Identification of Organic Admixtures in Cement Dry Mix Systems Using MDRS

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Organic admixtures for industrial mortars and concretes, such as superplasticizers, retarders, or organic lubricants, are widely used to modify and control the processing properties of hydraulic bonded systems. A precise and accurate analytical statement about the presence of organic ingredients is required to design high-performance engineered castables, such as refractories.

The present paper describes the application of Morphologically Directed Raman Spectroscopy (MDRS) to monitor organic admixtures in cement dry mix systems. Received spectra of MDRS investigations of organic and inorganic ingredients show characteristic Raman patterns of distinct peaks allowing the classification of spotted particles. MDRS provides highest sensitivity since it is applied to individual particles of the present matrix, allowing the detection of admixture components in lowest concentration.

1 Introduction

Cement is one of the most important building material of today's time [1]. Especially in the refractory industry, Calcium Aluminate Cement (CAC) is well-established as a special application cement. A broad portfolio of multi-purpose CAC-based cements for construction projects in extreme-condition areas has been developed [2–8] (Fig. 1).

As a key component of such formulae, organic admixtures are commonly used to selectively modify and influence the processing properties of functionalized binder, mortar, and concrete systems [9–11].

Common admixtures, such as retarders, accelerators, or superplasticizers, comprise carboxylic acids, paraffins, or polymeric molecular chains consisting primarily of esters, carboxylate salts, and ether groups. Organic acids like citric acid are often used as retarder for calcium aluminate hydration [12]. Paraffin wax might occur in some mortars as rheology modifier or temporary binder. Superplasticizers like polycarboxylate ether (PCE) function as hydrophilic surfactants which deflocculate and disperse particles of cement when dissolved in water [13, 14]. To ensure required cement performance attributes and thus an efficient design and use of high-performance engineered refractories, even elusive amounts of organic substances embedded in cementitious mineral systems need to be reliably identified, as organic admixtures are generally used in small concentrations of some tenths of a percent.

This article describes the use of Morphologically Directed Raman Spectroscopy (MDRS) as an efficient way to identify organic ad-

Fig. 1 Some exemplary cement dry mix systems

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Tab.1 Materials used in this stud.

Material	Abbreviation	Manufacturer	Purity [%]	Type
Citric acid	AC	Brenntag UK & Ireland	≤100	Retarder
Tartaric acid L(+)	AT	Merck Chemicals KgaA	≤100	Retarder
Organic acid	AO	Merck Chemicals KgaA	≤100	Retarder, Self-curing compound
Paraffin wax		Shell UK Oil Products Limited	>99	Organic binder, Lubricant
Polycarboxylate ether 1	PCE1	Peramin	N/A	Superplasticizer
Polycarboxylate ether 2	PCE2	Peramin	N/A	Superplasticizer
Crosslinked acrylic polymer	CLAP	BASF Construction Polymers	N/A	Deflocculant, Superplasticizer
Secar71 (CAC)	S71	Kerneos	N/A	
Ordinary Portland Cement	OPC	Lafarge	N/A	
Anhydrite		Francis Flower	>97	
Calcite		Omya	>95%	

mixtures present in high-functionalized cement-based systems.

2 Experimental procedure

2.1 Materials

A wide range of organic admixtures commonly used for refractory castables and specialty mortars were investigated, mixed in dosages of 0,025 % up to 5 % by the weight of the cement (Tab. 1). This includes polycarboxylate ethers (PCE), crosslinked acrylic polymers (CLAP), carboxylic acids, and paraffin wax (Fig. 2). Kerneos' calcium aluminate cement Secar71 served as a model dry-mix system. Besides, investigated cement-additive matrices cover a wide spectrum of industrially used mineral components of binder systems (Tab. 1).

2.2 MDRS methodology and procedure

The term Raman spectroscopy refers to spectroscopic investigations of inelastic scattering of light (Fig. 3). When light traverses a material, some of the light changes in wavelength. In quantum mechanics, this phenomenon is described as Raman- or Stokes-scattering. To be measured by Raman spectroscopy, a change in polarizability of molecules while rotating and vibrating, initiated by a monochromatic laser, is necessary. This results in Stokes lines characteristic for a certain material and allows differentiating even closely-related chemical species with similar chemical structures to give a high molecular specificity.

Morphologically directed Raman spectroscopy is an analytical tool to chemically identify individual particles based on image analysis. MDRS uses Raman spectroscopy in conjunction with static image analysis obtained by morphological investigation.

