OCDO--97 001482

NEW HIGH-CAPACITY, CALCIUM-BASED SORBENTS-
CALCIUM SILICATE SORBENTS

Department of Chemistry
Case Western Reserve University
Cleveland, OH 44106-7078

Malcolm E. Kenney
Hurlbut Professor of Chemistry

Gwanghoon Kwag
Research Assistant

Ray-Kuang Chiang
Research Assistant

Kerry L. Fillgrove
Research Assistant

FINAL REPORT

OCRC/94-1.8

RECEIVED

MAY 29 1996

DEPARTMENT OF DEVELOPMENT
OHIO COAL DEV OFFICE

This project was funded in part by the
Ohio Coal Development Office
Department of Development
State of Ohio

February 28, 1996

MASTER

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

DISCLAIMER

**Portions of this document may be illegible
in electronic image products. Images are
produced from the best available original
document.**

1. TABLE OF CONTENTS

1.	Table of Contents	2
2.	List of Figures	3
3.	List of Tables	4
4.	List of Symbols and Abbreviations	5
5.	Executive Summary	6
6.	Introduction	9
7.	Hydrated Portland Cement Sorbent	11
8.	Experimental Details	18
9.	Syntheses	22
10.	Results and Discussion	25
11.	Conclusions	45
12.	Collaborations	47
13.	References	48

2. LIST OF FIGURES

1.	Structure of 11-Å tobermorite	14
2.	Structure of $\text{Ca}(\text{OH})_2$	14
3.	Schematic structure of $[\text{Ca}_2(\text{Al,Fe})(\text{OH})_6]_2(\text{SO}_4, \text{CO}_3, 2\text{OH}) \cdot 6\text{H}_2\text{O}$ or AFm	15
4.	Portion of unit cell of $\text{Ca}_3\text{Al}_2(\text{O}_4\text{H}_4)_3$, hydrogarnet, showing $\text{Al}(\text{OH})_6$ and $(\text{OH})_4$ units in structure	16
5.	Schematic drawing of sorption apparatus	21
6.	Infrared spectra of portland cement sorbent produced in pressure vessel with MgO-stabilized ZrO_2 beads, runs 2 and 4, Table III	34
7.	X-ray powder patterns of portland cement sorbent produced in pressure vessel with MgO-stabilized ZrO_2 beads, runs 2 and 4, Table III	35
8.	X-ray powder patterns of portland cement sorbent produced in pressure vessel with MgO-stabilized ZrO_2 beads, runs 5 and 8, Table III	36
9.	X-ray powder patterns of portland cement sorbent produced in stirred ball mill with Y_2O_3 -stabilized ZrO_2 beads, runs 16-18, Table IV	37
10.	X-ray powder patterns of portland cement sorbent produced in pressure vessel with Y_2O_3 -stabilized ZrO_2 beads, runs 19-21, Table IV	38
11.	X-ray powder patterns of clinker sorbent produced in glass flask with MgO-stabilized ZrO_2 beads, runs 22, 23 and 27, Tables V and VI	39

3. LIST OF TABLES

I.	Weight Percent Composition of Type I Portland Cement	13
II.	Atom Percent Composition of Type I Portland Cement	13
III.	Portland Cement Sorbent Produced in Pressure Vessel with MgO-Stabilized ZrO_2 Beads	40
IV.	Portland Cement Sorbent Produced in Stirred Ball Mill with Y_2O_3 -Stabilized ZrO_2 Beads	42
V.	Crushed Clinker Sorbent Produced in Glass Flask with MgO-Stabilized ZrO_2 Beads	43
VI.	Clinker Fines Sorbent Produced in Glass Flask with MgO-Stabilized ZrO_2 Beads	44

4. LIST OF SYMBOLS AND ABBREVIATIONS

A	Al_2O_3
AFm	a phase in hydrated cement which can be approximated as $[\text{Ca}_2(\text{Al,Fe})(\text{OH})_6]_2(\text{SO}_4, \text{CO}_3, 2\text{OH}) \cdot 6\text{H}_2\text{O}$
BET	Brunauer-Emmett-Teller
C	CaO
$\bar{\text{C}}$	CO_2
C_3ASH_4	$\text{Ca}_3\text{Al}_2(\text{SiO}_4)(\text{O}_4\text{H}_4)_2$
C_3S	alite, Ca_3SiO_5
C_2S	belite, $\beta\text{-Ca}_2\text{SiO}_4$
C-S-H	the phase $\text{CaO-SiO}_2\text{-H}_2\text{O}$
C_2SH	$\alpha\text{-Ca}_2(\text{SiO}_3\text{OH})(\text{OH})$
F	Fe_2O_3
H	H_2O
S	SiO_2
$\bar{\text{S}}$	SO_3

5. EXECUTIVE SUMMARY

Aim

A search is being carried out for new calcium-based SO_2 sorbents for induct injection. More specifically, a search is being carried out for induct injection calcium silicate sorbents that are highly cost effective.

Current Year Objectives

The current year objectives include the study of sorbents made by hydrating ordinary or Type I portland cement or portland cement clinker (a cement intermediate) under carefully selected conditions.

Current Year Results

During the current year, the hydration of portland cement in a stirred pressure vessel at temperatures up to 180°C , and in a high speed, stirred ball mill at stirring rates of 3000 rpm has been studied. In addition, the hydration of clinker (a cement intermediate that is ground with a small amount of gypsum to make cement) has been studied. The apparatus that has been used in this work is a stirred glass flask apparatus. The grinding medium that has been used in these experiments is MgO -stabilized ZrO_2 beads or Y_2O_3 -stabilized ZrO_2 beads. The variables studied have included hydration time, hydration temperature, stirring rate, slurry concentration and

SiO₂ addition. The sorbents have been characterized by infrared spectroscopy, X-ray powder diffractometry, BET surface area measurement, and SO₂ uptake measurement (as determined with a bench scale sand-bed sorber).

