# Analysis of microstresses in cement paste by fluorescence piezospectroscopy

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An experimental method to measure microstresses in cement paste, as a typical granular medium, was developed employing a fluorescence microprobe spectroscopy method. Stresses were recorded with a Raman spectrometer making use of ($Cr^{3+}$ fluorescence lines of) alumina as a piezospectroscopic stress sensor. In a two-dimensional stress map, fluctuations in the stress distribution led to stress chains, indicating the granular character of cement paste. Due to these fluctuations, microforces much higher than the macroscopic strength of the material existed. The presented technique is proposed as a general tool to analyze stresses in cementitious systems. In practice, the method supports the development of toughening additives to materials like cement paste.

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## I. INTRODUCTION

For cementitious materials—in common with most materials of industrial interest—the key dependence between microscopic features and macroscopic properties must be understood in order to gain control over the material in use [1]. In this comprehensive process, we expect the granular behavior of cement paste to play a key role, since the general stress distribution properties of granular materials should be strongly correlated to the physical mechanism originating fracture. As a consequence, we need to develop a reliable tool for measuring microscopic stresses in granular materials.

Since the grain size in our model material is on a micrometer scale, a high-resolution stress analysis would be most suitable. Regarding microstresses, the application of piezospectroscopic techniques experienced a tremendous development over the last few years [2–5]. Fluorescence and Raman microprobe spectroscopy have been used to measure directly the microscopic stress fields in fine ceramics, e.g., silicon nitride [6], zirconium oxide [7], and hydroxyapatite [8]. Moreover, piezospectroscopy was applied to a number of materials of notable industrial interest, e.g., glasses [9], fibers [10] or biomaterials [11].

The evaluation of microstresses in cementitious materials, as well as granular materials in general, was another previously neglected aspect of piezospectroscopy, which must be blamed on the lack of appropriate stress sensor systems. Here we report on a closure of this gap by taking advantage of a particularly suitable phenomenon for stress analysis: the fluorescence of chromium ($Cr^{3+}$) in several oxygen polycrystalline environments. Even in the case of crystalline alumina, where $Cr^{3+}$ is naturally contained in the $Al_2O_3$ lattice only as trace impurity, chromium provides a sharp and intense line and functions well as a stress sensor [12]. Thus, intimately mixing ultrafine grained alumina into a grained system such as cement paste should provide a capable stress sensor system. Experimental processing and preliminary results of a stress mapping experiment are described in the present paper.

## II. EXPERIMENTAL PROCEDURES

### A. Preparation of cement paste samples for stress analysis

Cement paste samples for stress mapping analysis were prepared by mixing ordinary Portland cement (OPC) with commercially available ultrafine alumina ($Al_2O_3$, particle size 0.1 $\mu$m). This homogeneous mix was treated with water, resulting in a cement:water:alumina ratio of 4:1.6:1. The freshly prepared paste was placed into minimolds manufactured from polyacrylate to achieve an acceptable smooth surface. In order to prevent generation of artificial residual stresses, cutting of the cement paste samples was strictly avoided by choosing the appropriate size of the mold (typically $3\times4\times45$ mm).

After curing, optical microscopic observation of the samples revealed that the size of the cement grains was typically bimodal with main fractional size values of 0.2 and 2 $\mu$m. Moreover, the microstructure of the samples was found to be intact and especially no surface cracking occurred. The compressive and tensile strength of the cement paste was 53 and 15 MPa, respectively. The overall volume fraction of porosity in the cement paste was 0.2.

In order to obtain a biaxial stress distribution and stress intensification upon subjecting the samples to a simple external bending stress [13], a notch of depth 0.2 mm, sharpened to a radius of less than 5 $\mu$m at its tip, was placed at the center of a bending bar.

