Pergamon

Cement and Concrete Research, Vol. 28, No. 9, pp. 1335–1345, 1998

0008-8846/98 $19.00 + .00

PII S0008-8846(98)00109-4

DETERMINATION OF GRINDING AIDS IN PORTLAND CEMENT BY PYROLYSIS GAS CHROMATOGRAPHY-MASS SPECTROMETRY

A.A. Jeknavorian,[1]* E.F. Barry,† and F. Serafin*
*Grace Construction Products, 62 Whittemore Avenue, Cambridge, MA 02140, USA
†University of Massachusetts-Lowell, Department of Chemistry, Lowell, MA 01854, USA

(Received April 14, 1998; in final form June 25, 1998)

ABSTRACT

The pyrolysis of Portland cement followed by gas chromatography/mass spectrometry is described for the determination of chemical additives interground with cement clinkers known as grinding aids. This technique, coupled with in situ derivitization using BSTFA-TMCS reagent, has been found to be readily applicable for detecting phenol, along with five glycol and alkanolamine-type compounds in cement. The recovery rate was found to be highly dependent upon the grinding process and the binding capacity of the various additives. Using a relatively short grinding process conducted at ambient temperature, most of the additives tested can be recovered at greater than 85% of their originally added concentration. However, in the case of a longer, more intense grinding procedure conducted at 105°C, only phenol had recovery rates greater than 50%. The formation of salts or stable complexes between the grindings aids and cations at the freshly fractured cement surfaces, is proposed as the major cause of the variable recovery rates for the various grinding aid compounds. *© 1998 Elsevier Science Ltd*

Introduction

Energy utilization during the grinding process of Portland cement clinker and gypsum can be significantly improved by adding polar organic compounds (referred to as grinding aids) in concentrations less than 500 ppm (1). Because of their highly polar nature, grinding aid compounds preferentially adsorb on surfaces formed by the fracture of electrovalent bonds (i.e., Ca-O and Si-O). The adsorbed molecules act to reduce the surface energy forces which cause agglomeration of the newly produced cement particles. The resultant dry dispersion of cement increases cement fluidity and reduces mill retention time (2). With the consumption of electric energy per unit time held constant during the application of grinding aids, the capacity of the mill is increased, resulting in more efficient consumption of energy (3).

Methods for the determination of commercially available grinding aids in Portland cement are required to fulfill the ASTM C 465 Specification for Processing Additions for Use in the Manufacture of Hydraulic Cements (4). According to this specification, vendors of grinding

---

[1] To whom correspondence should be addressed.

aids must provide a means for the quantitative determination of the addition in the finished cement. Cements may also be analyzed for grinding aid content to check mill operation, verify that the correct additive was used, and troubleshoot cement performance problems.

Numerous difficulties are associated with the analysis of cement for interground additions: a) additive concentrations generally range from 50 to 500 ppm; b) the additives may no longer be present in their original chemical form after the grinding process, during which mill temperatures can reach as high as 115°C; c) harsh extraction procedures required to solubilize strongly adsorbed compounds can cause decomposition; and d) grinding aid compositions may not consist of mixtures of pure compounds, but rather more complex raw materials containing oligomers (5).

Most of the few published methods concerned with the analysis of Portland cement for interground organic compounds deal with measuring functional additions, i.e., water-reducing and air-entraining agents (6–9), as opposed to additives specifically designed to improve grinding efficiency. These procedures normally involve both aqueous and organic solvent extractions followed by titration or spectrophotometric techniques. With regard to common grinding aid compounds, several unpublished wet chemical methods can be obtained from the ASTM C465 certification report. Grinding aid formulations containing a known amount of a specific amino compound have been measured by oxidation of the amine to ammonia by alkaline $KMnO_4$ solution, followed by treating the liberated ammonia by nesslerization and colorimetry (10). A method for ethylene glycol content in Portland cement involves aqueous extraction, conversion of the extracted glycol to formaldehyde using iodate and arsenite reagents, and finally reaction with chromatropic acid to form a chromophore measurable at 570 nm (11).