The results obtained show that an excellent portland cement sorbent can be prepared by milling cement at 120°C at 600 rpm for 15 minutes with MgO-stabilized ZrO₂ beads. They also show that clinker, which is cheaper than cement (since it is an intermediate in the preparation of it) can be used interchangeably with cement as a starting material. Further, it is clear that while a high surface area may be a desirable property of a good sorbent, it is not a requisite property. Among the hydration reaction variables, milling time is highly important, reaction temperature is important and stirring rate and silicate-to-H₂O ratio are moderately important. The components of hydrated cement sorbent are various combinations of C-S-H, calcium silicate hydrate: Ca(OH)₂; AFm, a phase in hydrated cement which can be approximated as [Ca₂(Al,Fe)(OH)₆]₂(SO₄,CO₃.2OH).6H₂O; α-Ca₂(SiO₃OH)(OH); Ca₃Al₂(SiO₄)(O₄H₄)₂; alite, ~ Ca₃SiO₅; and belite, ~ β-Ca₂SiO₄; with C-S-H, Ca(OH)₂ and AFm being the desirable components. The addition of active SiO₂ to the reaction mixture can increase the amount of C-S-H and reduce the amount of Ca(OH)₂ in the sorbent. Overly vigorous conditions can reduce the amount of C-S-H and increase the amount of α-Ca₂(SiO₃OH)(OH) in it.

The hydration times have been decreased from a previously reported minimum of 3 hours to the above stated 15 minutes. This results in a much lower projected process costs since stirring is energy intensive.

In sum, the project has proceeded as anticipated to the extent a research project can be expected to, and it has yielded valuable results.

Work To Be Done

In the coming year, efforts will be made to find ways to make calcium silicate hydrate (C-S-H) type sorbents that have still better combinations of SO₂ uptake, calcium utilization and projected cost. Specifically, the objectives of the work to be done are to find ways to make hydrated portland cement sorbents for SO₂, or similar sorbents for SO₂, that are still simpler to make, require still less power to make and utilize still shorter milling times. Additional objectives are, as necessary, to install instrumentation, construct apparatus and carry out studies of pure reference compounds designed to yield base-line data.

Collaborations

Analytical work was done on samples of hydrated cement sorbent for Prof. Keener of the University of Cincinnati. Also help on the preparation of hydrated cement sorbent was obtained from personnel of Union Process Corporation (Akron) in the grinding laboratories of Union Process.

6. INTRODUCTION

Desulfurization of Flue Gas from Power Plants

About 20% of the coal known on earth is in the United States.¹ Much of the U.S. coal can be extracted relatively inexpensively. As a consequence of this, coal is widely used in the U.S. to fire electric power plants.

Much of the coal used to fire power plants contains considerable sulfur. The use of such high-sulfur coal in power plants leads to the emission of large amounts of SO_2 (about 70% of the SO_2 released in the U.S. is from coal-fired power plants²). Because of laws enacted as a result of public demand, particularly the Clean Air Act Amendments of 1990, the coal and power industries are in the process of developing and implementing cost-effective abatement procedures and technologies for SO_2 emissions from power plants. The abatement procedures that are currently of interest include coal switching and coal blending. The abatement technologies of interest include pre-furnace sorbent addition, in-furnace sorbent injection, in-duct sorbent injection, in-duct sorbent-slurry injection (spray drying), and in-duct sorbent-slurry scrubbing (wet scrubbing).³

In-Duct Sorbent Injection

Each of these procedures and technologies has its advantages, and each has been studied or already adopted in some form. A technology of particular interest is

in-duct sorbent injection.⁵ This has low capital costs and low space requirements. These features of it are attractive for use in retrofitting older plants with limited expansion space and for use in new plants with moderate SO₂ abatement requirements. Sorbents such as Ca(OH)₂, NaHCO₃ and a Ca(OH)₂-fly ash product have been considered for use in this technology, but none of these sorbents combines low cost, high reactivity and the ability to give environmentally acceptable sorption byproducts.⁵⁻⁷

Objectives of Work

This situation has led to the current multiyear study. The main objective of this work has been, and continues to be, that of finding one or more good induct injection sorbents. This effort has been focused on Ca-based sorbents because Ca is nontoxic and abundant (it is 5th in abundance in the earth's crust, and constitutes 5% of it⁸).

The objectives of the current year include the study of sorbents made by hydrating portland cement.

The co-sponsor of the project is Case Western Reserve University. It contributed some of the time of the principal investigator.

7. HYDRATED PORTLAND CEMENT SORBENT

Portland Cement

Portland cement is a complex mixture. It is produced by a two-step process. In this process, a limestone-clay or a limestone-shale mixture is first partially fused at about $1450^{\circ}\text{C}^{9a}$ and then the resultant, clinker, a hard, rock-like product, is ground with a small proportion of gypsum, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$.

The second step in this process is energy intensive, requiring about 125-185 kJ/kg. Thus, clinker is less expensive than cement.^{9b}

The main components of cement are a phase called alite, $\sim\text{Ca}_3\text{SiO}_5$; a phase called belite, $\sim\beta\text{-Ca}_2\text{SiO}_4$; an aluminate phase, $\sim\text{Ca}_3\text{Al}_2\text{O}_6$; a ferrite phase, $\sim\text{Ca}_3\text{AlFeO}_5$; and gypsum $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$. On a weight basis of ordinary or Type I portland cement is composed of about 50-70% alite, 15-30% belite, 5-10% aluminate phase, 5-15% ferrite phase and 3-4% gypsum.^{9a} Cement thus contains about 45% Ca on a weight-percent basis and about 30% Ca on an atom-percent basis, Tables I and II.

Hydration of Portland Cement

Under ordinary hydration conditions, that is, with a H_2O :cement ratio of 0.5 to 1, the alite of cement gives the calcium silicate hydrate C-S-H and also $\text{Ca}(\text{OH})_2$.¹⁰

or in cement chemist's notation

C-S-H is an amorphous phase having a layer structure similar to that of

11 Å-tobermorite. Figure 1.^{10,11} $\text{Ca}(\text{OH})_2$ is a crystalline compound with a layer structure. Figure 2.^{10,11} Under ordinary conditions, the rate of hydration of the alite in cement is low, essentially complete hydration taking about a year.¹⁰

The belite of cement gives C-S-H and $\text{Ca}(\text{OH})_2$ under ordinary conditions:

or

This hydration is very slow, essentially complete hydration taking more than four years.¹⁰

The hydration of the mixture of the aluminate phase, ferrite phase and gypsum present in cement in the presence of atmospheric CO_2 gives an aluminate phase called AFm:

or

Table I. Weight Percent Composition of Type I Portland Cement

	source	Ca	Mg	Fe ^a	Al	Si	Mn ^b	K	Na	Sr	Ti	O	P ^c	S ^d	total ^e
cement	Medusa	45.53	0.80	2.31	2.75	9.65	0.09	0.69	0.11	0.13	0.16	34.89	0.07	1.05	100

^a Reported as Fe₂O₃. ^b Reported as Mn₂O₃. ^c Reported on P₂O₅. ^d Reported SO₃. ^e Calculated on basis of composition after ignition.