The methodology of MDRS can be broken down into three main stages:

(1) Morphological imaging of dispersed sample particles;
(2) Raman spectral analysis acquisition;
(3) Chemical identification.

MDRS provides information about Raman chemical correlation scores to pre-determined library spectra. Via correlation calculation, the strength of association between

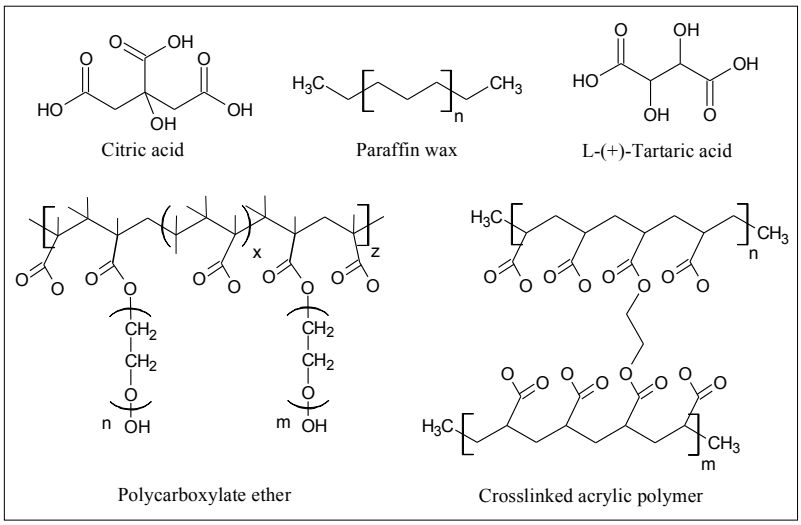

Fig. 2 Structural formulae of investigated organic admixtures

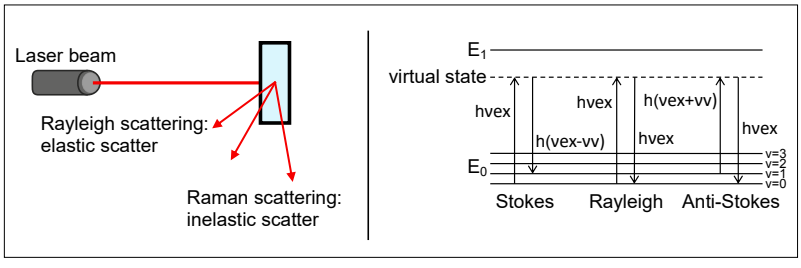

Fig. 3 Demonstration of scattering phenomena (l.), and quantum mechanical model of Raman scattering (r.)

Fig. 4 Photo of the Malvern Morphologi G3SE-ID equipped with a Raman RXNN1 semiconductor laser

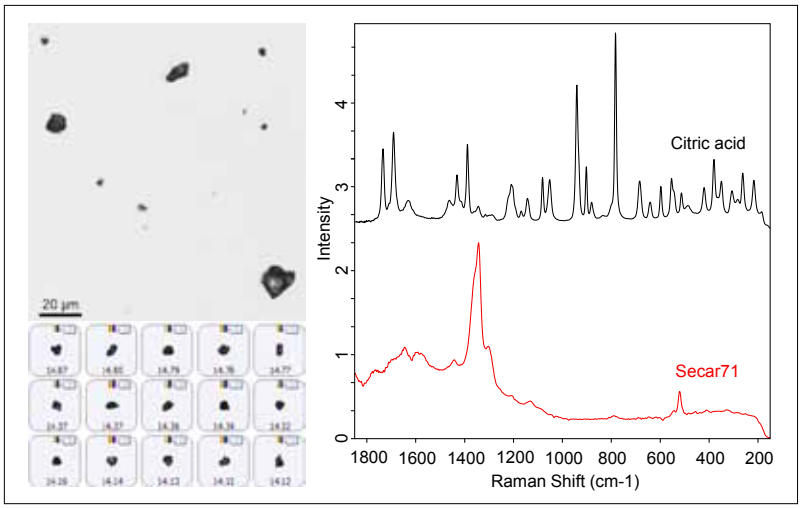

Fig. 5 MDRS analysis of citric acid and Secar71: morphological imaging of dispersed sample particles (l.); Raman spectral analysis acquisition (r.)

a particle spectrum and in-house reference library spectra can be measured.

MDRS in a spectral range from 150 cm^{-1} to 1850 cm^{-1} was obtained using the Malvern Morphologi G3SE-ID, equipped with a Raman RXNN1 semiconductor laser operating at 785 nm and a high resolution 5 mega pixel digital camera Nikon CFI60 Optics with 50x objective magnification (Fig. 4). Morphology data was acquired for around 50 000 particles, where 1000–5000 particles were targeted for spectral analysis. In total, the process took about 48 h.