Modern methods of instrumental analysis have also been applied for grinding aid determination in cement. Acetate-based cement additives can be measured by phosphoric acid extraction followed by concentration and analysis by gas chromatography (12). Triethanolamine (TEA), a common grinding aid component, has been measured by polarography after extraction with water and complexation with Fe^{3+} (13). Laser desorption fourier transform mass spectrometry (LD-FTMS) was applied for the detection of TEA and triisopropanolamine (TIPA) in cement and pure mineral phases of cement clinker (14). Peak intensity data indicated that TEA and TIPA have lower surface affinity for C_3A (tricalcium aluminate) and C_3S (tricalcium silicate) versus C_2S (dicalcium silicate) and C_4AF (tetracalcium aluminoferrite). However, information on the grinding process (i.e., mill configuration, grinding time, and operating temperature) and recovery rates for the TEA and TIPA were not indicated. A pyrolysis gas chromatographic/mass spectrometric (pyr-GC/MS) method was reported for the determination of diethylene glycol (DG) in cement (15,16). The pyrolysis temperature was 764°C; however, information concerning recovery rate, response linearity over a range of concentrations, and clinker grinding conditions were not reported.

The present study is an extension of a recently submitted paper (17,18) concerning the use of pyr-GC/MS for the determination of chemical additives in Portland cement and hardened concrete. In that report, among the interground additives that were evaluated by pyr-GC/MS, only phenol was found to be readily detectable at a recovery rate of 50%. DG and TEA were either not detected, or only a fraction ($< 5\%$) of their original concentration was present in the pyrolysate. In this study, the pyr-GC/MS method for the grinding aids was modified to include in situ pretreatment of the cement with a mixture of N,O-bis(trimethylsilyl)trifluoroacetamide (BSTFA) and trimethylchlorosilane (TMCS) to improve the recovery rate of the following common grinding aid additives: phenol, ethylene glycol (EG), diethylene

TABLE 1
Chemical composition and fineness
of cement samples, mass %.

Cement sample →	HT*	SW*
SiO_2	21.6	21.1
A_2O_3	6.3	4.8
Fe_2O_3	2.3	3.3
CaO	66.8	64.6
MgO	1.4	4.7
SO_3	2.5	2.6
LOI	1.0	1.1
Na_2O_{eqvt}	0.5	0.83
Bogue Compounds		
C_3S	61	62
C_2S	16	14
C_3A	13	8
C_4AF	7	10
Blaine Surface Area, cm^2/g	2630	3710

*Cement HT was used with the Spex Mill, while grinds with the rotating custom mill were conducted with SW cement.

glycol (DG), propylene glycol (PG), triethanolamine (TEA), and triisopropanolamine (TIPA). The effect of the milling process was also evaluated whereby each additive was interground with clinker and gypsum using a relatively low energy, vibrating bench-top ball mill versus a floor-mounted, more energy- intensive rotating ball mill operated at elevated temperatures. Various pyrolysis temperature programs were also investigated to maximize desorption of the additives from the cement. To further understand the thermal desorption behavior of cement interground with DG, the reaction product formed from mixing DG with a saturated solution of calcium hydroxide was also analyzed by pyr-GC/MS.

Experimental Program

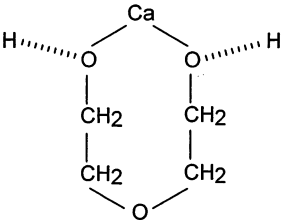
Preparation of Cement Samples with Grinding Aid

200 ppm each of phenol, EG, DG, PG, TEA, TIPA, and a phenol/TEA blend were interground with gypsum and two commercially available Portland cement clinkers using two milling apparatus: 1) a bench top vibrating SPEX 8000 Mixer/Mill (SPEX Industries, Edison, N.J.), and 2) a custom fabricated rotating ball mill with temperature control, which more closely simulates an industrial scale cement milling process. The composition of the cements after the clinkers were interground with gypsum is reported in Table 1.