Table II. Atom Percent Composition of Type I Portland Cement

	source	Ca	Mg	Fe ^a	Al	Si	Mn ^b	K	Na	Sr	Ti	O	P ^c	S ^d	total ^e
cement	Medusa	29.12	0.84	1.06	2.61	8.80	0.04	0.45	0.12	0.04	0.08	55.93	0.06	0.84	100

^a Reported as Fe₂O₃. ^b Reported as Mn₂O₃. ^c Reported on P₂O₅. ^d Reported SO₃. ^e Calculated on basis of composition after ignition.

Figure 1. Structure of 11-Å tobermorite (from Ref. 12, used with permission).

Figure 2. Structure of Ca(OH)₂ (from Ref. 12, used with permission).

AFm has a layer structure. Figure 3.^{9d,10,12-17} This hydration-carbonation reaction is slow, taking about 100 days.¹⁰

Related Species

Ca₃Al₂O₆ by itself hydrates within 30 minutes to a mixture of [Ca₂Al(OH)₆](OH)·6H₂O and [Ca₂Al(OH)₆][Al(OH)₄]·3H₂O:¹⁰

Figure 3. Schematic structure of $[\text{Ca}_2(\text{Al,Fe})(\text{OH})_6]_2(\text{SO}_4, \text{CO}_3, 2\text{OH}) \cdot 6\text{H}_2\text{O}$ or AFm (from Ref. 12. used with permission).

or

These compounds then react with each other within one to two days to give hydrogarnet:

Figure 4. Portion of unit cell of $\text{Ca}_3\text{Al}_2(\text{O}_4\text{H}_4)_3$, hydrogarnet, showing $\text{Al}(\text{OH})_6$ and $(\text{OH})_4$ units in its structure (from Ref. 12, used with permission).

or

Hydrogarnet is an end member of the hydrogarnet garnet-grossular garnet series,

$\text{Ca}_3\text{Al}_2(\text{SiO}_4) - \text{Ca}_3\text{Al}_2(\text{O}_4\text{H}_4)$.^{18,19} It contains unusual tetrahedral $\text{O}_4\text{H}_4^{4-}$ ions. Figure 4, while grossular garnet contains tetrahedral SiO_4^{4-} ions. A phase in this series is katoite.¹⁹ It contains, as implied, both $\text{O}_4\text{H}_4^{4-}$ and SiO_4^{4-} ions.

Another species of interest in connection with the hydration of cement is $\alpha\text{-Ca}_2(\text{SiO}_3\text{OH})(\text{OH})$. This silicate contains tetrahedral $\text{SiO}_3\text{OH}^{3-}$ ions.^{9a}

Hydration of Clinker

The hydration of the alite and belite of ground clinker under ordinary conditions gives C-S-H and Ca(OH)_2 . The hydration of the mixture of the aluminate and ferrite phases in clinker in the presence of atmospheric CO_2 yields AFm which is devoid of SO_4^{2-} ions under ordinary conditions.^{9f}

Portland Cement Sorbent

Recently it has been shown that a good sorbent for SO_2 can be prepared by hydrating portland cement at a H_2O :cement ratio of 10 to 1.⁴ This sorbent can be prepared moderately rapidly if vigorous agitation and elevated temperatures are used.

8. EXPERIMENTAL DETAILS

Infrared Spectroscopy

The infrared spectra were obtained with a commercial Fourier Transform infrared spectrophotometer (Model 16 PC; Perkin-Elmer, Norwalk, CT) interfaced to a PC (DEC 433dx LP 486 PC; Digital Equipment, Westminister, MA). Samples were ground in Nujol, and the resulting mulls were supported on KBr plates. Typical relevant instrument settings used are:

range	4,000-400 cm^{-1}	resolution	4 cm^{-1}
background scans	2	number of scans	8

Powder X-Ray Diffractometry

The powder X-ray diffraction patterns were obtained with a commercial diffractometer (Philips APD 3520 Diffractometer, equipped with a Philips XRG 3100 Generator (Cu target) and a Philips graphite monochromator: Philips Electronic Instruments, Mahwah, NJ) interfaced to a PC (International Business Machines). Pertinent instrument settings used are :

generator power	40 kV, 30 mA	scan mode	step scan
scan rate	2 $^{\circ}$ /min	step size	0.05 $^{\circ}$
scan range	4-60 $^{\circ}$		

Surface Area Techniques

BET nitrogen-adsorption surface area values were obtained with a commercial instrument (Gemini II 2370 Surface Area Analyzer; Micromeritics Instruments, Norcross, GA) interfaced (RS 232) to a PC (Gateway 2000 386/25 PC; Gateway 2000, North Sioux City, SD). Samples were degassed with an ancillary degasser (Micromeritics FlowPrep 060 Degasser; Micromeritics). Helium was used as the free space adsorbate and N₂ was used as the surface area adsorbate. Relevant instrument settings used are:

degassing step

drying temperature 105 °C

drying time 2 h

surface area determination step

temperature -195.8 °C

relative pressure 0.05-0.3

number of points 5

SO₂ Uptake Techniques

A previously described, custom built sorption apparatus⁴ was modified by the replacement of its peristaltic H₂O pump with a syringe pump (74900 series; Cole-Parmer, Niles, IL) in which was mounted a suitable syringe (10 mL; Glenco, Houston, TX). The apparatus, Figure 5, is designed to simulate typical bag-house conditions in a power plant. The SO₂ uptake of the products was determined as described by Chiang.⁴ The temperature of the sand-bed reactor was 60 °C. The composition of the

simulated flue gas used was 0.2 % SO₂ (2000 ppm SO₂), 12 % H₂O (relative humidity 60 % at 60 °C) and 88 % N₂.

Estimation of Composition of Sorbents

The composition of the products was estimated from inspection of their infrared spectra and their X-ray powder diffraction patterns. The values in Tables III-VI given for the composition of the products are subject to considerable error and should not be take as precise.

Figure 5. Schematic drawing of sorption apparatus (from Ref 12, used with permission).

9. SYNTHESSES

Chemicals

Unweathered clinker and Type I portland cement were obtained as a gift from a local cement producer (Medusa Cement, Cleveland, OH). Byproduct fumed SiO_2 (Microsilica EMS 960) was obtained as a gift from a regional producer (Elkem Materials, Pittsburgh, PA).

