Using an intrinsic, exposed core, optical fibre sensor to quantify chemical scale formation

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Abstract. An intrinsic, exposed core, optical fibre sensor has been used for directly monitoring surface crystal growth in-situ. A negative, linear relationship ($R^2=0.98$, $n=44$) was observed between radial loss of radiation at sites of crystal growth and radiation transmitted along the fibre as guided modes. A positive, linear response ($R^2=0.99$, $n=8$) was also observed between measured crystal thickness (on the surface of the fibre core) and attenuation of radiation guided within the fibre. An empirical geometric ray-model, based on the refraction of guided modes out of the exposed fibre core into the crystals of higher refractive index supported the experimental observations. Results point to the potential of using an optical fibre as a fully-recoverable, quantitative sensor of crystal growth.

1. Introduction

Scale formation, or crystallization fouling, is caused by inorganic salts and is a common problem in industrial processes [1]. Crystallization of these inorganic salts occurs on surfaces when the solubility limits of these salts exceed their saturation levels [2]. These inorganic salts are known to be inverse solubility salts, meaning their solubility decreases with increasing temperature [3]. Inverse solubility leads to an increase of scale deposit on heat exchanger surfaces, reducing the performance and efficiency of the heat exchanger due to the poor heat conductance of the scale [4]. Scale formation causes surface blockage, reduced process efficiency [2], equipment failure and requires maintenance intervention [5]. Surface cleaning requires system shut down. Scale related problems cost industry millions of dollars per year [6]. The principal scale-forming metals are calcium and magnesium which react with dissolved anions such as carbonates or sulphates to form a precipitate [1]. Prevention of scale involves either reducing the amount of calcium and magnesium in the water (softening) [7], or treatment with chemicals, known as anti-scalants or scale-inhibitors [1]. Both processes involve additives to the water; however, scale detection methods are necessary in order to assess the effectiveness of proposed scale-inhibitors and in setting dosage rates. Scale monitoring systems include in-situ measurements of liquid electrical conductivity, turbidity [2] or measurement of the heat transfer coefficient of the scaled surface [3].

Optical fibre sensors that have a section of cladding removed, therefore allowing the light, which is totally internally reflected inside the core, to interact with the environment surrounding the core could provide an alternative method. Intrinsic exposed core sensors (IECS) are able to sense physical
modifications at the surface of the exposed core as a result of changes in the surface refractive index and the interaction of guided radiation with the surface modification. In the case of, for example, crystal growth on the surface, the higher refractive index of the crystals will mean some of the guided radiation in the core will be refracted out into the crystals with a concomitant reduction in radiation transmitted through to the end of the fibre. Furthermore, previous work of Lamb et al [8] has demonstrated that the evanescent field component of radiation guided through an exposed core is not affected by the presence of (non-resonance) scattering particles in solution. One immediate advantage of this technique over conventional methods of scale detection is that the obtained signal is a direct measure of the amount of crystal growth on a surface that is independent of homogenous, or bulk-liquid, crystal growth.

The use of an unclad section of optical fibre for the measurement of crystal formation and crystal growth has been proposed by Philip-Chandy et al. [9] to monitor the scale formation in industrial applications however this work did not relate the sensor output to the actual crystal growth process.

In this paper, the use of an unclad optical fibre as a monitoring device for scale formation is described. An empirical geometrical ray-model is proposed to explain the sensor response to crystal growth and some key characteristics behind the measurement of signal attenuation in relation to the crystal growth are reported including the impact of crystal size and crystal distribution.

2. Materials and methods

Measurements of crystal formation were conducted using either a PUV-600T and PUV-200T optical fibre from Ceram Optec, USA. The fibres have 600 and 200 µm diameter fused silica core, respectively, with refractive index 1.457 and are surrounded by a silicone cladding with refractive index of 1.408. The cladding and core are surrounded by a Tefzel® or nylon jacket. Both the Jacket and cladding were physically removed and the bare core treated with a tissue soaked in ethanol to remove any oily substances and remaining cladding. Measurements were performed in a metal cell which holds the fibre horizontal and immersed in 150 ml of solution. Radiation from a 5 mW He/Ne laser (λ = 632.9 nm, Uniphase, CA USA) was coupled into the fibre using a precision optical coupler (M-F-91TS, Newport, Irvine CA USA). The radiation exiting the optical fibre was detected using a UDT PIN 10DP photodetector (United Detector Technologies, CA USA). The attenuation of the guided light was calculated using

\[ A(t) = -10 \log_{10} \left( \frac{I(t)}{I_0} \right) \]  