Sample preparation with the SPEX Mill involved pipetting 1.00 mL of a 0.53% solution of each additive diluted in acetonitrile (ACN) into a 50-mL tungsten carbide grinding vial containing 25 g of HT clinker precrushed to an approximate Blaine Surface Area (BSA) of 3000 cm^2/g, 1.25 grams of powdered gypsum, and two stainless steel balls with diameters of 2.0 and 1.6 cm. The vial was then mounted on a wrist action shaker and operated for 15 min. at ambient temperature (22°C). At the end of the grinding process, the charge had reached a temperature of approximately 40 to 45°C.

The custom fabricated rotating ball mill consists of a cylindrical hardened steel chamber having a volume of 13 L. The distribution of tungsten carbide coated steel ball sizes and their corresponding diameters used for the grinds were as follows: 350 at 20 mm, 450 at 16 mm, and 650 at 12 mm. During the grinding process, the mill is placed in a wooden box equipped with adjustable heat lamps which allow operating temperatures from ambient to 150°C, and a motorized shaft which rotates the mill at 60 rpm. The removable cover of the mill has a small sealable opening in which grinding aid solutions can be injected. The grinds were performed by first heating the mill and balls to 105°C. 3325 g of clinker and 175 g of gypsum, both precrushed to an approximate 3000 cm^2/g BSA, were added to the mill, which was then sealed with a near air tight cover. For the 200 ppm dosage, 0.7 g of neat grinding aid solution was quickly added through the small opening on the cover. The mill was then mounted on a clamp and allowed to rotate at 105°C for 110 min. In the case of additive DG, an additional grind was conducted where no heat was applied to the mill. Considering that the fineness of the two clinkers were similar before the respective grinding processes (just passing 850 μm sieve), the final Blaine Surface areas indicate that the SW clinker particles experienced far greater fracture energy due to the difference in the weight ratio of grinding media to clinker (6 for the rotating mill versus 2 with the SPEX), and length and temperature of grinding.

In order to understand the possible role of calcium salt formation with grinding aid compounds during milling operations, a 1:1 molar mixture of DG and saturated $Ca(OH)_2$ solution was stirred at ambient temperature for 3 hours, and then dried at 125°C for 3 h. The infrared spectrum and thermalgravimetric analysis suggests the presence of the following calcium alkoxide salt:



The CaDG salt was interground with the HT clinker and gypsum using the SPEX Mill, and later analyzed by pyr-GC/MS.

Pyrolysis Gas Chromatography-Mass Spectrometry Instrumentation

Grinding aid determination in cement was performed with a CDS 2000 Pyrolyzer (CDS Analytical, Oxford, PA) operated in tandem with a Hewlett-Packard (HP) 5890 GC equipped with an HP mass selective detector (MSD). The CDS 2000 pyroprobe, which includes a coiled platinum element where pyrolysis occurs, was interfaced with the GC injection port using a heated CDS 1500 Valved Interface (Figure 1). This pyrolysis system was found to be especially useful for grinding aid content as the temperature and time programming capability of the pyroprobe provided for flexible heating rates up to a final pyrolysis temperature