Analysis of Cement

The analysis of the cement was furnished by its supplier.

Syntheses of Cement and Clinker Sorbents

Typical Pressure-Vessel Synthesis. In a typical pressure-vessel synthesis (Table III, run 2), a mixture of cement (Type I, 3.0 g), H_2O (30 mL) and ZrO_2 beads (MgO-stabilized, 1.4 mm diameter, 180 g; Union Process, Akron, OH) was stirred (600 rpm) with a shaft stirrer (alloy C-276 (6.5% Fe 53% Ni, 15.5% Cr, 16% Mo, 1% Mn, 4% W, 2.5% Co)) in a bomb (alloy C-276, 300 mL, Teflon-lined, Parr 4842; Parr Instrument Co., Moline, IL) while being heated (heating mantle, 100 °C) for 2 h, and then cooled (H_2O bath) for 15 min. The resulting mixture was filtered (60-mesh bronze screen) and the beads were washed with H_2O (~ 20 mL). The filtrate and

washings were combined and filtered (Whatman #50), and the solid was dried (~ 60 °C, ~ 60 torr) for ~ 16 h, weighed (2.9 g) and crushed.

The product was a light gray powder.

Typical Stirred-Ball Mill Synthesis. In a typical stirred-ball mill synthesis (Table IV, run 16), a mixture of cement (Type I, 12.5 g), H_2O (125 mL) and ZrO_2 beads (Y_2O_3 -stabilized, 1.0 mm diameter, 935 g, Union Process) was stirred (3000 rpm) with a shaft stirrer (delta alloy discs) in a stirred ball mill (750 mL, stainless steel, 01HD-DM Attritor; Union Process) while being heated (steam, 100 °C) for 20 min. The resulting mixture was filtered (60-mesh bronze screen) and the beads were washed with H_2O (~ 50 mL). The filtrate and washings were combined and filtered (Fisher #4), and the solid was dried (~ 60 °C, ~ 60 torr) for ~ 16 h, weighed (13.1 g) and crushed.

The product was a light gray powder.

Typical Glass-Flask Synthesis. In a representative glass-flask synthesis (Table V, run 22), a mixture of clinker (Type I, -60 mesh, 5.0 g), H_2O (50 mL) and ZrO_2 beads (MgO-stabilized, 1.4 mm diameter, 300 g; Union Process) was stirred (~ 500 rpm) with a shaft stirrer (Teflon banana-type blade, Trubore, lubricated with STIR-LUBE, Ace Glass, Vineland, NJ), in a two-necked glass flask (500 mL) fitted with a condenser and a CO_2 trap (NaOH-filled drying tube) while being heated (oil

bath, 100 °C) for 3 h. The resulting mixture was filtered (60-mesh bronze screen) and the beads were washed with H₂O (~ 30 mL). The filtrate and washings were combined and filtered (Whatman #50), and the solid was dried (~ 60 °C, ~ 60 torr) for ~16 h, weighed (5.2 g) and crushed.

The product was a light gray powder.

10. RESULTS AND DISCUSSION

HYDRATED CEMENT SORBENTS

A series of 27 experiments was done on cement and clinker. These experiments were carried out in one of three reactors, the pressure vessel, the stirred ball mill or the glass flask.

Cement Sorbent Produced in Pressure Vessel with MgO-Stabilized ZrO₂ Beads (Table III)

A set of fifteen experiments was done on portland cement in the pressure vessel. In these experiments, the stirring rate was moderate and the beads were MgO-stabilized ZrO₂ (density 5.4 g/cm³).

Variation of Reaction Time. A group of four experiments was done in which the reaction time was varied from 180 to 30 minutes. The cement:H₂O:beads ratio in these experiments was 1:10:60, the reaction temperature was 100 °C and the stirring rate was 600 rpm, runs 1-4, Table III.

Various combinations of C-S-H, Ca(OH)₂, AFm, α -Ca₂(SiO₃OH)(OH), Ca₃Al₂(SiO₄)(O₄H₄)₂, alite and belite were present in the products of the experiments, Figures 6 and 7 and Table III. The alite and belite were from unhydrated cement. The presence of more alite and belite in the shortest run product than the longest run one shows that over a 30 to 180 minute time span the degree of hydration of a product

is dependent on the reaction time under the conditions used. Since C-S-H and $\text{Ca}(\text{OH})_2$ are ordinary products of the hydration of cement, their presence in the products obtained is not surprising. The presence of AFm in the shortest run product but not in the longest run one, the absence of $\alpha\text{-Ca}_2(\text{SiO}_3\text{OH})(\text{OH})$ in the shortest run product but its presence in the longest run one, and the presence of less $\text{Ca}_3\text{Al}_2(\text{SiO}_4)(\text{O}_4\text{H}_4)_2$ in the shortest run product than longest run one are consistent with probable favorable kinetics for the formation of AFm and the probable thermodynamic stability of $\alpha\text{-Ca}_2(\text{SiO}_3\text{OH})(\text{OH})$ and $\text{Ca}_3\text{Al}_2(\text{SiO}_4)(\text{O}_4\text{H}_4)_2$ under the conditions used.^{9c, 18,20-25}

The good surface areas of the four products are as expected since C-S-H and AFm can have high surface areas. Because $\alpha\text{-Ca}_2(\text{SiO}_3\text{OH})(\text{OH})$ and $\text{Ca}_3\text{Al}_2(\text{SiO}_4)(\text{O}_4\text{H}_4)_2$ are typically crystalline and compact and because milling can be expected to increase the surface area of a product, the differences in the surface areas of the four products are probably attributable to the opposing effects of the amounts of $\alpha\text{-Ca}_2(\text{SiO}_3\text{OH})(\text{OH})$ and $\text{Ca}_3\text{Al}_2(\text{SiO}_4)(\text{O}_4\text{H}_4)_2$ present and the length of the reaction time.

