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Remote characterization of the rheological properties of sludges and slurries—preliminary investigations into a novel *in situ* sensor

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Multiphase process design and optimization often depends upon the rheological properties of sludges and slurries. In practice the task of determining these important properties is usually carried out by removing small samples from a process line or process unit and performing tests with proprietary bench-top analysers near to site or at a remote laboratory. Sampling will remain an important procedure in industrial processes, but there is also a strong case for augmenting the routine information obtained using an *in situ* sensor, as suggested below.

- Sampling protocols can result in extensive turnaround periods from sample collection to the generation of results. The delay can have an effect on a variety of factors such as product quality, process operability and efficiency.
- Sampling of toxic or radioactive material can prove an even greater challenge to minimize human involvement.
- Removal often changes the rheology of a specimen, and might lead to incorrect conclusions being drawn about the condition of a sludge.
- Sludge and slurry in a containment suffers a gravitational gradient, so that a removed sample should be paired with its location, particularly in the vertical dimension.
- Sludge or slurry removed from a duct or from siphoning tubes suffers a velocity gradient such that lighter fractions are preferentially represented in the sample, causing an underestimate of coarser particles.

• Many more data points can be collected by a remote instrument, improving the sampling statistics of the measurement.

This paper presents results of an investigation using a small piezo-electric driven AT-cut quartz crystal to measure changes in suspension stability. Mono-dispersed silica suspensions were prepared in several different chemical environments, with the conditions chosen from examination of the zeta potential and sedimentation data. The study shows that by varying the suspension stability, the resonating frequency of a 5 MHz AT-cut quartz silica crystal significantly deviates as the amplitude of oscillation is increased for a coagulated suspension, while remaining unchanged for a dispersed suspension.

Keywords: rheology, *in situ*, resonance

Introduction

An understanding of the rheological properties of sludges and slurries and the ability to manipulate colloidal suspension stability are of great importance in industries such as, petroleum, pharmaceutical, paint, food, nuclear, wastewater and mining, to name a few. In certain industries the particle-particle interactions are continually adjusted throughout the process to improve the transportation or separation efficiencies, which can result in substantial environmental and cost savings. A number of laboratory-based techniques are readily employed to determine the degree of destabilization in a suspension. Sedimentation columns provide an indication of the aggregation behaviour in a suspension by monitoring the relative rates at which the solid-liquid interfaces descend, while measurement of the zeta potential, which is a measure of the net surface charge on a particle, provides a method for quantifying the stability behaviour. Challenges with these techniques include the determination of an adequate sample volume, their portability and field robustness. Many of the current techniques are expensive to set up and operate. Where regular scrutiny of suspension stability is essential, a sensible progression would be to measure the suspension stability *in situ* and online, relieving any time delays associated with laboratory practice. The introduction of the quartz crystal microbalance technique to measure suspension stability would overcome some of the issues already highlighted, and with further development provide an opportunity for *in situ*, online measurement.

Quartz crystal microbalances (QCMs) have evolved significantly from an early technique in 1959[1], when it was first used in a sensing mode to show a linear relationship between the frequency decrease of an oscillating quartz crystal and the bound elastic mass of deposited metal. The measurement technique is sensitive to solution-surface interface interactions, possessing a wide detection range capable of detecting monolayer surface coverage by polymer films and large bounded masses on the surface. Its usefulness in such areas has been highlighted by a ‘boom’ in its application to study such systems over the past decade. Continual development of

QCMs had led to the current research interest of the authors in detecting the interaction length scales between solid particles, inferring information about the stability of a colloidal suspension.

A QCM consists of a piezoelectric AT-cut quartz crystal disc a few tenths of mm thick, cut to a geometry that provides a stable oscillation with frequency relatively unaffected by temperature fluctuations at room temperature[2]. Electrodes that are coated on the upper and lower surfaces are connected to an oscillator circuit. An AC-voltage applied across the electrodes vibrates the quartz crystal laterally 1–2 nm, by the piezoelectric effect. The oscillation induces an acoustic wave, which propagates into the bulk media to a solution penetration depth of 250 nm, decaying exponentially due to the viscous damping of the solution[3, 4]. The penetration region is very sensitive to changes in the physical and structural properties of fluid or slurry in contact with the crystal surface. These changes introduce an amount of damping in the crystal resonance, and the resultant frequency shift can provide an indication of the physical/structural properties within the media investigated.