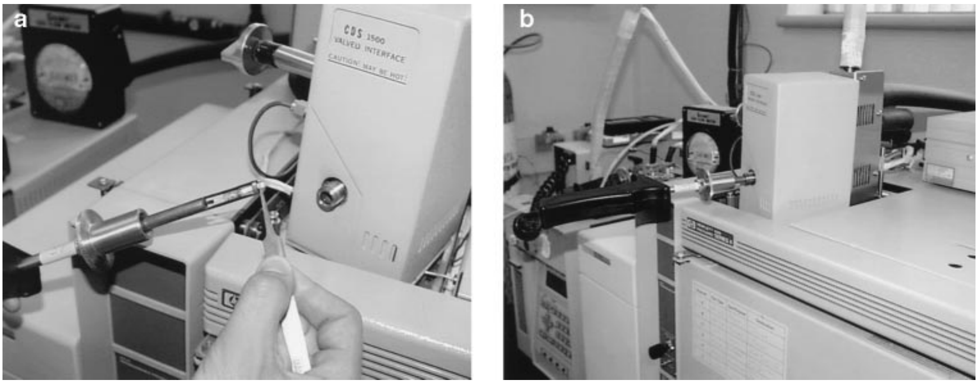


FIG. 1.
Pyroprobe and valved interface mounted on gas chromatograph. (*a*) Pyroprobe with quartz sample boat. (*b*) Pyroprobe inserted into valved interface.

of 1400°C. The platinum coiled element allowed the use of quartz tubes (15 mm long × 6 mm dia.) which can hold up to 70 mg of powder after gentle tapping. This sample size was found suitable for homogeneous powders such as Portland cement.

In the case of in-situ treatment of the cement with the BSFTA-TMCS derivitizing agent, the thermally desorbed organic additions, upon being swept from the pyrolysis chamber with helium carrier gas, were immediately trapped at the inlet of a 30 m × 0.25 mm DB-5 column, 0.25 μm film thickness (J&W Scientific), held at 35°C until the pyrolysis program was complete. The GC column temperature was then programmed at 10°C/min to a final temperature of 280°C with the eluted compounds detected by MSD. The capability to obtain mass spectra on the eluted compounds was found to be quite useful for identifying the pyrolysis products from cement, especially since the grinding aid additives could possibly be transformed to other compounds either during the grinding process or when desorbed from the cement. Pyrolysis products obtained without pretreatment of the cement were chromatographed on a 30 m × 0.25 mm i.d. HP-INNOWAX (crosslinked polyethylene glycol) column with 0.25 μm film thickness.

Pyrolysis Methods

The determination of interground additions of phenol, EG, DG, PG, TEA, TIPA, and phenol/TEA blend were carried out by direct pyrolysis of the cement, after the cement was pretreated with BSTFA-TMCS reagent. For both methods, 70 mg of cement were loosely packed into the quartz tubes with small amounts of quartz wool inserted at the ends of the tube to prevent sample blowout. Various pyrolysis temperature programs were applied that involved both ballistic (instantaneous) heating up to temperatures of 900°C coupled with variable hold times at final temperature, and ramp heating starting at 200°C and applying a range of heating rates (120 to 600 C°/min) to a final temperature of 900°C.

Pipetting the silylating reagent solution directly onto the cement sample, which is loosely packed in the quartz pyrolysis tube (i.e. in-situ method), was found to be the most convenient

TABLE 2
Pyrolysis variables for grinding aid analysis.

Parameter	Range
Pyrolysis temperature	300–900°C
Heating rate	Ballistic; 120–600°C/min
Hold time at final pyr. temp	0–2 min
BSTFA-TMCS derivitization	
reagent concentration	10–60%
reagent volume	10–40 μL
reagent-cement contact time prior to heating	30–120 s

and efficient means to conduct the derivitization step. To assure complete contact of the silylating reagent solution with the cement sample, 15 μL of reagent was added at both ends of the packed quartz tube prior to insertion in to the pyroprobe. The complete pyrolysis variables examined in this study are listed in Table 2.

Direct Pyrolysis of Cement

A systematic evaluation of pyrolysis temperature and heating rate over the ranges listed in Table 2 found that among the six grinding aid compounds only phenol could be readily desorbed and identified by direct pyrolysis of Portland cement. GC-MS results from the pyrolysis of cement samples interground with the 200 ppm dose of the other additives did not significantly differ from those obtained with a control cement, regardless of the grinding process used. In the case of DG, a previous study (17) found that only trace amounts (<3 ppm) could be detected by direct pyrolysis of 200 and 400 ppm DG cement samples at 700°C.