### B. Fluorescence spectroscopy

The general piezospectroscopy fluorescence technique, its accuracy, and calibration procedures have been described previously [5]. In brief, a Raman spectroscopic apparatus (T-64000, Jobin-Ivon/Horiba Group, Tokyo, Japan) was op-

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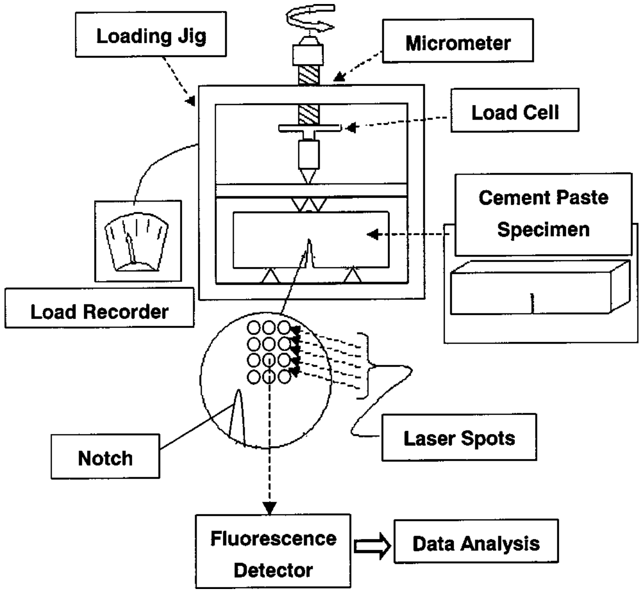


FIG. 1. Schematic experimental setup for microstress measurement of cement paste.

erated with an Ar laser ($\lambda = 488$ nm) with a power of 20 mW, while an optical microscope was used both to focus the laser and to collect the fluorescence light. Light frequencies were analyzed using a single monochromator equipped with a charge-coupled device camera. The slit width was 5950–6200 $cm^{-1}$ to detect the maxima of the $Cr^{3+}$ (alumina) doublet at 6052 and 6084 $cm^{-1}$, respectively. A four-point bend loading jig (with inner and outer spans of 10 and 20 mm, respectively) was equipped with a 100 N load cell. Notched samples were spanned into the jig and placed into the Raman apparatus (Fig. 1).

Physical and experimental foundations for stress analysis by fluorescence microprobe spectroscopy have been rigorously established in a recent paper [14] and we report here only on the salient topics. In stress mapping experiments, the laser was focused on the center of the sample nearby the notch tip. In a typical procedure, a map of $40 \times 70\ \mu m^2$ (with a lateral resolution of 1 $\mu$m) on a precisely specified surface area of the sample was recorded at zero external load. This map was used to establish a $40 \times 70$ matrix of local "zero-stress" wave numbers for the fluorescence peak frequency. Next, a congruent map was collected at the same location, but with an external load of $\approx$14.5 N. Throughout the fluorescence measurements, the load was kept constant with a maximum fluctuation of less than 1 N. The neat (local) peak shifts were then calculated by subtracting at any location the frequency recorded at zero external load from that recorded at the onset load for bending. The collected Raman data were analyzed by standard curve-fitting algorithms.

The local stresses at the monitored locations were calculated from the respective frequency shifts according to the piezospectroscopic coefficients [15] $\Pi_c$ and $\Pi_a$ given as 2.75 and 2.10 $cm^{-1}$ GPa for *a*- and *c*-axis oriented sapphire crystals, respectively [16,17]. An average equibiaxial piezospectroscopic coefficient $2(\Pi_c + 2\Pi_a/3)$ for an alumina crystallite was employed to linearly relate the frequency shift

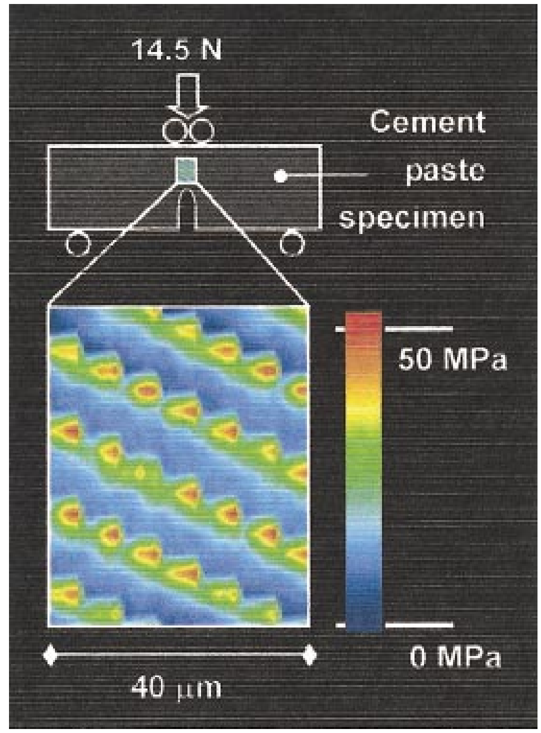


FIG. 2. (Color) Typical $40 \times 70\ \mu$m stress map of the surface area of hardened cement paste.

