

EVALUATION OF PHOTOACOUSTIC SPECTROSCOPY FOR QUALITY CONTROL OF CEMENT

Final Report
for Iowa DOT Project TR-409

Sponsored by the
Iowa Department of Transportation
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January 1998

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FINAL REPORT
IDOT Research Project TR-409

ABSTRACT

This report discusses the feasibility of using infrared photoacoustic spectroscopy (PAS) as a viable technique that can quickly provide information on cement composition prior to use. The PAS technique is of interest because the cost is much lower than for other type of instrumentation used for mineral analysis, it requires virtually no sample preparation, and it can perform multi-component analysis in a matter of minutes. Feasibility of the technique was based on the ability of PAS to identify and quantify sulfate species and major cement matrix components. Strengths and limitations of the technique are presented.

FINAL REPORT

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OBJECTIVE

The objective of this project was to determine the feasibility of using a low-cost photoacoustic spectrometer as a rapid nondestructive analytical tool to determine important mineral species in cement prior to use. Strengths and limitations of the photoacoustic approach for mineralogical analyses of interest were identified and the utility of the technique for routine cement analyses assessed.

INTRODUCTION

Portland cement is commonly used in construction projects within the Iowa Department of Transportation (IDOT). Failures are typically the result of variability in cement composition and can be minimized by analytically screening the cement prior to hydration. The scope of work in this project went to establishing the feasibility of photoacoustic spectroscopy (PAS) as an analytical technique for routine cement analysis. Feasibility was determined by assessing PAS's ability to (1) identify and quantify sulfate species in a cement matrix and (2) identify and quantify the major cement matrix components. The work in this project consisted of essentially three tasks:

- Establish sample preparation and sample analysis protocols.
- Acquire spectra of pure individual cement components.
- Demonstrate utility of the technique for cement analysis.

EXPERIMENTAL

The sulfate compounds examined in this study were gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), bassanite ($\text{CaSO}_4 \cdot 0.5 \text{H}_2\text{O}$), anhydrite (CaSO_4), and arcanite (K_2SO_4). High-purity gypsum and high-purity bassanite samples were obtained from the Celotex Corporation and the National Gypsum Company, respectively. The purity of the standard sulfate samples were assessed by x-ray diffraction (XRD) and weight loss analysis. It was determined that the Celotex gypsum was approximately 93% pure and the bassanite was $\geq 98\%$ pure. Standard anhydrite was prepared by heating the high purity bassanite at 1000°C for 6 hours in a muffle furnace. Analysis of the prepared anhydrite by XRD indicated that the resulting compound was "synthetic anhydrite" with no residual bassanite present. The purity of the synthetic anhydrite was assumed to be $\geq 98\%$. Anhydrous CaSO_4 produced by lower heating temperatures was not used because of the potential of absorbing ambient moisture and converting to other CaSO_4 compounds. Reagent grade K_2SO_4 from Fisher Scientific was used for the arcanite. XRD analysis showed that the K_2SO_4 was arcanite rather than a polymorph of that compound. The arcanite was powdered with a mortar and pestle prior to use, while the calcium sulfate compounds were used as received (already powdered).

The major cement matrix components investigated were tricalcium silicate (C_3S), dicalcium silicate (C_2S), tricalcium aluminate (C_3A), and tetracalcium aluminoferrite (C_4AF). These compounds were obtained from Construction Technology Laboratories (Skokie, IL). Only the monoclinic form of the C_3S (the mineral alite) was used in this study.

Sample Preparation

Samples were prepared by accurately weighing various mineral components on a Mettler AE100 analytical balance. A total sample weight of 0.5g was used for each analyte concentration prepared. Samples were stirred and tumbled before taking ~20mg aliquots and mounting them in small aluminum cups. The mounted samples were not dried prior to PAS analysis.

Sulfate standards were prepared by adding known amounts of the respective sulfate to a separately prepared synthetic cement matrix. Sulfate concentrations were corrected based on purity levels of the standard used. This correction was only significant for gypsum. The concentration range investigated for each of the sulfate components was 0 to 4% (weight percent). The synthetic cement matrix used for the sulfates consisted of 60% C_3S , 20% C_2S , 10% C_3A , and 10% C_4AF and was used both for the sulfate standards and mixtures.