Results and Discussion

The thermal desorption profile of phenol from cement as a function of pyrolysis temperature (Fig. 2) exhibits a plateau in the 500–600°C range, suggesting that some portion of the interground phenol may exist as a thermally stable complex or salt with the cations at the cement surface (i.e. calcium phenolate). This finding is also somewhat indicated by the very low recovery rate of phenol using various solvent extraction procedures. For example, sonicating a 25:1 mixture of 2-propanol with a cement interground with phenol, whereby the solvent was heated to just below its boiling point (80°C), yielded only 8% of the original phenol content.

For this study, recovery rates for the various grinding aids were determined by comparing the MSD response obtained from the pyrolysis of the interground cements to that produced by pyrolyzing cement samples onto which had been doped 3 μL of a 4 μg/μL of grinding aid/ACN solution. The maximum achievable recoveries for phenol were 41% for the cement ground by the lesser energy intensive mild SPEX Mill process, and 25% for cement samples prepared with the heated rotating ball mill operated at 105°C. (The effect of grinding process

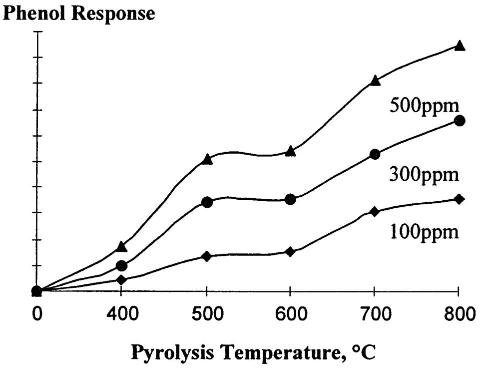


FIG. 2.
Thermal desorption profiles for phenol at various pyrolysis temperatures. Cement samples interground with 200 ppm phenol/TEA blend.

on recovery rate will be discussed later.) The corresponding pyrolysis conditions were ballistic heating at 800°C for 2 min.

The inability to detect the other additives by direct pyr-GC/MS could be the result of irreversible adsorption through the formation of non-volatile complexes and salts, possibly combined with partial decomposition to other compounds during either the grinding and/or pyrolysis processes. These two factors are supported by the following findings: 1) pyrolysis of the proposed calcium-DG reaction product did not yield any detectable DG, and 2) the GC-MS results for cements interground with DG feature several compounds such as 3,4-hydropyran, dibenzofuran, and benzaldehyde, which are not among the pyrolysis products observed with control cements (18).

In Situ Derivitization with BSTFA-TMCS

The poor recovery rates observed with the direct pyrolysis method prompted an evaluation of derivitizing agents to enhance desorption and volatility of the tightly bound grinding aid compounds. Previous reports on the use of derivitizing agents found tetramethylammonium hydroxide (TMAH) useful for detecting fatty and rosin acids and sodium gluconate in concrete (15–18). Silylation, regarded as the most widely used derivitization procedure for GC analysis, was considered because silylating agents are able to replace active hydrogen atoms associated with alcohols and amines to form very volatile, thermally stable silyl derivatives (19,20). The combination of BSTFA-TMCS, 99:1, was chosen because: a) BSTFA is among the most reactive silylating agents whereby derivitization can often occur rapidly and completely at ambient temperature, b) heating under ramping pyrolysis temperatures can help drive slower reactions to completion, c) BSTFA and its by-products are among the most volatile silylating reagents causing less chromatographic interference, and d) TMCS, while rarely used alone, is considered to be a silylating catalyst by increasing the reactivity of BSTFA.

An evaluation of the earlier described derivitization variables (Table 2) indicated one particular set of parameters to provide optimum recovery for the various grinding aid

TABLE 3
Optimum derivitization parameters.