The suspensions under investigation consist of colloidal particles that are extremely small and have very low inertial forces; as a result, particle-particle interaction forces play a significant role in their behaviour. The DLVO theory[5, 6] is used to describe the stability of colloidal particles in an aqueous environment, with the total interaction energy (V_T) between two identical colloidal particles calculated as a function of particle separation, through the summation of the van der Waals force (V_A) and the electrostatic repulsion force (V_R):

$$V = V_R + V_A = \frac{32\pi\varepsilon a k^2 T^2 \gamma^2}{e^2 z^2} \exp[-\kappa H] - \frac{Aa}{12H} \quad [1]$$

where V_R is the repulsive force and V_A the attractive force. ε is the dielectric constant, a the particle radius, k the Boltzmann constant, T the absolute temperature, $\gamma = \tanh(ze\psi_o/4kT)$ (Ψ_0 *Stern potential*), e is the electronic charge, z the counter ion charge number, H the separation distance, A the Hamaker constant and, K the inverse Debye length.

It is important to note that the attractive component is effectively constant with changes in the electrolyte concentration and depends on the bulk properties of the particulate, whereas the repulsive component arises from the presence of the diffuse electrical double layer around each particle and is strongly influenced by the electrolyte according to:

$$\kappa \propto (z^2 c)^{1/2} \quad [2]$$

where, c is the electrolyte concentration and z the counter-ion charge valency. Therefore under high electrolyte concentrations, the double layer will be significantly suppressed and the particle dispersion is expected to coagulate.

Experimental details

Suspension characterization

A sample of Angstromsphere, mono-dispersed silica powder (see Figure 1), was obtained from Fiber optic center Inc., with a particle density of 2.2 gcm^{-3}. Millipore Milli-Q® grade water, free of organics and other impurities was used in all sample preparations. Prior to QCM-D analysis, the suspensions were characterized using traditional methods for monitoring stabilities, recording the zeta potential using the Malvern Nano ZetaSizer®, and the sedimentation characteristics using the LUMiFuge® 114 Separation Analyser.

Zeta potential

The Malvern Nano ZS calculates the zeta potential by determining the electrophoretic mobility of the particles before applying the Henry equation. Silica suspensions (15 ml) were prepared to a concentration of 1 000 ppm, in 10^{-1} M and 10^{-3} M KNO_3 solutions. The samples were prepared 24 hours in advance and tumbled for the duration, to reach equilibrium. The pH of the suspension was then adjusted using an appropriate concentration of KOH, to pH 9. The zeta potential was recorded as a function of electrolyte concentration and pH, with the pH of the suspensions adjusted down to pH 3 using analytical grade HNO_3. Each experiment was completed using the auto-titration function on the Nano ZS, which allowed the pH to be adjusted by half a unit between each zeta potential measurement. At each interval, 10 measurements were recorded to produce an average value.

Sedimentation rate

The sedimentation properties of the suspensions were determined using a LUMiFuge®. The LUMiFuge® enhances the rate of sedimentation, by exerting a centrifugal force on the particles. Local alterations in particle concentration are detected due to changes in the light transmission. A concentrated region will absorb the light, so transmission is low; consequently as the concentration reduces transmission increases. The resulting

