

Chen et al. [47] described how it was possible to utilize the fuel calorific value of the carbonaceous shale used as secondary raw material by feeding the shale directly to the calciner.

5. SPECIAL CLINKER AND MANUFACTURING PROCESSES

Kupper et al. [48] describe experience and operating data for plants producing white cement. By comparing with grey cement plants, the differences in technology are seen, but also the possibilities of controlling the cement quality. Uchikawa et al. [49] studied the influence of minor components, such as Cr, Fe, and Mn, on the colour of white cement. The importance of burning condition control (atmosphere, cooling) as well as the effect of mineralizers are reported. The possibility of manufacturing white cement in Albania using local raw materials was demonstrated by Pecani [50]. A patent [P3] describes the production of white clinker from limestone and a silica gel waste from the production of AlF_3 .

A patent for production of white clinker [P4] describes an apparatus, where the clinker is cooled in the fuel gas to recover a considerable part of the heat content in the gas.

Belite cement was the subject of several papers. Müller et al. [51] studied cement properties, such as strength and setting of differently cooled belite clinker. Gies et al. [52] reported on the composition of belite clinker and found that high proportions of K_2O could be incorporated in C_2S and stabilize the hydraulically active α' - and α - C_2S . The effect of K_2O and MgO addition was investigated by Sychev et al. [53]. The addition decreased the sintering temperature without decreasing the activity of the clinker. The effect of K_2O , MgO , and SO_3 in the production of belite clinker was studied by Chimaev et al. [54], and the effect of SO_3 alone was reported by Mielke et al. [55,56].

A new method of mechanical activation for producing oil well cement without burning, using industrial wastes as raw materials was reported by Karimov et al. [57].

Two patents [P5] and [P6] use $CaCl_2$ in combination with other raw materials for burning cement clinker.

6. KILN PARAMETERS

6.1 Preheaters and Precalciners

Kwech [58] described 28 different calcining systems, and the problems of calciner design, choice of air supply system, fuel feed-in points, position of raw meal feed-in, as well as the mixing of combustion air, fuel and raw meal.

A mathematical model describing the thermal performance of a cyclone preheater was reported by Fei [59], while the energy savings by conversion of a four-stage into a five-stage cyclone preheater were described by Igawa et al. [60]. Unland [61] described the design of the calciner to achieve complete burn-out of various fuels. Rosemann [62] developed a mathematical model that indicated the combustion rate of the fuel could be raised by supplying only a part of the raw meal to the calciner. Warshawsky et al. [63] reported that the calcination increased when a major part of the calcined meal was recirculated to the calciner.