The excellent SO_2 -uptake values of the three longest run products and the good SO_2 -uptake value of the shortest run product are not surprising since C-S-H, $\text{Ca}(\text{OH})_2$ and AFm are all good sorbents.⁴ Because $\alpha\text{-Ca}_2(\text{SiO}_3\text{OH})(\text{OH})$ is probably only a moderately good sorbent and $\text{Ca}_3\text{Al}_2(\text{SiO}_4)(\text{O}_4\text{H}_4)_2$ is probably a poor sorbent,⁴ and because the amount of SO_2 a product can take up can be expected to be partly

governed by its surface area. the variation in the SO_2 -uptake values of four products are likely explainable partly on the basis of the amounts of $\alpha\text{-Ca}_2(\text{SiO}_3\text{OH})(\text{OH})$ and $\text{Ca}_3\text{Al}_2(\text{SiO}_4)(\text{O}_4\text{H}_4)_2$ present in them and partly on the basis of their surface areas.

Variation of Reaction Temperature. A series of four experiments was carried out in which the temperature was varied from 180 to 120 °C. The cement: H_2O :beads ratio in these experiments was 1:10:60, the reaction time was 30 minutes and the stirring rate was 600 rpm, runs 5-8, Table III.

Various combinations of C-S-H, $\text{Ca}(\text{OH})_2$, $\alpha\text{-Ca}_2(\text{SiO}_3\text{OH})(\text{OH})$, $\text{Ca}_3\text{Al}_2(\text{SiO}_4)(\text{O}_4\text{H}_4)_2$, alite and belite were present in the products of these experiments. Figure 8 and Table III. The presence of C-S-H in the lowest temperature product but not in the highest temperature one, and the presence of more $\alpha\text{-Ca}_2(\text{SiO}_3\text{OH})(\text{OH})$ in the highest temperature one than in the lowest temperature one show that over the 120-180 °C temperature range the types of species produced are dependent on the hydration temperature. This is consistent with the known ability of elevated temperatures to accelerate conversion of C-S-H to $\alpha\text{-Ca}_2(\text{SiO}_3\text{OH})(\text{OH})$.^{9c}

Variation of Stirring Rate. In addition, a group of three experiments was done in which the stirring rate was varied from 500 to 300 rpm. In these experiments, the cement: H_2O :beads ratio was 1:10:60, the reaction time was 180 minutes and the reaction temperature was 100 °C. These three experiments together with the first one of the previous group gave a group of four comparable experiments in which the stirring rate varied from 600 to 300 rpm, runs 1 and 9-11, Table III.

The similar composition of the four products shows that over the 300-600 rpm range the influence of stirring rate on the hydration reaction is small under the conditions used. The relatively small variations in the surface areas of the products arise from unknown factors. Probably the relatively small variations in the SO_2 -uptake values of the products are partly attributable to the differences in their surface areas.

The differences in the surface areas of the products can be ascribed partly to the relative amounts of C-S-H, $\alpha\text{-Ca}_2(\text{SiO}_3\text{OH})(\text{OH})$ and $\text{Ca}_3\text{Al}_2(\text{SiO}_4)(\text{O}_4\text{H}_4)_2$ in them since, as already noted, C-S-H can have a high surface area and $\alpha\text{-Ca}_2(\text{SiO}_3\text{OH})(\text{OH})$ and $\text{Ca}_3\text{Al}_2(\text{SiO}_4)(\text{O}_4\text{H}_4)_2$ typically have low surface areas. Perhaps they can also be partly ascribed to crystal digestion at elevated temperatures. The excellent SO_2 -uptake values of the three highest temperature products are not understood since these products are not rich in C-S-H and AFm. and have low surface areas. However, they do show that a high surface area is not requisite a characteristic of a high-uptake product.

In an extension of this group of experiments, a further group of experiments was done which were parallel except that the reaction time was 15 minutes instead of 30 minutes, runs 12-15, Table III.

In the products of these experiments, various combinations of the species that were present in the products of the previous group of experiments were present. The patterns of occurrence of these species are similar to patterns of occurrence of the

species in the products of the previous group. The results of these experiments show that with a 15-minute reaction time as well as with a 30-minute one, the influence of temperature on the types of species produced over the range of 180-120 °C is important.

Cement Sorbent Produced in a Stirred Ball Mill with Y_2O_3 -Stabilized ZrO_2 Beads (Table IV)

A second set of experiments was carried out on portland cement in the stirred ball mill. In these experiments, the stirring rate was high, the beads were Y_2O_3 -stabilized ZrO_2 (density 6.0 g/cm³) and the rotors were delta alloy (a steel alloy with 12% Cr, 1.5% C, 0.5% Mn, 0.8% Mo, 0.3% Si and 0.9% V).

Variation of Reaction Time. A group of three experiments was carried out in which the reaction time was varied from 20 to 5 minutes. The cement:H₂O:beads ratio in these experiments was 1:10:80, the reaction temperature was 100 °C and the stirring rate was 3000 rpm, runs 16-18, Table IV.

Various combinations of C-S-H, Ca(OH)₂, AFm, Ca₃Al₂(SiO₄)(O₄H₄)₂, alite and belite were present in the products. Figure 9 and Table IV. Comparison of the composition of the 20 minute product with the 30-minute-100 °C product of the time-variation experiments done with the pressure vessel, run 4, Table III, suggests that a high rate of stirring under the conditions used is only somewhat more effective in the hydration of cement. The variations in the amounts of C-S-H, Ca(OH)₂, AFm and

$\text{Ca}_3\text{Al}_2(\text{SiO}_4)(\text{O}_4\text{H}_4)_2$, alite and belite show that the length of reaction time influences the degree of hydration of the products under the conditions used. The variations in the amounts of C-S-H, $\text{Ca}(\text{OH})_2$, AFm and $\text{Ca}_3\text{Al}_2(\text{SiO}_4)(\text{O}_4\text{H}_4)_2$ in the products are consistent with the variations in the amounts of alite and belite in them. the relative ease of formation of AFm. and the stability of $\text{Ca}_3\text{Al}_2(\text{SiO}_4)(\text{O}_4\text{H}_4)_2$.

The differences in the surface areas of the products are in accordance with the amounts of alite and belite present. and the differences in the SO_2 -uptake values are also in rough accordance with the amounts of alite and belite present.

In an extension of this group of experiments, a group of experiments was carried out which were parallel except that the reaction temperature was $\sim 25^\circ\text{C}$ instead of 100°C . runs 19-21. Table IV.

Here. various combinations of C-S-H, $\text{Ca}(\text{OH})_2$, AFm, $\text{Ca}_3\text{Al}_2(\text{SiO}_4)(\text{O}_4\text{H}_4)_2$, alite and belite were present. Figure 10 and Table IV. The patterns in the composition and uptake data for these experiments and the previous group of experiments show that at 25°C as well as 100°C the reaction time over the time span of 5-20 minutes does influence the degree of hydration of the products.

