PROCEEDINGS
OF THE
THIRTEENTH INTERNATIONAL CONFERENCE
ON
CEMENT MICROSCOPY

International
Cement
Microscopy
Association

April 8-11, 1991
Tampa, Florida

INTERNATIONAL CEMENT MICROSCOPY ASSOCIATION
1206 COVENTRY LANE, DUNCANVILLE
TEXAS, 75137, USA

PROCEEDINGS OF THE THIRTEENTH INTERNATIONAL CONFERENCE ON CEMENT MICROSCOPY

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INTERNATIONAL CEMENT MICROSCOPY ASSOCIATION
1206 COVENTRY LANE, DUNCANVILLE
TEXAS, 75137, USA

WYNDHAM HARBOUR ISLAND HOTEL
TAMPA, FLORIDA
APRIL 8-11, 1991

A WORD OF THANKS TO OUR CORPORATIONS AND COMPANIES

Centex Cement, Inc., USA

Lafarge Corporation, USA

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Portland Cement Association, USA

Construction Technology Laboratories, Inc., USA

Coplay Cement Company, USA

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FROM THE ENTIRE COMMITTEE OF THE INTERNATIONAL CEMENT MICROSCOPY ASSOCIATION

FOREWARD

ICMA actually started in October 1978, when Ken Earhard, Vice President of the Gifford-Hill Cement Company, suggested that a gathering of cement microscopists for the mutual exchange of ideas and technical data would be a good idea. A meeting was proposed and held in Arlington, Texas, with appromately 45 people in attendance. The primary speaker for this meeting was Don Campbell of PCA. John Marlin of O.K.C. also gave a demonstration of staining and etching techniques. The whole tone of the meeting was kept very informal and application techniques were stressed as our focal point.

In March 1980, a second meeting was held. Gifford-Hill was joined this time by Southwestern and General Portland as sponsoring companies. Approximately 175 people attended the meeting held in Dallas, Texas. The meeting's highlight was an address by Dr. Yoshio Ono. Application techniques were also stressed at this meeting and a small workshop and exhibition of equipment were held in conjunction with the meeting. There were no proceedings published for the first and second meetings.

The actual formation of the ICMA occurred at the third meeting (1981). At this meeting, we gave up our company sponsorship and went independent. Following 1980, ICMA met annually as follows:

- Third Annual Meeting - March 16-19, 1981, Houston, Texas
- Fourth Annual Meeting - March 28-April 1, 1982, Las Vegas, Nevada
- Fifth Annual Meeting - March 14-17, 1983, Nashville, Tennesee
- Sixth Annual Meeting - March 26-29, 1984, Albuquerque, New Mexico
- Seventh Annual Meeting - March 25-28, 1985, Fort Worth, Texas
- Eighth Annual Meeting - April 6-10, 1986, Orlando, Florida
- Ninth Annual Meeting - April 5-9, 1987, Reno, Nevada
- Tenth Annual Meeting - April 11-14, 1988, San Antonio, Texas
- Eleventh Annual Meeting - April 10-13, 1989, New Orleans, Louisiana
- Twelfth Annual Meeting - April 2-5, 1990, Vancouver, B.C., Canada
- Thirteenth Annual Meeting - April 8-11, 1991 Tampa, Florida

- The Fourteenth Annual Meeting is scheduled for April 6-9, 1992 in Costa Mesa (Orange County), California.

The proceedings of each meeting, containing all the papers, are published annually and available from the ICMA headquarters address.

INTRODUCTORY REMARKS

These are the Proceedings of the Thirteenth International Conference on Cement Microscopy, held in Tampa, Florida, USA, from from April 8–11, 1991. The papers presented in this edition address the results of work completed by different experts in the field from throughout the world. The main focus of these papers is the relationship between processing techniques and the properties of the product, with an emphasis on microscopic techniques.

These Proceedings, as well as the previous ones, offer both a comprehensive reference and the best authoritative picture available of knowhow and experience in cement microscopy gathered from all over the world. It is meant to serve as a working tool and source of informative references for problem solving in the areas of clinker, cement and concrete.

I wish to express my personal thanks and gratitude to the authors for their continuous scientific contributions which have made this conference and post-conference possible.

On behalf of the ICMA Committee, I extend a warm welcome to all attendees of ICMA's 1991 conference. I wish each of you a happy stay, enjoyable time and lasting memories of Tampa.

George R. Gouda

NOTES

The following abbreviated formulae, commonly used in cement technology, are used in these proceedings:

$S = SiO_2$ $A = Al_2O_3$ $F = Fe_2O_3$ $C = CaO$

C_3S = $3\,CaO.SiO_2$

C_2S = $2\,CaO.SiO_2$

C_3A = $3\,CaO.Al_2O_3$

C_4AF = $4\,CaO.Al_2O_3.Fe_2O_3$

C_2A = $2\,CaO.Al_2O_3$

C_2F = $2\,CaO.Fe_2O_3$

S.M. = Silica Modulus

A.M. = Alumina Modulus

H.M. = Hydraulic Modulus

L.S.F.= Lime Saturation Factor

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REPLACEMENT OF SILICA BY SANDSTONE IN A RAW MEAL - ITS EFFECT ON THE CLINKER MICROSTRUCTURE

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ABSTRACT

A dry process cement plant that was originally using silica as one of the components for its Type II cement raw meal decided to replace it by sandstone in order to prolong the life of the quarry. This led to distinct changes in the clinker microstructure. These differences are described in this paper.

