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Quartz crystal microbalance as a device to measure the yield stress of colloidal suspensions

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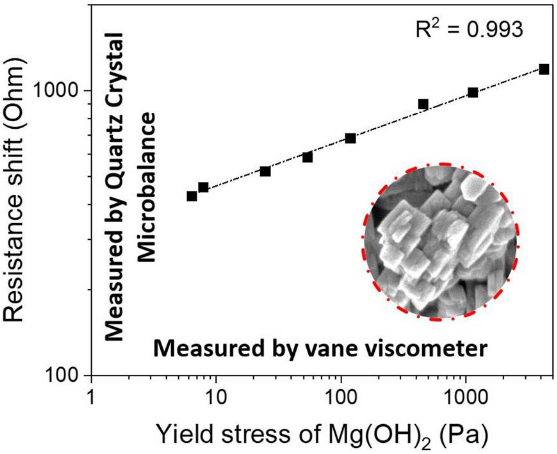
GRAPHICAL ABSTRACT



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ABSTRACT

The application of quartz crystal microbalance (QCM) as a device to measure the rheology of colloidal suspensions has been studied. Using a commercial dip-probe QCM, the yield stress of magnesium hydroxide suspensions has been correlated to the resonance properties of a 5 MHz AT-cut quartz sensor. A stable resonance baseline was first established in air before submerging the sensor into the colloidal suspension. The response of the sensor resistance was shown to correlate to changes in the suspension yield stress, while the frequency response was found to result from more complex contact mechanics and suspension viscoelasticity contributions. Since the QCM is a relatively simple technique with no mechanically moving parts, this approach offers the potential for rapid in situ rheology assessment.

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1. Introduction

The UK nuclear industry is currently entering a phase of post operational clean out (POCO) to safely remove and store legacy wastes which have accumulated over several decades of nuclear power generation. A particular concern for the UK is the legacy sludge waste which has been stored in open air ponds and silos and now needs to be retrieved for further interim storage or ultimate disposal. To ensure the safe recovery of the wastes, design guides for sludge retrieval will be proposed based on the physical and chemical properties of the materials to be recovered. Understanding the rheology of the legacy sludge, along with its modification during handling is therefore of great importance. However, conventional rheometer techniques are often unsuitable due to issues of sample handling (radioactivity and methods of extraction), and the requirement to frequently collect data in confined spaces. With its simple design, small size and no mechanical parts, a quartz crystal microbalance (QCM) has the potential to directly measure rheology in challenging environments.

In its standard configuration, a QCM consists of a piezoelectric AT-cut quartz sensor with electrodes coated on each surface. Applying an oscillating electric field across the piezoelectric sensor generates an internal mechanical stress that vibrates the sensor [1]. Interpretation of the vibrational motion reveals the viscosity-density product of the deposited material from which other physical properties such a deposited film thickness and viscoelasticity can be determined [2–6].

The baseline data includes QCM resonance frequency and motional resistance. The resonance frequency is often quoted due to the simplicity of the Sauerbrey equation (Eq. (1)) which provides a simple conversion of resonance frequency shift to deposited mass:

$$\Delta f = -\frac{2f_0^2\Delta m}{A\sqrt{\rho_q\mu_q}} \tag{1}$$

where Δf is the measured frequency shift, f_0 is the fundamental frequency, Δm is the mass change, A is the sensor area, ρ_q is the density of quartz sensor (2.648 $\mathrm{g\,cm^{-3}}$), and μ_q is the shear modulus of quartz sensor ($2.947 \times 10^{11}\ \mathrm{g\,cm\,s^{-2}}$).

While a Sauerbrey conversion is often useful, the underlying principle as an extension of the resonating sensor is only truly valid when the added mass satisfies: i) no slip, ii) rigid deposition, and iii) even deposition on the sensor surface [2].

Nomura and Bruckenstein demonstrated the stable resonance of QCM when one surface of the sensor was intimately in contact with a bulk liquid [7–9]. Gordon-Kanazawa-Mason [3,10,11] derived a simple relationship correlating the change in resonance frequency to changes in the density and viscosity of a non-adsorbing fluid (Eq. (2)):

$$\Delta f = -f_{0*}^{\frac{3}{2}}\left(\frac{\rho_L\mu_L}{\pi\rho_q\mu_q}\right)^{1/2} \tag{2}$$

where f_{0*} is the fundamental resonance frequency, and ρ_L and μ_L are the absolute density and viscosity of the fluid, respectively. More recently, studies based on the Mason equivalent circuit theory [12] or the Voigt-Voinova theory [13] have demonstrated the applicability of QCM to measure the viscoelastic properties of bulk fluids and deposited layers on the sensor surface.