Crushed Clinker Sorbent Produced in Glass Flask with MgO-Stabilized ZrO_2 (Table V)

A third set of experiments was done on -60 mesh crushed clinker in the glass flask apparatus. In these experiments, the stirring rate was moderate and the beads were MgO-stabilized ZrO_2 .

Variation of Clinker to H_2O Ratio. A group of three experiments was done in which the clinker: H_2O ratio was varied from 1:10 to 1:3. The clinker:beads ratio in these experiments was 1:60, the reaction time was 3 hours, the reaction temperature was 100 °C, and the stirring rate was ~500 rpm, runs 22-24, Table V.

In the products, various combinations of C-S-H, $\text{Ca}(\text{OH})_2$, AFm, $\alpha\text{-Ca}_2(\text{SiO}_3\text{OH})(\text{OH})$, $\text{Ca}_3\text{Al}_2(\text{SiO}_4)(\text{O}_4\text{H}_4)_2$ alite and belite were present. Figure 11 and Table V. Since the composition of clinker is the same as that of cement except for the absence of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, the existence of these species in the products is as expected. The presence of $\alpha\text{-Ca}_2(\text{SiO}_3\text{OH})(\text{OH})$ in the 1:3 ratio product but not the 1:10 ratio product, and the greater degree of milling expected with the more viscous 1:3 ratio mixture suggest that the use of hydration mixtures with a smaller proportion of H_2O promotes completion of the hydration. The moderate or high surface areas of the products are consistent with the length of the milling time used and the amounts of C-S-H and AFm present in them. Their excellent SO_2 -uptake values are in accordance with the amounts of C-S-H, $\text{Ca}(\text{OH})_2$ and AFm present in them, and their high surface areas.¹²

Clinker Fines Sorbent Produced in Glass Flask with MgO-Stabilized ZrO_2

(Table VI)

A fourth set of experiments was done on -60 mesh clinker fines. In these experiments, the stirring rate was moderate and the beads were MgO-stabilized ZrO_2 .

Variation of Clinker to H_2O Ratio. A pair of experiments was done in which the clinker: H_2O ratio was 1:10 or 1:5. The clinker:beads ratio in these experiments was 1:60, the reaction time was 3 hours, the reaction temperature was 100 °C, and the stirring rate was ~500 rpm, runs 25 and 26, Table VI. These experiments were, as apparent, like the crushed clinker mix-ratio experiments except that -60 mesh clinker fines were used instead of -60 mesh crushed clinker.

Both of the products of this pair of experiments contained C-S-H, $\text{Ca}(\text{OH})_2$, AFm, $\text{Ca}_3\text{Al}_2(\text{SiO}_4)(\text{O}_4\text{H}_4)_2$, alite and belite, and the 1:5 ratio product also contained $\alpha\text{-Ca}_2(\text{SiO}_3\text{OH})(\text{OH})$. The results from these experiments again suggest that the use of reaction mixtures containing less H_2O promotes completion of hydration. In addition, they show that clinker fines are interchangeable with crushed clinker as a reactant. This is as expected since the two types of clinker have the same composition.

Variation of Reactants. An experiment was done in which fumed SiO_2 was added to the reaction mixture. The clinker: H_2O :beads: SiO_2 ratio in this experiment was 1:6.5:60:0.3, the reaction time was 3 hours, the reaction temperature was 100 °C, and the stirring rate was ~500 rpm, run 27, Table VI.

C-S-H, AFm, alite and belite were present in the product. Figure 33 and Table VI. The absence of Ca(OH)_2 in the product is attributable to the ability of fumed SiO_2 to react with Ca(OH)_2 to give C-S-H.^{9d} The high surface area of the product and its excellent SO_2 -uptake value are in accordance with the presence of a large amount of C-S-H and some AFm in it.

Figure 6. Infrared spectra of portland cement sorbent produced in pressure vessel with MgO-stabilized ZrO₂ beads, runs 2 and 4, Table III.

Figure 7. X-ray powder patterns of portland cement sorbent produced in pressure vessel with MgO-stabilized ZrO₂ beads, runs 2 and 4, Table III.

Figure 8. X-ray powder patterns of portland cement sorbent produced in pressure vessel with MgO-stabilized ZrO₂ beads. runs 5 and 8. Table III.

Figure 9. X-ray powder patterns of portland cement sorbent produced in stirred ball mill with Y₂O₃-stabilized ZrO₂ beads, runs 16-18, Table IV.

Figure 10. X-ray powder patterns of portland cement sorbent produced in stirred ball mill with Y₂O₃-stabilized ZrO₂ beads, runs 19-21, Table IV.

Figure 11. X-ray powder patterns of clinker sorbent produced in glass flask with MgO-stabilized ZrO₂ beads, runs 22, 23 and 27. Tables V and VI.

Table III. Portland Cement Sorbent Produced in Pressure Vessel with MgO-Stabilized ZrO₂ Beads

variable	wt ratio	time (min)	temp (°C)	press ^b (psi)	stir media	stirrer	vessel	CSH	CH	AFm ^{c,d}	C ₂ SH	C ₃ ASH ₄	C ₃ S	C ₂ S	SO ₂ uptake
					conditions			estimated composition ^a							BET area (m ² /g)
					cem H ₂ O beads										(mmol/g)
1 time	1 10	60	180	100	8	600	ZrO ₂ (M) ^e	alloy ^f	Teflon ^g	++	++	++	+	+	60
2 time	1 10	60	120	100	7	600	ZrO ₂ (M) ^e	alloy ^f	Teflon ^g	++	++	++	+	+	73
3 time	1 10	60	60	100	7	600	ZrO ₂ (M) ^e	alloy ^f	Teflon ^g	++	++	++	+	+	76
4 time	1 10	60	30	100	5	600	ZrO ₂ (M) ^e	alloy ^f	Teflon ^g	++	++	++	++	++	66
5 temp	1 10	60	30	180	100	600	ZrO ₂ (M) ^e	alloy ^f	Teflon ^g	++	+++	++	+	+	17
6 temp	1 10	60	30	160	60	600	ZrO ₂ (M) ^e	alloy ^f	Teflon ^g	++	+++	++	+	+	20
7 temp	1 10	60	30	140	25	600	ZrO ₂ (M) ^e	alloy ^f	Teflon ^g	++	+++	++	+	+	20
8 temp	1 10	60	30	120	15	600	ZrO ₂ (M) ^e	alloy ^f	Teflon ^g	++	++	++	+	+	44
9 stirring	1 10	60	180	100	8	500	ZrO ₂ (M) ^e	alloy ^f	Teflon ^g	++	++	++	+	+	66
10 stirring	1 10	60	180	100	8	400	ZrO ₂ (M) ^e	alloy ^f	Teflon ^g	++	++	++	+	+	70
11 stirring	1 10	60	180	100	8	300	ZrO ₂ (M) ^e	alloy ^f	Teflon ^g	++	++	++	++	++	65
12 temp, time	1 10	60	15	180	90	600	ZrO ₂ (M) ^e	alloy ^f	Teflon ^g	++	+++	++	+	+	11
13 temp, time	1 10	60	15	160	55	600	ZrO ₂ (M) ^e	alloy ^f	Teflon ^g	++	+++	++	++	++	13
14 temp, time	1 10	60	15	140	20	600	ZrO ₂ (M) ^e	alloy ^f	Teflon ^g	++	++	++	++	++	24
15 temp, time	1 10	60	15	120	10	600	ZrO ₂ (M) ^e	alloy ^f	Teflon ^g	++	++	++	++	++	46