INTRODUCTION

A dry process cement plant that had been using the raw meal composition (given below in Table 1) in the past to produce Type 20 (ASTM Type II) cement decided to modify the composition in order to prolong the life of the quarry.

The silica component (2.7%) in the raw meal was replaced by 12.7% sandstone, and the resultant modified composition was as follows (Table 1):

Table 1

Raw meal composition before and after modification

Before modification		After modification	
Limestone	46.3%	Limestone	59.7%
Shale	49.5%	Shale	26.2%
Silica	2.7%	*Sandstone*	12.7%
Iron oxide	1.5%	Iron oxide	1.4%

In order to determine the effect of this modification on the clinker a detailed comparative microstructural study of the two clinkers, one made with silica and the other with sandstone was carried out by the authors. Their findings are presented in this paper.

METHODS

Three methods that were used for the microstructural investigation are as follows:

1) X-ray diffraction analysis (XRDA) - for mineralogical phase identification
2) Optical microscopy - for examination of microstructure of clinkers
3) Scanning electron microscopy/energy dispersive X-ray analysis (SEM/EDXA) - (a) for examination of microstructure using fractured surfaces of clinkers, (b) qualitative phase composition, (c) quantitative microanalysis of phases (d) elemental X-ray mapping to study the distribution pattern of important minor elements in these clinkers, and (e) backscattered electron imaging (BEI) of interstitial matrix.

1) XRDA - Proper identification of all the major and minor phases in an as-received clinker is virtually impossible because of the innumerable peak overlaps of major phases (1). Therefore, a commonly adopted practice among diffractionists is to treat the as-received ground clinker in salicyclic acid + methanol solution (2) to dissolve out the silicate phases, leaving the interstitial matrix phases and the minor cement compounds such as sulfates, periclase and freelime unaffected. The silicate phases are first identified on the as-received sample, followed by identification of the other phases on the treated sample. XRDA was carried out with a Rigaku D-Max X-ray diffractometer run at 30 kV, 25 mA.

2) Optical microscopy - Polished sections of clinkers embedded in epoxy resin were prepared. These were then chemically etched with dilute succinic acid, followed by dilute nitric acid etch (3) for distinction between the various phases.

3) SEM/EDXA - A JEOL 840A SEM with a Link 100085 EDXA was also used for examination and analysis of the clinker samples.

RESULTS

The chemical analysis of all the raw meal ingredients, the raw meal itself, the clinkers and cements before and after the raw meal modification are shown in Table 2. It is obvious that the limestone is slightly siliceous. The silica used in the original raw meal was extremely rich in SiO_2, whereas the sandstone in the modified raw meal contains substantial amounts of Al_2O_3, K_2O and MgO. Its MgO content (9.6%) is exceptionally high, suggesting the association of dolomite with sandstone, and the high proportions of K_2O and Al_2O_3 indicate the presence of feldspar in the sandstone.

XRDA

From Fig. 1 it is evident that all the four major phases (C_3S, C_2S, C_3A and C_4AF) that constitute portland cement clinker are present in both the clinkers studied. From peak integration, the amount of C_3S in the silica clinker is lower than the sandstone clinker (Table 3). This, however, does not appear very clearly in the Bogue composition given in Table 4. Monoclinic alite is present in both the clinkers. β-C_2S was positively identified in both, but C_2S content in the silica clinker was found to be slightly higher (Table 3). A similar trend is seen in the Bogue composition (Table 4). Figure 2 represents the XRD traces of the SAL treated samples that show the presence of C_3A, C_4AF, MgO and CaO. The C_3A in these two clinkers form a mixture of cubic and orthorhombic types. From Table 4 total C_3A is slightly lower in the silica clinker.

From peak integrtion periclase in the sandstone clinker is distinctly higher (Table 3). This is also clear in the XRD traces (Fig. 2). The amount of freelime is very low in both the clinkers. Arcanite (K_2SO_4) was identified in the sandstone clinker (Fig. 2).

No difference in the aluminoferrite phase was observed. There is very little difference in the LSF, SM, and AM values (Table 4) before and after modification.