Cement, mass	70 mg
BSTFA-TMCS	30 μL of 60% solution in ACN
Soak time	30 s at 22°C
Pyrolysis Program	200–800°C at 600°C/min with 1 min hold at 800°C

compounds (Table 3). Typical pyrograms for a control cement and one interground with a phenol/TEA blend are shown in Figure 3. The chromatographic peaks represent the silylated derivatives of phenol and TEA. The presence of several other compounds in the cement does not necessarily indicate they are originally in the cement, but should be considered as resulting from a combination of trace organics adsorbed by the clinker (i.e., possible kiln fuels) and possible reaction products created from the pyrolysis of the grinding aids.

The identity of the thermally desorbed grinding aid compounds was confirmed by comparing their mass spectra with the spectra of compounds obtained by conducting pyr-GC/MS analysis on the control cement doped with solutions of the individual additives. For example, Figure 4 illustrates a comparison of the mass spectra of silylated TEA derivative from a cement sample prepared on the rotating mill at 105°C vs. a cement sample doped with a phenol/TEA blend. The excellent spectral match provides confirmation of the identity of the originally interground TEA additive.

The benefits provided by derivitization are readily evident from Table 4, which compares the recovery rates for the various interground additives using direct pyrolysis and in-situ derivitization methods. Also included are results for cements interground with the phenol/TEA blend and the calcium-DG salt. Recovery rates are listed for cement samples prepared

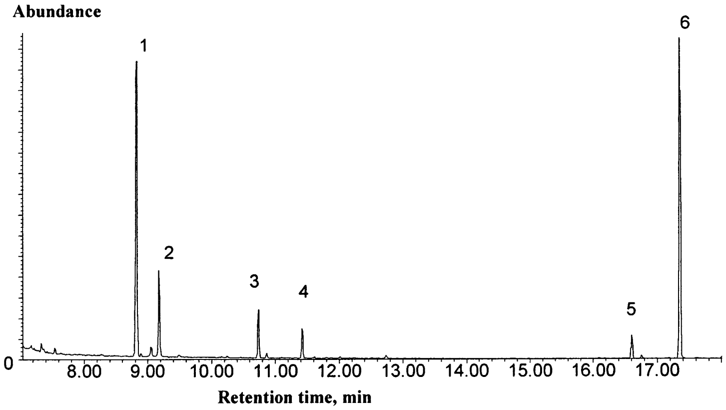


FIG. 3.

Total Ion Chromatogram (TIC) obtained from pyr-GC/MS of BSTFA-TMCS-treated cement sample interground with phenol/TEA blend. Peak identification (as silyl derivative): 1 = phenol; 2 = BSTFA-TMCS reagent; 3; 4; and 5 = background; and 6 = TEA.