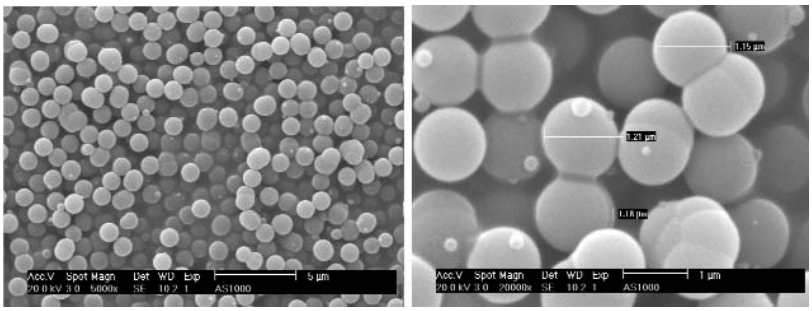

Figure 1. Scanning electron micrographs, showing the size, shape and polydispersity of the angstromspheres

transmission profiles display the intensity of light transmitted as a function of the radial co-ordinates. The samples were prepared as previously described, but with a particle concentration of 10 000 ppm, so that any changes in transmission could be clearly detected by the sensor. The LUMiFuge® was rotated at 300 rpm (generating 11 'g') and transmission profiles through the cell were recorded every 10 seconds.

Quartz crystal microbalance

Samples were prepared as previously described to a particle concentration of 1 000, 10 000 and 10 0000 ppm. Prior to sample addition, the quartz crystal and the QCM were subjected to a rigorous cleaning procedure to remove any impurities. The silica crystal was sonicated for 15 minutes in 2% Decon before being washed with Milli-Q water, dried with nitrogen and placed in a UV-ozone chamber for 15 minutes. This procedure was carried out 3 times before the crystal was mounted in the cell. The resonance frequencies and dissipation values for all overtones are recorded in air, before the system is further cleaned by flushing 10 ml of 60°C Milli-Q water and 10 ml of 60°C 2% Decon through the whole system 3 times, finally rinsing with 20 ml of Milli-Q water. The resonance frequencies and dissipation values were then recorded in water to verify system performance. The system was then left to reach stability, so that changes in the frequencies for the third and fifth overtones were negligible with time, less than 0.2 Hz h^{-1}.

Once stable, the silica suspensions are then adjusted to the required pH and sonicated for 45 minutes to degas the suspension to avoid the formation of air bubbles in the measurement chamber. The suspension is then fed through the QCM under gravity, before the system is locked off, holding approximately 300 ℓ of suspension in the cell. The particles were then allowed to settle for 16 hours under gravity to form a sediment bed. Schematics of the QCM-D and 5 MHz silica quartz crystal are shown in Figure 2.

To monitor the suspension stability, the resonating frequency of the crystal was recorded as the amplitude of oscillation was ramped up, increasing the energy input into the bulk medium. The amplitude was increased linearly between 0.0 and 4.0 a.u. and was adjusted when the recorded frequencies at the third and fifth overtones had reached a plateau.

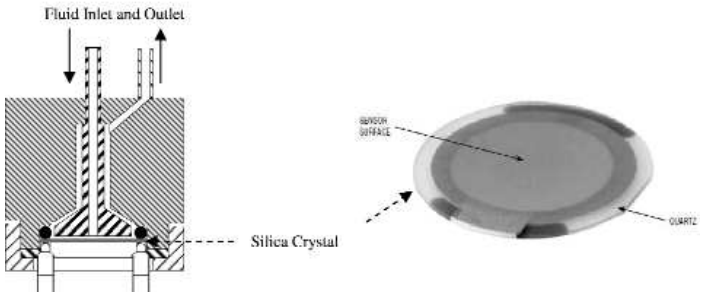

Figure 2. Schematic of the QCM-D measurement cell and silica quartz crystal

Results and discussion

Figure 3a, shows the zeta potential curves for a 10^{-1} M and 10^{-3} M KNO_3 silica suspension, showing the iso-electric point (net zero surface charge) of the silica to be around pH 2. The measured zeta potential as a function of pH for the 10^{-1} M KNO_3 suspension is significantly lower than that for the 10^{-3} M KNO_3 suspension, owing to diffuse electrical double layer (edl) suppression as a result of the increased ion concentration in the system. A 'rule of thumb' for the transition in stability of a colloidal suspension is often taken to be around ±30 mV. Between these two values we predict the suspension to be unstable; outside of this range we predict the suspension to be stable. This, however, should not be taken as a definitive boundary, with the transition more likely to be gradual. Using the 30 mV boundary, analysis of the zeta potential data shows that for the 10^{-3} M suspension, the system can be classified as stable if the pH is greater than 3 and unstable below. In comparison, the 10^{-1} M KNO_3 suspension exhibits instabilities over the majority of the pH range investigated, with the transition in stability being identified around pH 7.5.