Table III. Portland Cement Sorbent Produced in Pressure Vessel with MgO-Stabilized ZrO₂ Beads

^a C₂SII, CaO-SiO₂-H₂O; CH, Ca(OH)₂; AFm, [Ca₂(Al,Fe)(OH)₆]₂(SO₄,CO₃,2OH)·6H₂O or a related amorphous phase; C₂SII, α-Ca₂(SiO₃OH)(OH); C₃ASH₄, Ca₃Al₂(SiO₄)(O₄H₄)₂; C₃S, alite; C₂S, belite. ^b Pressure above atmospheric. ^c Amount inferred from cement composition and literature data. ^d Relatively amorphous. ^e ZrO₂(M), 1.4-mm diameter MgO-stabilized ZrO₂ beads. ^f Alloy, alloy C-276 (6.5% Fe, 53% Ni, 15.5% Cr, 16% Mo, 1% Mn, 4% W, 2.5% Co). ^g Teflon-lined alloy steel pressure vessel.

Table IV. Portland Cement Sorbent Produced in Stirred Ball Mill with Y₂O₃-Stabilized ZrO₂ Beads

variable	wt ratio			conditions							estimated composition ^a							BET area (m ² /g)	SO ₂ uptake (mmol/g)
	cem	H ₂ O	beads	time (min)	temp (°C)	press ^b (psi)	stir (rpm)	media	rotor	vessel	CSH	CH	AFm ^{c,d}	C ₂ SH	C ₃ ASH ₄	C ₃ S	C ₂ S		
16 time	1	10	80	20	100	0	3000	ZrO ₂ (Y) ^e	alloy ^f	steel	+++	++	+		+		+	56	6.8
17 time	1	10	80	10	100	0	3000	ZrO ₂ (Y) ^e	alloy ^f	steel	++	++	++		+		++	20	4.8
18 time	1	10	80	5	100	0	3000	ZrO ₂ (Y) ^e	alloy ^f	steel	+		++				+++	16	3.7
19 time, temp	1	10	80	20	25	0	3000	ZrO ₂ (Y) ^e	alloy ^f	steel	++	+	+				++	19	5.4
20 time, temp	1	10	80	10	25	0	3000	ZrO ₂ (Y) ^e	alloy ^f	steel	+	+					+++	19	4.3
21 time, temp	1	10	80	5	25	0	3000	ZrO ₂ (Y) ^e	alloy ^f	steel	+						+++	10	3.6

^a CSH, CaO-SiO₂-H₂O; CH, Ca(OH)₂; AFm, [Ca₂(Al,Fe)(OH)₆]₂(SO₄,CO₃,2OH)·6H₂O or a related amorphous phase; C₂SH, α-Ca₂(SiO₃OH)(OH); C₃ASH₄, Ca₃Al₂(SiO₄)(O₄H₄)₂; C₃S, alite; C₂S, belite. ^b Pressure above atmospheric. ^c Amount inferred from cement composition and literature data. ^d Relatively amorphous. ^e ZrO₂(Y), 1.0-mm diameter Y₂O₃-stabilized ZrO₂ beads. ^f Alloy, delta alloy (steel alloy with 12% Cr, 1.5% C, 0.5% Mn, 0.8% Mo, 0.3% Si, 0.9% V).

Table V. Crushed Clinker Sorbent Produced in Glass Flask with MgO-Stabilized ZrO₂ Beads

variable	wt ratio		conditions				estimated composition ^a						BET area	SO ₂ uptake				
	clnk	^b H ₂ O:beads:SiO ₂	time (h)	temp (°C)	press ^c (psi)	stir (rpm)	media	stirrer	vessel	CSH	CH	AFm ^{d,e}	C ₂ SH	C ₃ ASH ₄	C ₃ S	C ₂ S beads	(m ² /g)	(mmol/g)
22 ratio	1	10 60	3	100	0	~500	ZrO ₂ (M) ^f	Teflon glass	+++	++	+	+	+	+	+	+	118	7.2
23 ratio	1	5 60	3	100	0	~500	ZrO ₂ (M) ^f	Teflon glass	++	++	+	++	+	+	+	+	65	7.1
24 ratio	1	3 60	3	100	0	~500	ZrO ₂ (M) ^f	Teflon glass	++	++	+	++	+	+	+	+	94	6.4

^a CSH, CaO-SiO₂-H₂O; CH, Ca(OH)₂; AFm, [Ca₂(Al,Fe)(OH)₆]₂(SO₄,CO₃,2OH)·6H₂O or a related amorphous phase; C₂SH, α-Ca₂(SiO₃OH)(OH); C₃ASH₄, Ca₃Al₂(SiO₄)(O₄H₄)₂; C₃S, alite; C₂S, belite. ^b -60 mesh. ^c Pressure above atmospheric. ^d Amount inferred from cement composition and literature data. ^e Relatively amorphous. ^f ZrO₂(M), 1.4-mm diameter MgO-stabilized ZrO₂ beads.