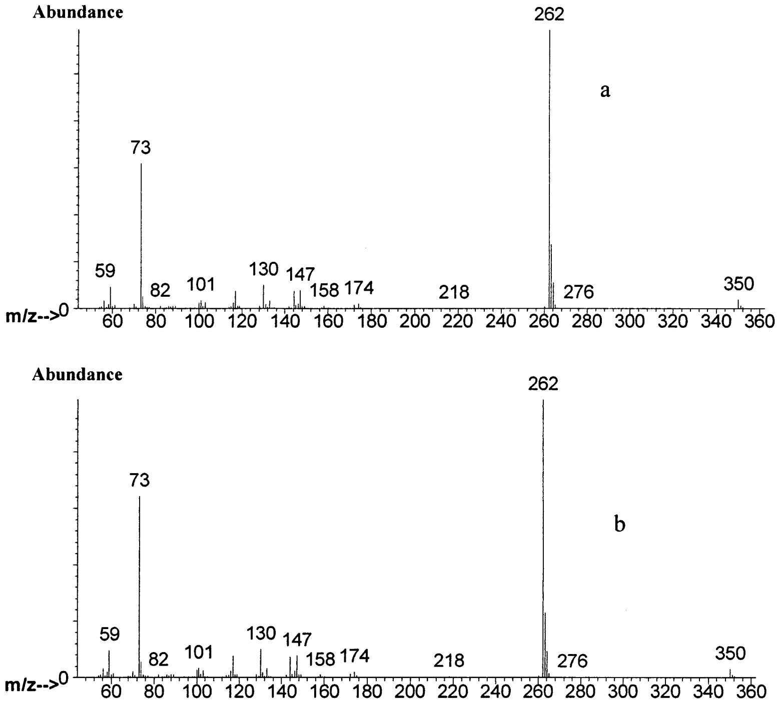


FIG. 4.
Comparison of mass spectra for the silylated derivative of TEA produced from the pyr-GC/MS of control cement doped with phenol/TEA blend versus cement interground with the grinding aid.

both with the SPEX and temperature controlled rotating mills. In the case of the rotating mill, results are provided for DG grinds conducted at both 22 and 105°C.

For the samples prepared with the SPEX Mill, the silylation procedure made detection possible for all the grinding aids except phenol, and in the case for 3 of the 6 compounds recovery rates increased over 80%. The fact that phenol could be detected for cement samples prepared with both the SPEX and rotating mills, without silylation, vs. the glycols and alkanolamines suggests that a) phenolic-type additives probably have less binding capacity with cement cations; and b) phenol would appear to be more thermally stable during pyrolysis. Similarly, incomplete recovery of the alkanolamine and glycols suggests that these compounds have either formed complexes at the cement surface during the grinding process that can not be completely silylated under the selected derivitization conditions, or that the alkanaolamines and glycols could possibly be partially altered and rendered undetectable during both the milling and pyrolysis processes. The relatively low recovery rate of DG from a clinker interground with the calcium-DG salt further underscores the possibility of thermally stable complexes or salts forming between polar compounds interground with clinker and gypsum. Furthermore, in the case of the SPEX-ground cements, the relatively low

TABLE 4
Percentage recovery of grinding aid compounds from cement.*

Process →	SPEX mill 45°C		Rotating mill		
			105°C	105°C	22°C
Grinding aid†	Direct	Derivitized	Direct	Derivitized	
Phenol	41%	93%	25%	80%	—
EG	ND‡	57%	ND	8%	—
DG	2%	86%	ND	19%	35%
PG	ND	31%	ND	6%	—
TEA	ND	85%	ND	5%	—
TIPA	ND	30%	ND	3%	—
Phenol/TEA§	69%	100%	25%	60%	—
CaDG	ND	32%	—	—	—

* Recovery based on ratio of MSD response obtained from doping control cement with 200 ppm grinding aid to response produced from thermally desorbed grinding aid from cement.

† Each additive interground at 200 ppm concentration.

‡ Not detected.

§ Recovery rate based on phenol response.

recoveries obtained for PG and TIPA could be a result of the steric hindrance associated with their secondary alcohol structures.

The samples prepared at 105°C with the rotating ball mill consistently yielded lower recovery rates indicating that certain grinding parameters such as mill temperature and configuration and grinding time appear to play an important role for the quantitative determination of grinding aids in cement. Possible causes for the relatively lower recovery include: a) irreversible adsorption of the grinding aid on the heated steel chamber and balls; b) partial evaporation from the mill; c) formation of certain complexes or salts could be favored at elevated mill temperatures; and d) partial decomposition of the grinding aid during the milling process. In the case of DG, the operating temperature of the rotating mill appears to have had a significant impact on recovery rate, which may have in part resulted from all these factors.