Figure 3b, shows sedimentation profiles for 10^{-1} M silica suspensions as a function of

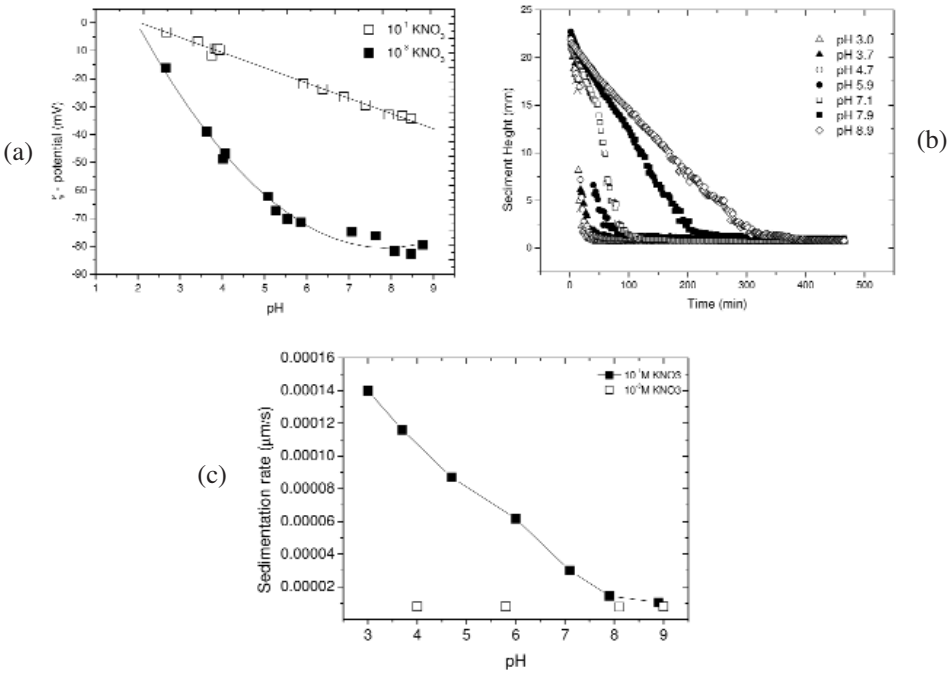

Figure 3. (a) zeta potential measurements as a function of pH and electrolyte concentration; (b) 10^{-1} M KNO_3 silica suspension sedimentation profiles as a function of pH; (c) relative settling rates for a 10^{-1} M and 10^{-3} M suspension as a function of pH (rates determined from constant sedimentation period)

pH. The curves show the sediment height of the sample as a function of time. Analyses of these data show a change in the settling characteristics between pH 7.1 and pH 7.9. A 10^{-1} M KNO_3 silica suspension at pH 7.9 shows the sediment height interface moving at a constant rate, characteristic of a mono-dispersed settling suspension, indicating no cluster formation in the suspension. However, for a 10^{-1} M KNO_3 silica suspension at pH 7.1, the settling trend is characteristic of a poly-dispersed system, with an initial rapid rate of settling dissipating as the sediment bed is formed[7]. Such a settling characteristic indicates cluster formation of the mono-dispersed particles in the suspension, highlighting destabilisation of the suspension. Figure 3c further emphasizes the destabilization of the 10^{-1} M silica suspension at pH 7–8, with the settling rate profile diverging from the 10^{-3} M profile, which remains constant (indicating stability) across the pH range investigated.