For the studies on C_3S , C_2S , C_3A and C_4AF , varying amounts of each were spiked into a matrix consisting of the three other major components. The concentration ranges investigated for the major matrix components were 50-70% for C_3S , 15-30% for C_2S , 2-15% for C_3A , and 5-15% for C_4AF .

RESULTS

The first step in the project was to determine the optimum parameters for the spectrometer. Parameters were selected to provide the best quality spectra in a reasonable period of time. The experimental parameters selected are listed in Table I.

Table I. Experimental Parameters.

Spectrometer:	Perkin-Elmer Paragon FTIR Spectrometer
Detector:	MTEC Model 300 Photoacoustic Detector ¹
Spectral Range:	4000 cm^{-1} to 650 cm^{-1}
Resolution:	8 cm^{-1}
Mirror Velocity:	0.1 OPD
Scans Co-added:	64 (~4 mins.)
Sample Size:	~20 mg

1. All samples were purged in the detector with helium prior to analysis to remove CO_2 and ambient moisture.

The sample preparation procedure was evaluated by taking triplicate aliquots of the high and low concentrations of each of the prepared calcium sulfate standards and checking the reproducibility of the acquired photoacoustic spectra. The reproducibility for each triplicate set was quite good.

The variance averaged about 1.5% for the sets and did not exceed 2.8% in the spectral regions of interest. This indicates that the developed sample preparation procedure is suitable for quantitative analysis.

Sulfate Analysis

Infrared photoacoustic spectra of the individual cement components was acquired in order to identify spectral interferences and select suitable regions in the spectrum to use for analysis. Investigation of the pure calcium sulfate component spectra showed that each had a unique spectral region for analysis with no spectral overlap within the concentration ranges investigated. It was determined that arcanite, although having a characteristic spectrum, did not have any distinctive bands that could be used for analysis. The respective absorption bands and spectral regions chosen for the calcium sulfate components are listed in Table II.

Table II. Peak Positions used for Area Analysis

	Anhydrite	Bassanite		Gypsum	
Peak Center (cm ⁻¹)	2135	3605	1616	2300	1700
1st Baseline Point (cm ⁻¹)	2190	3631	1660	2400	1687
2nd Baseline Point (cm ⁻¹)	2103	3584	1587	2168	1672

Once spectral regions were identified for each of the sulfate species, standards/calibration sets were prepared with varying “known” amounts of sulfate for each of the species to be determined. Concentrations of those standards varied from 0 to 4% in order to mimic real world samples. The samples were then analyzed by linear regression (LR) and partial least squares (PLS) analysis techniques.

Linear regression analysis was performed by measuring the peak areas of the sulfate bands in the calibration set spectra. The peak areas and concentration values were then used to determine calibration coefficients to generate calibration curves. The square of the calibration coefficients (or regression coefficient) indicate the quality of fit of the data to a straight line. A value of 1 (one) indicates a perfect fit. The regression coefficients for the sulfate calibration sets are listed in Table III. Linear regression is well suited for single component analysis when there is little spectral interference and band overlap. When overlap and interferences become more prominent the accuracy of the results drops and other more sophisticated techniques are required.

Table III. Correlation Coefficients for PLS and Conventional LR Analysis

	<u>Partial Least Squares</u>		<u>Linear Regression</u>	
	Correlation Coefficient (R ²)	Average Error in Analysis	Regression Coefficient (R ²)	Average Error in Analysis
Anhydrite	0.9989	0.10%	0.9893	0.20%
Bassanite	0.9929	0.43%	0.9913	0.13%
Gypsum	0.9968	0.22%	0.8912	0.14%

The sulfate calibration sets were also analyzed by PLS. PLS differs from the LR technique in that typically the whole spectrum is used to fit the data, thereby improving sensitivity and facilitating analysis of multicomponent compounds such as cement. PLS is especially applicable to spectra which demonstrate severe spectral interference and band overlap. Similar to linear regression, a calibration model is generated and correlation coefficients ascertained to determine the quality of fit of the data. Again, a value of 1 (one) indicates a perfect fit. The correlation coefficients from the PLS analysis are also listed in Table III for comparison. Both sets agree quite well with each other. Since no spectral interference or band overlap was observed within the concentration ranges of interest for the sulfate analytes in this study, linear regression will be used as the analysis technique.