While those fundamental studies highlight the great potential of QCM when investigating solid, liquid and gaseous systems, until recently solid-liquid systems had received very little attention; in particular particle suspensions. The interaction of particles and the QCM sensor has been considered in detail by Johannsmann and co-workers [6,14], where the Mason model has been suitably modified to include point-contact loads that are relevant to non-uniform loads such as deposited particles on the resonating sensor. Of the few studies considering QCM and particles, other applications include i) measuring the particle concentration by drying suspensions onto the sensor [15] and ii) detecting particle deposition onto a heterogeneous surface [16,17], with the resonance properties correlated to the colloidal forces acting between the resonating sensor and suspension. When studying particle systems, researchers have reported positive frequency shifts during mass deposition, which is contrary to the mass deposition theories described by Sauerbrey and Voigt-Voinova [18–20].

Dybwad and Pomorksa [20,21] developed a model termed the 'coupled resonance model' to account for such interesting behaviour. The model states that for a sphere in contact with a resonating sensor of angular frequency, ω, the sphere will adopt its own resonance of angular frequency, $\omega_s = (\kappa/m)^{1/2}$, where κ is the contact stiffness and m the particle mass [20,21]. The contact stiffness is a function of both tangential and normal load contributions, although for a 5 MHz sensor the contact stiffness is strongly influenced by the normal oscillatory load due to the flexural contributions to the displacement pattern. If the sphere is small and the particle contact with the resonating sensor is sufficiently stiff, the condition $\omega_s > > \omega$ holds true and 'inertial loading' occurs where the mass of the sphere reduces the sensor resonance frequency, i.e. Sauerbrey behavior [2,20,21]. If the sphere is large however (typically > 1 μm) and is weakly bound to the sensor, the condition $\omega_s < < \omega$ holds true and the resonance frequency of the sensor increases, described as 'elastic loading' [20,21]. Pomorska et al. performed finite element calculations on relevant systems and concluded that this phenomena is plausible in liquid phase media, where the resonance frequency of the sensor is dependent on the strength of the sphere-sensor contact rather than the adsorbed mass [20].

The objective of the current study is to extend the application of QCM and correlate the frequency and resistance responses to changes in the rheology of particle suspensions, i.e. the shear yield stress. The measurement approach is quite simple and involves measuring the frequency and resistance shifts from the baseline resonance in air to the steady-state values once submerged into the test material. In particular, samples of two different types of magnesium hydroxide were investigated, as similar materials are thought to represent the major fractions of corroded fuel canister wastes, present in various nuclear legacy ponds and silos in the UK [22].

2. Materials and methods

2.1. Materials

Two magnesium hydroxide ($Mg(OH)_2$) samples were used as model test materials relevant to legacy nuclear waste in the UK. The first test material Versamag A was supplied by Rohm and Hass and the second test material Versamag B (sample labelling used throughout) was supplied by Martin Marietta. Both samples were chosen due to their varied magnesium oxide (MgO) contents leading to differences in aging behavior, see discussion below. The pH of all suspensions was maintained at pH 10.2 due to the natural buffering of the system, which corresponded to conditions close to the particle isoelectric point ($pH\ 10.2,\ \ \zeta = -7 \pm 4\,mV$). Both particle types were used as received and dispersed in deionised water with a resistivity of 18 MΩ cm.

2.2. Sample aging

80 g Versamag (A or B) was added to 120 g deionised water (solid content = 22 vol%) in a 250 mL glass beaker and hand mixed for 15 min until the suspension resembled a smooth paste. The suspension was left undisturbed for 5 min before measuring the yield stress and QCM response (separate samples). The objective of the aging tests was to measure the time-dependent changes in the suspension yield stress between 0 and 70 h. The suspension volume fraction was chosen such that the particle concentration exceeded the gelling concentration [23,24] (Fig. S1), hence no suspension consolidation would occur during sample aging. To avoid yield stress changes due to sample drying, a thin layer of mineral oil (ρ = 0.84 $\mathrm{g/cm^3}$) was gently pipetted onto the suspension (following immersion of the QCM sensor), before