Figure 4 shows typical frequency data recorded using the quartz crystal microbalance as the amplitude of oscillation of the quartz crystal is ramped up from 0.4 to 4.0 a.u. Two unstable and three stable silica suspensions are presented. The frequencies have been normalized by the square root of the harmonic number. In a liquid environment the frequency shift at any particular harmonic of the fundamental resonance is proportional to $\sqrt{n}\sqrt{\rho_L \eta_L}$ for a liquid with density and viscosity ρ_L , η_L

The plots clearly show that as the amplitude of oscillation is increased, significant frequency shifts are observed across all overtones for the unstable suspensions, compared to small shifts observed for the three stable suspensions. The frequency trends are most likely to be a combined consequence of the operational physics of the QCM and the physical nature of the particulate network. Summarizing the raw frequency data, Figure 5 represents the frequency shifts for a 10^{-1} M suspension at varying particle concentrations and pH. The shaded area represents the maximum and minimum frequency shift observed for a stable silica suspension (10^{-3} M KNO_3) over the pH range investigated. For 10 0000 ppm suspensions, a transition in suspension stability can be observed at approximately pH 6, where the recorded frequency shift for the 10^{-1} M

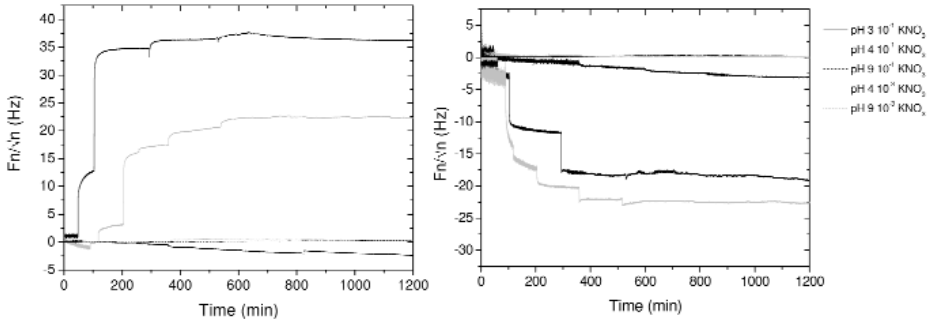

Figure 4. Recorded frequency shifts measured at the third and fifth overtones as a function of pH and electrolyte concentration (unstable suspensions pH 3 and 4 10^{-1} M KNO_3)

suspension deviates out of the stable region. Comparison with the 10 000 ppm and 1 000ppm suspensions, a similar drift out of the stable region also appears at approximately pH 6.

Analysis of the data shows that for all stable suspensions (shaded area) the resultant frequency shifts are negligible. This is probably an effect of the pathway in which the energy is transferred through the suspension, in between the dispersed particles, penetrating through the path of least resistance. As a result, the particles do not impede upon the shear wave, therefore not inducing a frequency shift in the crystal resonance. Such data is comparable to a situation when only water is investigated in the fluid cell. In the case of an unstable suspension, the particle-particle interactions will be mainly attractive, enabling the formation of large clusters that produce a sediment structure which is highly porous, containing many particle-particle contacts. As a result, the penetrating shear wave has to pass through the particle network, as a pathway of least resistance through the fluid phase may not be present. With the shear wave penetrating through paths of higher resistance, an effective change in the density/viscosity of the bulk medium is sensed, which in turn produces a shift in the resonating frequency of the quartz crystal.