Based on the sulfate standard analysis, it was determined that the minimal detectable level by PAS for bassanite and gypsum in the prepared synthetic cement matrix was 0.5% (weight percent). The minimal detectable level for anhydrite was 0.3%.

Examination of the matrix components indicated that elevated levels of C_3S could potentially interfere with the sulfate analysis. To test if C_3S would interfere, a series of calcium sulfate standards were prepared with the C_3S concentration raised to 80%. Analysis of this series yielded the expected sulfate concentrations. Other matrix components were not investigated because spectral analysis indicated that there would be little or no interference from them. To demonstrate that the PAS method can analyze mixtures, a series of samples were prepared in which all three calcium sulfate compounds were added. The samples were then analyzed by linear regression. The results of the analysis are presented in Table IV. The concentrations of the sulfates were able to be determined within experimental error except for gypsum in two of the mixtures. The experimental gypsum concentrations were lower than expected for the two mixtures.

Table IV. Analysis of Prepared Mixtures (wt. %)

	<u>Known Concentrations</u>			<u>Experimental Concentrations</u>		
	Anhydrite	Bassanite	Gypsum	Anhydrite	Bassanite	Gypsum
Mixture 1	0.98	0.96	2.79	0.88	1.08	2.72
Mixture 2	0.98	1.04	0.98	1.20	1.03	0.77
Mixture 3	0.96	3.00	0.95	1.13	2.86	1.09
Mixture 4	1.02	1.02	0.91	0.95	1.01	1.06
Mixture 5	2.94	0.98	0.91	2.91	1.30	0.60
Mixture 6	1.00	1.00	0.97	0.97	1.00	.99

Matrix Component Analysis

Evaluation of the major cement matrix component spectra indicated that there were no distinctive spectral regions that could be used for analysis for C_3S and C_4AF components. The C_2S and C_3A component spectra did show unique spectral regions that could be used for analysis. However,

the absorption bands for these compounds are weak and are located in spectral regions where potential interferences exist in real world samples. Examination of real world cements (e.g., Holnam) revealed that there may be minor matrix components which can spectrally interfere. For example, calcium hydroxide has an absorption band which overlaps the absorption band of C_3A .

As mentioned above, only the C_2S and C_3A matrix components had distinctive regions which could potentially be used for quantitative analysis. Calibration sets of these matrix components were prepared over the anticipated range of concentrations and analyzed by both PLS and LR. For each component the correlation and regression coefficients were better than 0.98.

Carbonate Formation

A Holnam cement sample obtained previously from the IDOT was re-analyzed by PAS about a year after our initial PAS analysis on that sample. It was of interest to note that the spectrum obtained a year later had some additional bands present that were absent in our initial analysis. After experimentally ruling out instrumental and sample preparation variables, a fresh Holnam cement sample was obtained from the IDOT. The spectrum obtained for this fresh sample matched the spectrum we initially obtained on the previous Holnam cement sample. Thus, some additional bands appeared in the spectrum due to sample aging. Although the source of the additional bands is not known with certainty, it is very likely that they are due to carbonate formation within the sample. IDOT personnel later noted that CaO and $Ca(OH)_2$ in the cement can convert to $CaCO_3$ as cements age. Thus, the PAS technique could potentially be used to monitor the carbonate bands as an indicator of cement aging and cement quality.

Unknown Analysis

The final step in this feasibility study was to examine samples prepared by IDOT personnel. Unknown samples were prepared by spiking NIST Portland cement clinkers with varying amounts of the calcium sulfate species. Original clinker samples were pulverized in a Spex shatterbox for 4 minutes. Blended samples were repulverized for 10 seconds in the Spex shatterbox. The sulfate concentration ranges for the spiked samples were to parallel the ranges used for the calibration sets. These samples were then submitted as unknowns for analysis by PAS, XRD and thermal analysis. The XRD and thermal analyses were to be performed by another laboratory. However, equipment failures and new equipment installations over the past month and a half have kept them from analyzing the samples prior to preparation of this report.