to the average stress inside each single laser spot [14], according to the following equation:

$$\langle \sigma \rangle = \Delta \nu / 2(\Pi_c + 2\Pi_a/3). \tag{1}$$

Considering that the $R_2$ line is less sensitive to the crystallographic orientation of individual $Al_2O_3$ grains [16] and also assuming that the value is determined by averaging over a large enough number of randomly oriented grains within one laser spot, the error related to the unknown crystallographic orientation of individual $Al_2O_3$ grains was smaller than 5%.

In all stress mapping experiments the dimension of the laser spot was 1 $\mu m^2$. Since alumina grains were an order of magnitude smaller than the laser spot, it was concomitantly assured that indeed one single laser spot averaged a relatively large number of grains of alumina.

## III. RESULTS AND DISCUSSION

When samples were prepared with the given mix proportion of OPC and alumina, the sensitivity of the sensor turned out to be sufficient throughout the entire sample to record fluorescence spectra of a good quality for fitting at any location within 1 s. The results of the piezospectroscopy experiment in the case of a $40 \times 70\ \mu m^2$ stress map, whose geometrical center was located 165 $\mu$m ahead of the notch tip and symmetrically with respect to the longitudinal notch direction, are displayed in Fig. 2. In this example, under the constant load of 14.5 N, fluctuations of internal stresses were observed, yielding a regular pattern of nearly perfectly aligned tensile stress chains. Areas of unexpectedly high tensile stresses of up to 50 MPa emerged in regular distances of

6.9±0.5 μm (intrachain) and 11.4±0.5 μm (interchain), respectively. The regular pattern was especially independent of the polycrystalline character of the material [18]. Furthermore, the geometric distance between two stress chains was 100 times longer than the diameter of the sensor, thus, the spatial dimension of the sensor did not interfere with the stress distribution. In a continuum and elastic material, the distribution of tensile stresses $\sigma_{\mathrm{tip}}$ along the abscissa $x$ with the origin at the root of a sharp notch and oriented towards the direction of crack propagation is described according to the following equation [19]:

$$\alpha_{\mathrm{tip}}=K_1/(2\pi x)^{1/2}, \tag{2}$$

where $K_1$ is a stress intensity factor, which depends on notch geometry, applied load magnitude, and loading configuration. When the stress map in Fig. 2 was recorded by fluorescence piezospectroscopy in the cement paste specimen, a stress intensity factor (under a load 14.5 N and in the presence of a notch 0.2 mm in depth for four-point flexure geometry) $K_1=0.9\ \mathrm{MPa\,m}^{1/2}$ was associated with the notch configuration. According to Eq. (2), an average stress $\sigma_{\mathrm{av}}=28.5\ \mathrm{MPa}$ can be calculated for the portion of abscissa $x$ between 130 and 200 μm ahead of the notch tip. This average stress value is found to be in good agreement with the average stress value, $\sigma_{\mathrm{av}}=25\ \mathrm{MPa}$, experimentally recorded by fluorescence piezospectroscopy along the same portion of abscissa $x$. The agreement between measured and calculated stress values can be positively regarded as a confirmation that our piezospectroscopic measurements provide a physically sound assessment of stress intensification at the notch tip. It should be noted, however, that the experimentally measured stress field is far from being a homogeneous and continuous field, as predicted by linear fracture mechanics. In other words, despite local stress fluctuations on a micrometric scale, the average stress field on a 100 μm scale (namely, a scale more than two orders of magnitude larger than the grain size of our cement paste) still obeys linear fracture mechanics.