Table 2

Chemical analysis of raw meal ingredients, raw meals, clinkers and cements

	L.O.I.	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	Na_2O	K_2O	Free CaO
Limestone	39.78	6.04	1.18	0.5	49.98	0.86	0.38	0.05	0.38	--
Shale	32.59	15.62	3.84	1.12	42.44	0.84	1.28	0.38	1.27	--
Sandstone	19.29	42.98	8.07	1.65	12.49	9.59	1.31	0.68	4.00	--
Silica	1.11	94.24	1.28	1.34	0.55	0.12	0.4	0.01	0.4	--
Iron	0.76	0.66	0.03	94.48	0	0.01	0.57	0	0.01	--
T20 raw meal with silica	---	14.32	2.87	2.16	42.47	1.1	1.15	0.22	1.14	--
T20 raw meal with sandstone	---	14.17	2.97	2.14	41.5	1.67	1.04	0.22	1.26	--
T20 clinker with silica	---	22.32	4.71	3.52	65.3	1.56	0.39	0.28	0.91	--
T20 clinker with sandstone	---	22.7	4.56	3.26	64.81	2.25	0.52	0.3	1.1	--
T20 cement with silica	0.76	21.83	4.49	3.39	63.79	1.60	2.49	0.28	0.90	0.32
T20 cement with sandstone	0.79	21.49	4.55	3.40	63.12	2.35	2.61	0.27	0.93	0.31

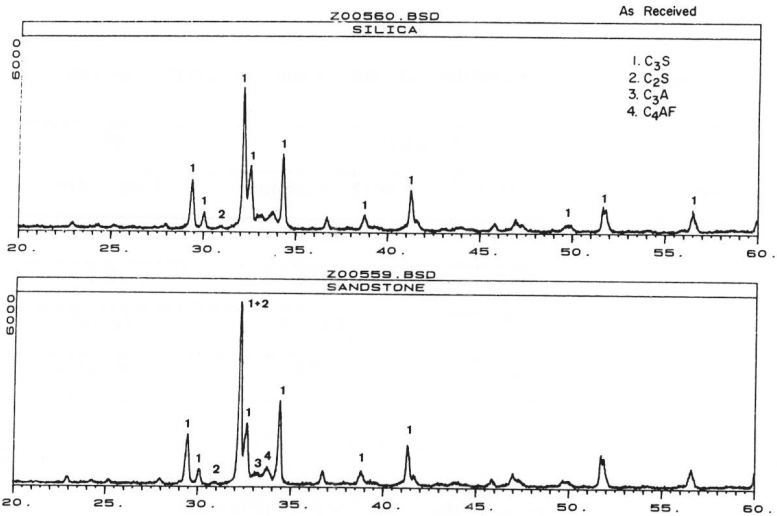

Fig. 1. XRD traces of as-received clinkers made with silica and sandstone

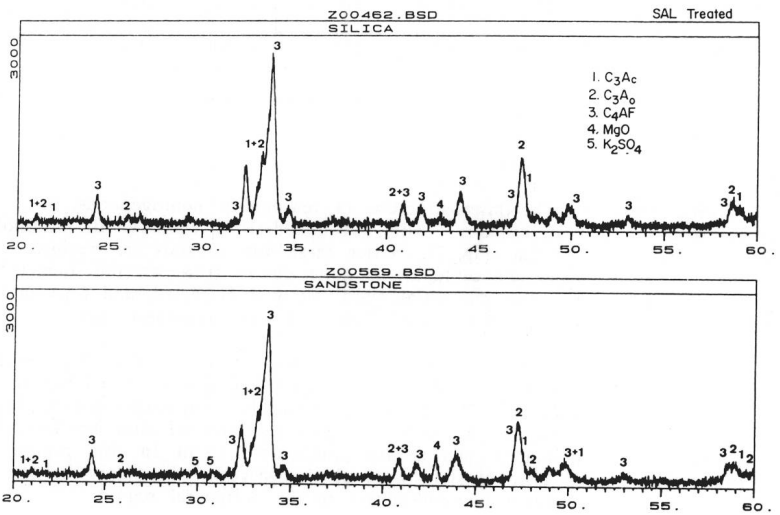

Fig. 2. XRD traces of SAL treated clinkers made with silica and sandstone

Table 3

Integrated peak intensities of determinable important phases

Phase	Clinker		XRD
	With silica	With sandstone	Peak (°2θ)
C_3S	28184	35613	51.7
C_2S	300	260	30.9
C_3S & C_2S (combined)	88777	104614	32.22
MgO	143	172	42.92

Table 4

Mineralogical composition and modulii of clinkers before and after raw meal modification

Clinker	C_3S	C_2S	C_3A	C_4AF	LSF	SM	AM
With silica	56.04	22.91	6.39	10.78	91.23	2.76	1.32
With sand-stone	56.19	21.50	6.81	10.53	91.84	2.71	1.37

Optical microscopic examination

Silica clinker: The microstructure is reasonably homogeneous in comparison to the sandstone clinker. Alite is subhedral to euhedral in morphology, the maximum size being 90 μm (Fig. 3). Often these alite crystals are fractured. The belite though round in shape and lamellar, is quite coarse (Fig. 4), the diameter varying from 15 to 80 μm. The interstitial matrix is well dispersed, and C_3A is finely crystallized. The clinker is slightly more porous in the peripheral region.

Sandstone clinker: This clinker is very heavily fused (Fig. 5), particularly in the core region. Alite is excessively coarse, often ranging from 120-150 μm. Highly corroded alite crystals are also present. Belite is compacted between fused alite crystals (Fig. 5). Owing to such a high degree of fusion of alite crystals in the central region, interstitial matrix phases are practically absent in this region. Alkali sulfate rims around alite crystals were also observed. Secondary belites can be seen in Fig. 6. The clinker is very porous in the peripheral region.