PAS spectra of the unknown samples were acquired under the same conditions as that of the synthetically prepared samples. The spectra were then analyzed by linear regression using the calibration curves generated with the synthetically prepared samples. The experimental and theoretical results are presented in Table V. The XRD and thermal analyses data were not available at the time this report was written and therefore not included. Samples C, G and K showed no evidence of any calcium sulfate present. The PAS spectra of these three samples were identical except in the region around 3642 cm^{-1} . This region corresponds to a characteristic absorption band of calcium hydroxide ($Ca(OH)_2$). Sample C had the largest concentration of $Ca(OH)_2$ and sample K the lowest. Because of the presence of $Ca(OH)_2$, which spectrally

interferes with C₃A, C₃A could not be determined. Likewise, there was a spectral interference observed in the absorption region of the C₂S species which prevented determination of that component.

Samples A, E, H, I, J, and L showed high concentrations of bassanite present. Based on visual examination of the PAS spectra, the bassanite levels were beyond the range used for the calibration set. Therefore, the bassanite values in these samples had to be extrapolated, reducing the confidence in their assigned value. Furthermore, the presence of high bassanite levels may also affect the determinations of the other sulfate species that may be present. At high concentration levels weaker bands become more prominent and can cause spectral interferences. The effect could result in false determinations, as seen for the anhydrite determination in samples E and I, or higher than actual determinations.

Since the majority of the determined sulfate values (by PAS) are higher than the theoretical values, it is believed that sample preparation variability (between IDOT prepared samples and ISU prepared sample) is suspect. Sample presentation is important in PAS measurements. Particle size is one variable, for example, that can effect results, producing slightly higher (or lower) concentrations. This may explain the differences for the anhydrite and gypsum values. The large differences between the bassanite values, however, cannot be explained at this time. Analysis of separate aliquotes of a given sample yielded very reproducible results, regardless of which sample preparation procedure was used. Therefore, sample homogeneity is not a major issue.

Table V. Analysis of IDOT Prepared Unknowns
(reported as wt. % sulfate)

Unk.	Theoretical			Photoacoustic			Thermal			XRD		
	Anh	Bas	Gyp	Anh	Bas	Gyp	Anh	Bas	Gyp	Anh	Bas	Gyp
A	3.0	2.0	0.0	5.2	11.5	0.0						
B	2.0	0.0	0.0	3.9	0.0	0.0						
C	0.0	0.0	0.0	0.0	0.0	0.0						
D	2.0	0.0	6.0	2.8	0.0	8.5						
E	0.0	2.0	3.0	(1.4)*	8.6	4.3						
F	0.0	0.0	2.0	0.0	0.0	3.0						
G	0.0	0.0	0.0	0.0	0.0	0.0						
H	1.0	2.0	2.0	2.2	12.9	3.3						
I	0.0	2.0	0.0	(1.1)*	8.5	0.0						
J	2.0	4.0	2.0	3.9	15.8	2.2						
K	0.0	0.0	0.0	0.0	0.0	0.0						
L	4.0	2.0	2.0	6.9	12.8	2.9						

*These experimental values are largely due to the large amount of bassanite present.
(See text.)

CONCLUSIONS

PAS does an excellent job at determining calcium sulfates when standards are prepared by adding sulfates to a synthetic cement matrix. Instrumental response is very linear with changes in concentration and the technique has suitable detection limits. However, for unknown reasons, the technique did not perform well on sulfate standards prepared by spiking and blending NIST Portland cement clinkers. Because the sample preparation procedures were much different between standards prepared at ISU (synthetic cement matrix) and IDOT (NIST clinkers), this is one area that requires consideration. As it currently stands, PAS is not a reliable technique for determining calcium sulfates in real world samples. However, because this may be related to largely or entirely to sample (i.e., standards) preparation procedures, the use of PAS for routine sulfate analyses on cements is still considered to be very feasible.

It also appears to be feasible to use PAS for determining C_3A , but only if $Ca(OH)_2$ levels are low or accounted for. C_2S also proved to be susceptible to interferences from the matrix clinker. The PAS method appears to be good for determining carbonate (sample aging) and $Ca(OH)_2$. However, the feasibility of doing quantitative analyses for those compounds still requires investigation.

PAS is not suitable for determining arcanite, C_4AF , C_3S or C_2S in cements due to lack of sensitivity or spectral interferences for those compounds.

RECOMMENDATIONS

ISU and IDOT personnel should meet to discuss these results further. PAS should not be used for cement analyses without further developmental work. IDOT personnel should consider supporting a follow-up study to examine the problem of standard preparation if it is believed that PAS may be of interest for calcium sulfate analyses alone.