The analysis of the stress distribution of 2800 stress-map data points provided additional information on the micromechanical behavior of the cement paste system: the stress-distribution $P(\sigma^*)$ of normalized stresses $\sigma^*$ with

$$\sigma^*=\sigma/\overline{\sigma} \tag{3}$$

($\sigma$ is measured stress, $\overline{\sigma}$ is the average of all measured stresses) shows that the quota of stresses reaches a sharp maximum at $\sigma^*=0.39$ (Fig. 3). The probability of compressive stress carrying grains ($\sigma^*<0$) vanishes, while a steep rise of probability is observed for $0<\sigma^*<0.39$. In a first approximation, $P(\sigma^*)$ decays exponentially for stresses $\sigma^*>0.39$. This is worth noting, because compared to a Gaussian distribution, the exponential decay implies a higher probability of finding large stress values $\sigma^*\gg 1$.

The formation of force chains and concomitant exponential decay of the distribution at high forces are specific and well-known features of granular materials [20,21]. Though mortar is regarded as a granular system [22], as well as cemented rocks are frequently considered [23], cement paste is hardly perceived from that perspective. This might be due to the fact that the morphology of cement paste is rather different from elementary granular systems, i.e., assemblies of spherical grains, commonly without or only minor cohesive forces. Instead, cement paste is a highly complex, polydisperse, chemically multifarious composite, where macroscopic cohesive forces are rather strong. Up to now, experimental approaches to stresses in granular media were restricted to photoelasticity [21] or carbon paper [20] evaluation. While the former technique requires either transparent or coated materials, the latter one can deal only with macrometer-size particles or beads and is incapable of detecting tensile forces, thus, both are not applicable to the present case. Combining results by former investigators on general granular media [20,24,25], we fitted the stress distribution by the following curve:

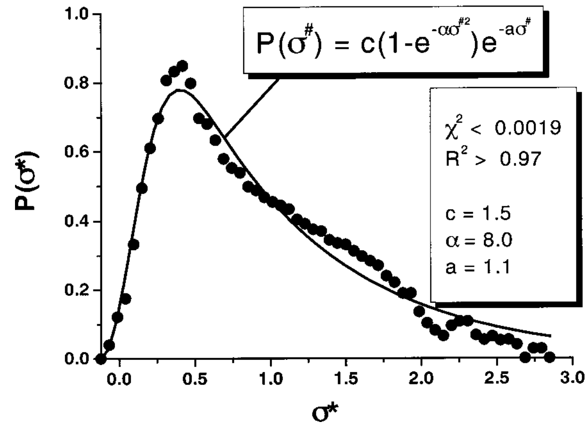


FIG. 3. Least-squares fitting of the experimental data according to Eq. (4). $\sigma^{\#}=\sigma^*-0.12$.

$$P(\sigma^{\#})=c(1-e^{-\alpha\sigma\#})e^{-a\sigma\#};\quad \sigma^{\#}=\sigma^*-0.12. \tag{4}$$

With $c=1.5$, $\alpha=8.0$, $a=1.1$, Eq. (2) yields a reasonable coefficient of determination $R^2>0.97$ and a value of fit $\chi^2<0.0019$. In addition, $P(\sigma^*)$ reaches its maximum for $\sigma^*_{\mathrm{max}}=0.39$, which is in conformity with the experimental data.

For example, Eq. (4) illustrates that ~15% of the mapped surface area carries stresses more than double as high as the average, and ~1.5% carry more than a fourfold stress. Though the quota of extraordinary high stresses was close to zero, we anticipate this small area fraction to initiate microcracking.

One should note that the decrease of $P(\sigma^*)$ for $\sigma^*\to 0$ is a controversial discussion [18,23–28]. Our fluorescence-microprobe experiments revealed a pronounced plunge of $P(\sigma^*)$ for small stresses, which we assume to correlate to the rather strong cohesive forces in cement paste [23]. However, such a complex correlation is far from being unfolded and out of the scope of this experimental paper.

## IV. CONCLUSION

Measuring microstresses in cement paste, we detected stress fluctuations giving rise to local stresses, which are much higher than the macroscopic strength of the material. This phenomenon suggests a considerable potential for strength control and optimization in cement paste. From the application side, the specific process of manufacturing cement pastes will provide a unique chance to study modified, tailor-made cement pastes and to control the result of each modification in terms of internal microscopic stresses.

The example of cement paste shows that employing fluorescence piezospectroscopy and alumina as a stress sensor enables one to measure microstress distributions in granular assemblies, which were not accessible by previous experimental techniques.

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