3 Results and discussion

MDRS principle is demonstrated in Fig. 5. First, dispersed sample particles are morphologically mapped and characterized followed by Raman spectral analysis acquisition. As an example, spectra of Secar71 (CAC) and citric acid (retarder) are given, indicating the change of intensity as a function of Raman shift.

The investigation of morphological data of a model system are shown in Fig. 6. The 3-way-plot illustrates that particles of cement and organic additions, in this case Secar71 and PCE1, are similar in shape and size, caused especially by particle interactions and the sample preparation and mixing processes. Independently, imaging cannot differentiate morphologically-similar species, thus does not indicate organic ingredients.

However, spectroscopic Raman data of MDRS investigations serve as a clear indicator for identifying the sample´s matrix components (Fig. 7–9). Since particles are mapped via morphological image processing and spotted by the Raman laser, each particle is analyzed individually. Therefore, the output of MDRS analyses are patterns of Raman shifts highly unique for the present substance.

Investigations of commonly used organic admixtures like carboxylic acids, or long chained organic structures indicate, that organic species generally show a series of sharp, distinct peaks. Even closely related chemical structures can be differentiated with highest sensitivity, since the obtained Raman shifts show exceptional uniqueness. Generally, a high fluorescence background of polymeric organic structures is to be note. Spectra of organic admixtures can be clearly distinguished from those of inorganic components of the cement system, as well, due to their unique patterns of Raman shifts. Assigned Raman shifts for Secar71 for example are spotted at 520 cm^{-1}, 1340 cm^{-1}, and 1650 cm^{-1} as broad bands, whereas citric acid gives sharp high-intensity peaks at 780 cm^{-1} and 950 cm^{-1}, for example.

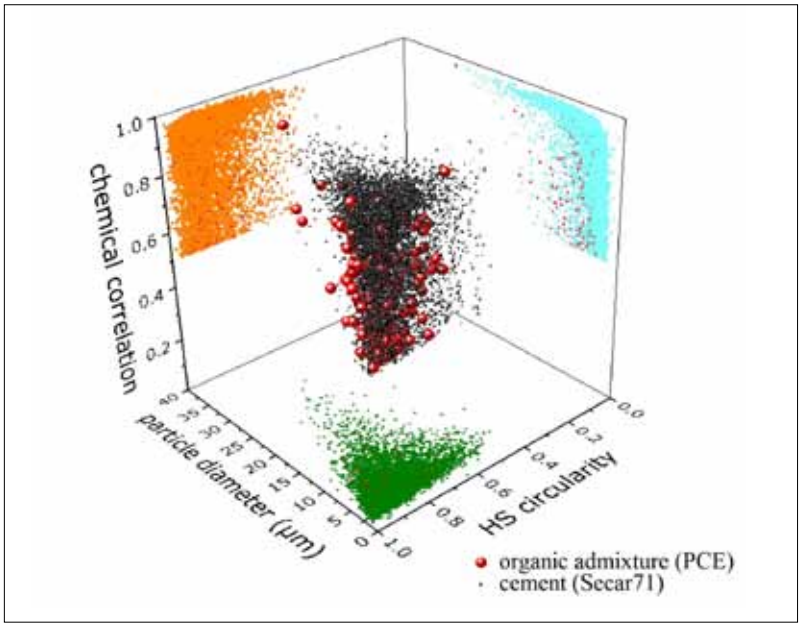

Fig. 6 3-way-plot of MDRS parameters chemical correlation, particle diameter, and HS circularity of Secar71 and a PCE

Thus, MDRS allows the identification of particles and indicates the presence of organic admixtures in the dispersed sample. A wide range of pre-determined library spectra serve as references, comparing the given data with the spectral output of the sample measurement as correlation scores.

Further investigations of exemplary dry mix systems comprising Secar71 and organic admixtures serve to outline limitations of MDRS (Fig. 10).

First, the laserbeam is only suitable for analysis of particles greater than 3 µm. Smaller particles can't be detected properly due to the high participation of the background material, leading to Raman shifts attributed to the carrier between 500 cm^{-1} and 200 cm^{-1}, as seen in the spectra. Thus, inaccuracies can occur when evaluating the spectrum.