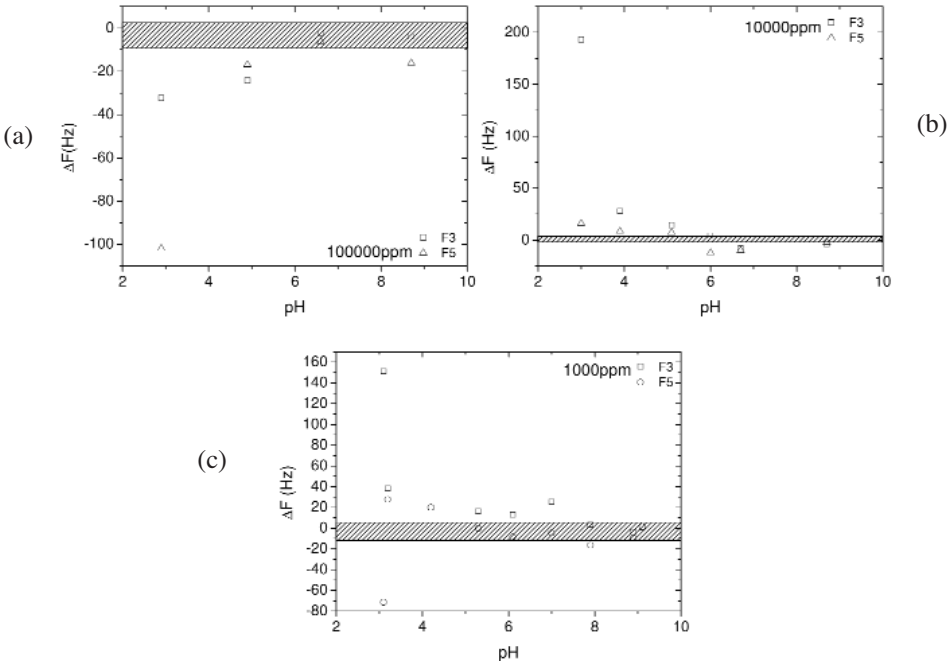

Figure 5. Frequency response of the resonating crystal during amplitude ramping, as a function of suspension chemistry and particle concentration. (a) 10 0000 ppm; (b) 10 000 ppm; (c) 1 000 ppm. (Shaded region represents the maximum and minimum frequency shift for a 10^{-3}M suspension)

Interpretation of the data also indicates that the frequency shifts across the overtones is not always consistent. Figure 4. shows that for an unstable suspension, the shift at the third overtone is observed to be positive as the amplitude is increased, while at the fifth the shift is negative. Figure 4 represents a situation where a bed has formed on the crystal surface from 16 h of gravitational settling and is then excited, while Figure 6 shows the reverse situation. Here, the resonating frequency of the crystal is recorded at a constant amplitude during particle sedimentation. The shift at the third overtone is negative, while the shifts at the fifth and seventh overtones are positive. From investigations that are not presented in this paper, it is believed that this characteristic frequency shift during amplitude ramping is concentration dependent and may be a result of slip between the particles and the crystal surface. Data recently collected have shown that the mirroring of frequency shifts diminishes as the mass loading on the crystal increases.

Conclusions

The application of QCM to monitor the stability of a colloidal suspension has been conclusively demonstrated (Figure 5), with negligible frequency shifts recorded for stable suspensions, compared to significant frequency shifts recorded for unstable suspensions. Although quantitative data cannot be collected using such a technique, this does not mean that the qualitative data is unreliable. As shown, the collected QCM data is comparable to the data collected using traditional techniques, indicating a transition in stability in the same pH region. With such a compact design and minimal sample volume required, the resonating technique may be a solution to measuring suspension stability *in situ* and online. Currently research in this area is very limited and a matrix of experiments is required to be completed to improve knowledge of the physics of operation, as well as to determine the limitations of this technique.

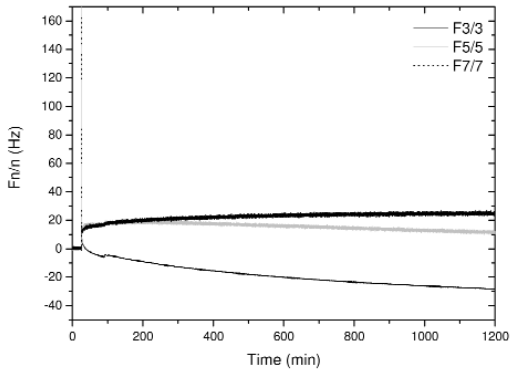

Figure 6. Recorded frequency shifts at the third, fifth and seventh overtone, for a 10^{-1} M KNO_3 pH 3 suspension. Amplitude of oscillation 0.8 a.u.

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