Table VI. Clinker Fines Sorbent Produced in Glass Flask with MgO-Stabilized ZrO₂ Beads

variable	wt ratio	conditions				estimated composition ^a				BET area (m ² /g)	SO ₂ uptake (mmol/g)		
		clnk ^b :H ₂ O:beads:SiO ₂	time (h)	temp (°C)	press (psi)	stir (rpm)	media	stirrer	vessel				
25	ratio	1 10 60	3	100	0	~500	ZrO ₂ (M) ^f	Teflon glass	+++ ++	+	+	134	7.4
26	ratio	1 5 60	3	100	0	500	ZrO ₂ (M) ^f	Teflon glass	++ ++	+	+	94	7.4
27	reactants	1 6.5 60 0.3	3	100	0	~500	ZrO ₂ (M) ^f	Teflon glass	++++	+	+	145	6.6

^a CSH, CaO-SiO₂-H₂O; CH, Ca(OH)₂; AFm, [Ca₂(Al,Fe)(OH)₆]₂(SO₄,CO₃,2OH)·6H₂O or a related amorphous phase; C₂SH, α-Ca₂(SiO₃OH)(OH); C₃ASH₄, Ca₃Al₂(SiO₄)(O₄H₄)₂; C₃S, alite; C₂S, belite. ^b -60 mesh. ^c Pressure above atmospheric. ^d Amount inferred from cement composition and literature data. ^e Relatively amorphous. ^f ZrO₂(M), 1.4-mm diameter MgO-stabilized ZrO₂ beads.

11. CONCLUSIONS

Portland Cement Sorbent

The results obtained show that an excellent portland cement sorbent can be prepared by milling cement at 120 °C at 600 rpm for 15 minutes with MgO-stabilized ZrO₂ beads. They also show that clinker, which is an intermediate in the preparation of cement and therefore cheaper, can be used interchangeably with cement as a starting material. Further, it is clear that while a high surface area may be a desirable property of a good sorbent, it is not a requisite property. Among the hydration reaction variables, milling time is highly important, reaction temperature is important, and stirring rate and silicate-to-H₂O ratio are moderately important. The components of hydrated cement sorbent are various combinations of C-S-H, Ca(OH)₂, AFm, α -Ca₂(SiO₃OH)(OH), Ca₃Al₂(SiO₄)(O₄H₄)₂, alite and belite, with C-S-H, Ca(OH)₂ and AFm being the desirable components. The addition of active SiO₂ to the reaction mixture can increase the amount of C-S-H and reduce the amount of Ca(OH)₂ in the sorbent. Overly vigorous conditions can reduce the amount of C-S-H and increase the amount of α -Ca₂(SiO₃OH)(OH) in it.

Milling Beads and Rotors

The most generally serviceable milling beads are Y₂O₃-stabilized ZrO₂ beads. These are dense, tough and ablation resistant. The most generally serviceable rotors

are delta alloy. These are reasonably wear resistant and give vigorous milling conditions.

12. COLLABORATIONS

In collaborative efforts, analytical work was done on a set of samples of hydrated cement sorbent for Prof. Keener of the University of Cincinnati. In addition help on the preparation of hydrated cement sorbent was obtained from personnel of Union Process Corporation of Akron in the grinding laboratories of Union Process.

13. REFERENCES

1. Kraushaar, J.; Ristinen, R. A. *Energy and Problems of A Technical Society*, 2nd ed., John Wiley: New York, 1993; pp. 48-50.
2. Corcoran, E. *Sci. Amer.* **1991**, 264, 105.
3. Makansi Power **1991**, June, 11.
4. Chiang, R.-K. Ph. D. Dissertation, Case Western Reserve University, 1994.
5. Makansi Power **1993**, October, 79.
6. McCarthy, G. J.; Solem-Tishmack, J. K. *Hydration Mineralogy of Cementitious Coal Combustion By-products*; American Society of Civil Engineers: New York, 1994, pp 103-121.
7. Jozewicz, W.; Chang, J. C. S.; Sedman, C. B.; Brna, T. G. *J. Air Pollut. Control Assoc.* **1988**, 38, 1027.
8. Greenwood, N. N.; Earnshaw, A. *Chemistry of the Elements*; Pergamon: New York, 1984, Chapter 5.
9. Taylor, H. F. W. *Cement Chemistry*; Academic: London, 1990, (a) Chapter 1, (b) Chapter 4, (c) Chapter 7, (d) Chapter 9, (e) Chapter 11 (f) Chapter 6.
10. Jawed, I.; Skalny, J.; Young, J. F. In *Structure and Performance of Cement*; Barnes, P., Ed.; Applied Science: New York, 1983, Chapter 6.
11. Double, D. D. *Phil. Trans. R. Soc. Lond. A* **1983**, 310, 53-66.
12. Chiang, R.-K.; Kwag, G.; Kenney, M. E. *New Calcium-Base Sorbents for Flue Gas Desulfurization*, in press.
13. Ahmed, S. J.; Taylor, H. F. W. *Nature* **1967**, 215, 622-623.
14. Skalny, J.; Tadro, M. E. *J. Amer. Ceram. Soc.* **1977**, 60, 174-175.
15. Hampson, C. J.; Bailey, J. E. *J. Mater. Sci.* **1983**, 18, 402-410.

16. Hampson, C. J.; Bailey, J. E. *J. of Mater. Sci.* **1982**, *17*, 3341-3346.
17. Ghorab, H. Y.; Fetouh, S. H. *Mat. Res. Soc. Symp. Proc.* **1987**, *85*, pp 255-260.
18. Macdowell, J. F. *Mat. Res. Soc. Symp. Proc.* **1991**, *137*, 437.
19. Passaglia, E.; Rinaldi, R. *Bull. Mineral.* **1984**, *107*, 605-618.
20. Zhong, B.; Yang, N.; Yoshiniko, O. Presented at the Proceedings of the Third International Symposium on Cement and Concrete., Beijing, China. 1993, pp 325-329.
21. Plowman, C.; Cabrera, J. G. *Cem. Concr. Res.* **1984**, *14*, 238-248.
22. Gupta, P.; Chatterji, S.; Jeffery, J. W. *Cem. Technol.* **1973**, *4*, 59-63.
23. Feldman, R. F.; Ramachandran, V. S. *Mag. Concr. Res.* **1966**, *18*, 185-196.
24. Double, D. D. *Phil. Trans. R. Soc. Lond. A* **1983**, *310*, 53-66.
25. Bailey, J. E.; Hampson, C. J. *Phil. Trans. R. Soc. Lond. A* **1983**, *310*, 105-111.