Second, agglomerations of particles may occur. The agglomeration of two particles (bottom spectra of Fig. 10) leads to a spectrum including both Secar71 and organic acid peaks. The broad Raman peaks at 520 cm^{-1}, 1340 cm^{-1}, and 1650 cm^{-1} are indicative for the presence of Secar71, while the organic acid gives distinct, sharp Raman peaks located over the whole spectrum. As shown, Raman analysis of agglomerated particles generates one spectrum with overlapping patterns of both particles. This results in low correlation scores of 0,5 and 0,8 respectively, even though the identification of the two components is positive.

Taking these difficulties into account, further measurements have been performed to value the accuracy of MDRS in terms of quantitative specification. The bar chart in Fig. 11 lists the obtained results of a MDRS measurement including 1 % of selected organic admixtures. The obtained values, ranging from 0,35 – 1,58 %, thus, are unacceptable quantitative statements. Seeing that the stated difficulties (particle size and agglomeration) lead to inaccuracies in terms of quantification, MDRS is not suitable to evaluate the concentration of organic admixtures in cement systems.

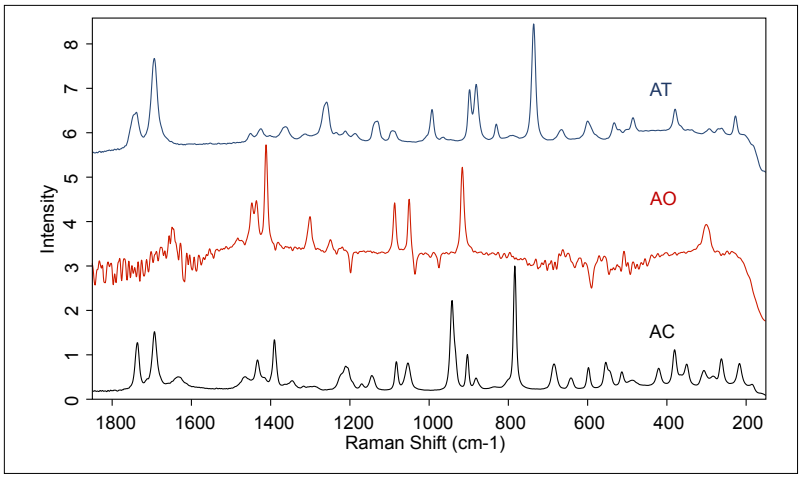

Fig. 7 Raman spectra of selected carboxylic acids

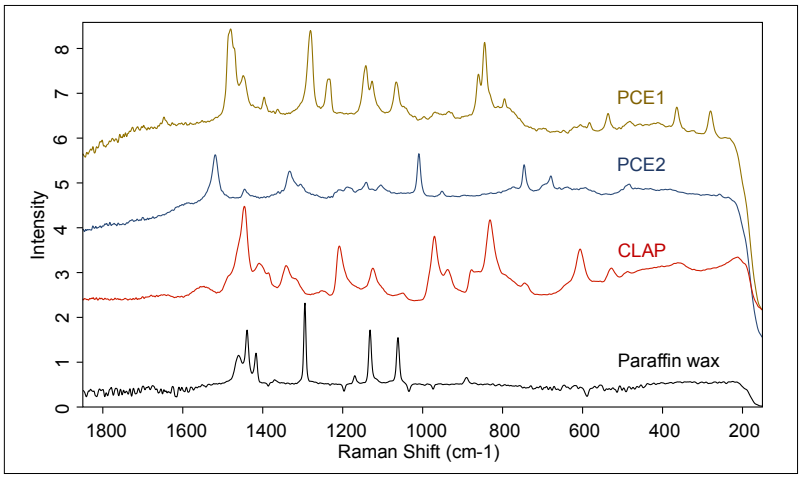

Fig. 8 Raman spectra of paraffin wax and selected polymers

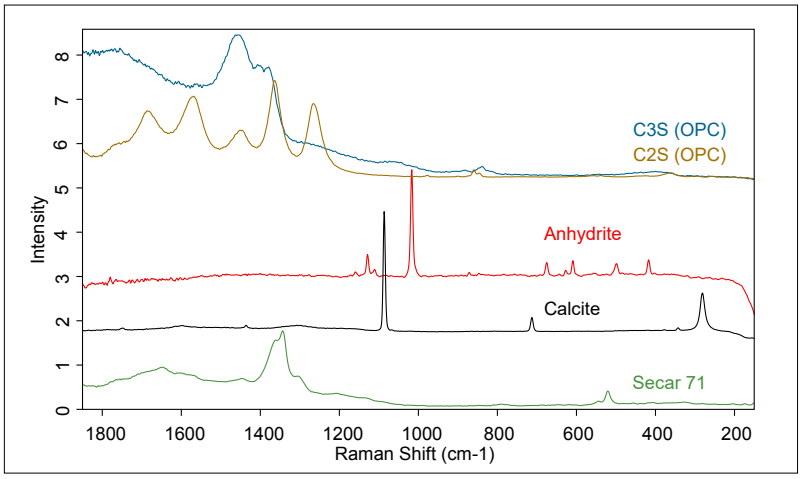

Fig. 9 Raman spectra of selected mineral compounds

4 Conclusion

This study provides an evaluation on the applicability of MDRS on monitoring organic admixtures as a part of dry-mix formulations of functionalized cement mixtures. It is stated that:

- independently, morphological imaging cannot differentiate organic and inorganic species of industrially mixed cement formulations;
- via Raman spectral analysis, organic components in lowest concentrations can be reliably identified by evaluating their unique Raman shift´s (peak location and shape);
- there is no need for additional sample preparation;

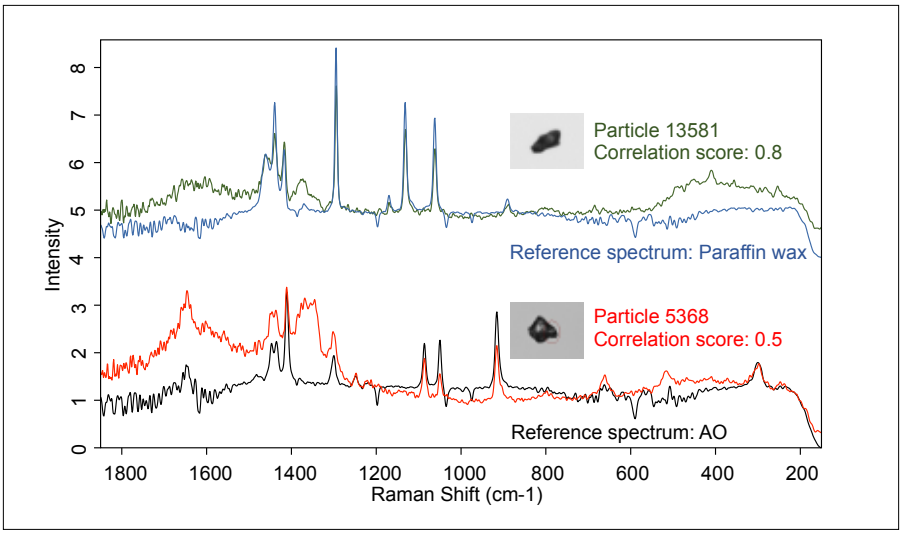

Fig. 10 Comparison of Raman spectra of agglomerated particles and reference spectra (correlation score)

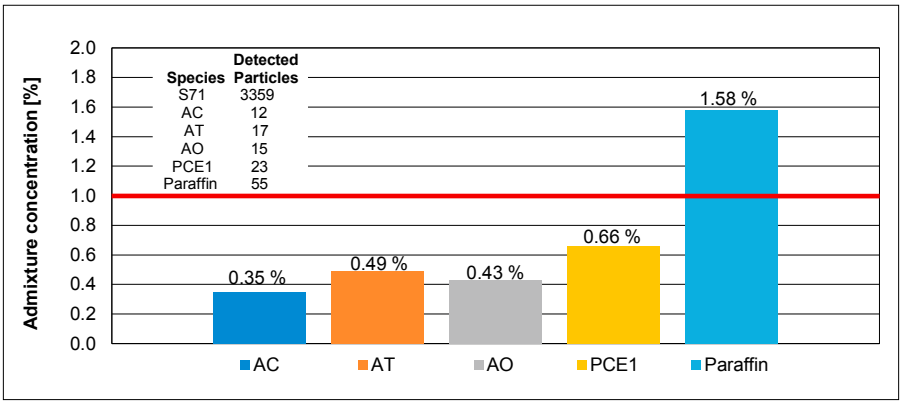

Fig. 11 Quantitative evaluation of MDRS investigations: mixture of Secar71 + organic admixtures with an initial value of 1 % each

- MDRS is unsuitable to quantify organic admixture concentrations due to agglomeration and particle sizes < 3 µm.

The method has proven to be a powerful tool for identifying organic admixtures, since organic structures show highly unique Raman patterns. MDRS allows the high-sensitivity detection of admixture components in lowest concentrations because it is applied to individual particles of the matrix. Outlined limitations of the method, though, reveal the need of a general analytical concept to provide detailed qualitative and quantitative information about organic admixtures present in cement matrices.

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