A linearity study performed with six cement samples interground with phenol, ranging from 0 to 400 ppm, and prepared with the SPEX Mill found the correlation coefficient, R, to be 0.99. A similar study using five DG cement samples containing 0 to 800 ppm also yielded a linear relationship, R = 0.98. An evaluation of cement samples prepared with the temperature controlled rotating mill has yet to conducted. Quantitative determination of various interground additions in cement for a particular milling process may be possible even when recovery rates are low as long as the recovery rate remains constant over the desired concentration range. The pooled standard deviation for 10 replicate measurements of thermally desorbed phenol as the silyl derivitive was 10 ppm. The RSD was 6%.

Conclusion

Pyr-GC/MS coupled with in situ derivitization using BSTFA-TMCS has been found to provide a unique capability for rapid and specific detection of six grinding aid compounds in cement. The recovery rate of the additives, as measured by a given set of pyrolysis conditions, was observed to be dependent upon both milling parameters and the chemical nature of the various grinding aids. Higher temperatures, longer grinding times, and more intense grinding conditions caused lower recovery rates through several possible mechanisms, i.e. salt or complex formation and partial thermal degradation resulting from either the milling process and/or pyrolysis procedure. The binding capacity of the various grinding aids, which in turn can be related to their hydroxy and amino functionalities, appears to play an important role with regard to the difference in recovery rates between phenol versus the glycols and alkanolamines.

Acknowledgment

The authors wish to thank Boris Gitlin for his assistance in performing the pyr-GC/MS analysis, and W.R. Grace for permission to publish this work.

References

1. W. Rechenberg, Zement-Kalk-Gips 12, 380 (1986).
2. F.J. Mardulier, Proc. Am. Soc. for Testing and Mat. 61, 1078 (1961).
3. F.W. Locher and H.M. v. Seebach, Ind. Eng. Chem. Process Des. Develop., 11, 190 (1972).
4. ASTM C465, Annual Book of ASTM Standards, Vol.04.01.
5. W.G. Hime, W.F. Milenz, and J.D. Connolly, Analytical Techniques for Hydraulic Cements and Concrete, ASTM STP 395, ASTM, 1965.
6. V.T. Yilmaz, A. Kindness, and F.P. Glasser, Adv. Cem. Res. 2, 107 (1989).
7. L. Bean and R.B. Peppler, Rock Products 49, 71 July (1946).
8. A.S. Wexler and F.D. Brako, Mat. Res. Stand. 3, 364, (1963).
9. V.T. Yilmaz, A. Kindness, and F.P. Glasser, Cem. Concr. Res. 22, 663 (1992).
10. A.S. Wexler, unpublished method from W.R. Grace for organic amines in cement, 1965.
11. Unpublished method from Union Carbide for determination of ethylene glycol in Portland cement.
12. A.S. Wexler, Analytical Techniques for Hydraulic Cements and Concrete, p. 58, ASTM STP 395, 1965.
13. V.T. Yilmaz, N. Menek, and M. Odabasoglu, Cem. Concr. Res. 23, 603 (1993).
14. P. Cassat, J.F. Muller, P. Manuelli, A. Vichot, and P. Colombet, Rapid Commun. Mass. Spectrom. 11, 1612 (1997).
15. A. Ohno and T. Yamamoto, 10th International Congress on the Chemistry of Cement, paper 3v015, June 1997.
16. A. Ohno, unpublished report by Sumitomo Osaka Cement Co., Ltd. July 1995.
17. A. Mabud, A. Jeknavorian, E.F. Barry, and J. Litzau, Proceedings of the 44th American Society for Mass Spectrometry (ASMS) Conference, p. 554, Portland, Oregon, 1996.
18. A. Jeknavorian, A. Mabud, E.F. Barry, and J.J. Litzau, J. Anal. Appl. Pyrol. In press.
19. K. Blau and J. Halket, Handbook of Derivatives for Chromatography, 2nd ed., pp. 57–8, John Wiley and Sons, New York, 1993.
20. D.R. Knapp, Handbook of Analytical Derivitization, p. 9, John Wiley and Sons, New York, 1979.