(1)

where \( A \) is the attenuation as a function of time measured in dB, \( I \) and \( I_0 \) are the intensity at \( t \) and \( t = 0 \), respectively. Following each set of measurements, crystals were removed from the fibre surfaces using 0.03 M HCl solution. After each measurement it was possible to ensure the fibres were returned to their original clean state by monitoring the radiation exiting the fibre until the intensity value returned to its original value. The photodetector outputs were digitised using a USB-6009 A-D converter (National Instruments, TX USA) and were recorded to a file by a program written in LabVIEW™ 7 Express (National Instruments, TX USA).

In order to measure the radial refraction of light from the fibre core, a 1 cm² section of cladding was removed, and a second photometer (Industrial Fiber Optics, AZ USA), hitherto referred to as the radial power meter, placed at 90° to the unclad section.

Calcium carbonate (CaCO₃) crystals were chemically deposited on the exposed core from a solution consisting of equal volumes of 0.0035 M CaCl₂ and Na₂CO₃. The size of the growing crystals on the fibre surface was determined using the diffraction pattern produced by a He-Ne laser directed at right angles across the fibre cross-section. The thickness was measured at 5 minute intervals using the distance between the diffraction minima (\( x \)) and

\[ D = \frac{I \lambda}{x} \]  

(2)
where \( l \) is the length between the screen and the fibre, \( \lambda \) is the wavelength of the light and \( D \) is the overall fibre and crystal thickness. The radiation exiting the fibre was detected with either a photodetector or a photometer, with the latter responsible for higher attenuation signals.

The distribution and size of crystals were observed using a Scanning Electron Microscope (SEM, Joel JSM5800-LV, Japan) pictures were taken from segments of fibres. The fibres were dried over silica gel for 2 days and then covered with a gold coating using an E5100 Polaron gold sputter coating device (Quorum Technologies, UK) for 4 mins at 2.2kV.

3. Results and discussion

The progressive attenuation of radiation from the 600 \( \mu \)m optical fibre, due to the growth of calcium carbonate crystals on its exposed core is depicted in Figure 1. The initial rapid rate of attenuation followed by a decreasing rate of attenuation is attributed to the depleting concentration of reactants in the solution. According to Figure 1 the technique remains sensitive to ongoing crystal growth beyond 200 minutes.

![Figure 1. Attenuation of guided radiation with progressive calcium carbonate crystallization on the exposed fibre core as a function of time at 25°C.](image)

Figure 2 is a plot of radiation radially exiting the fibre core into the 90° radial power meter, as a function of radiation exiting from the end of the optical fibre, acquired during progressive crystal growth. The linearity of this plot suggests the radiation lost at the end of the fibre is indeed a result of the radial emission of radiation from the region of crystal growth.
We propose an empirical geometric ray-model (Figure 3) to explain the response of the optical fibre sensor to surface crystal growth. In this model, all guided radiation strikes the core-crystal interface at incident angles between 66.2° (the critical angle for internal reflection of guided modes along the fibre core when immersed in solution) and 90°.

This radiation enters the surface crystals at angles in the range of 53.4°-61.4°. All of this radiation is internally reflected off the top crystal-liquid interface (since the critical angle at the crystal-solution interface is approximately 53.4°) and emerges from the side faces of the crystal at angles ranging from 36.7°-48.1° relative to the normal of the vertical crystal-solution interfaces (either directly or following an internal reflection step at the crystal-fibre core interface). These angles are effectively the same as that relative to the surface of the fibre at the location of the crystal. In preparing the exposed section of the fibre, cladding was removed from only the top ¼ of the fibre profile, meaning that all exiting radiation would be emitted in an arc of approximately 180° centred on the vertical in both the radial and axial directions. If the radial power meter has a collection area of approximately 1 cm², the...
collection head was located at a radial distance of 2.5 cm from the fibre surface, then the proportion of radially-emitted radiation intercepted by the power meter is estimated to be 1 cm$^2$ of the entire emission volume (here estimated to be a hemisphere) of 3.9x10$^{-3}$ m$^2$, namely a proportion of 0.025. If the power output from the fibre end is reduced exclusively by radial emission of guided modes at the crystal growth region, then the fraction of power intercepted by the radial power meter should be the same as the magnitude of the slope of the line in Figure 2. The similarity (<10% discrepancy) between the expected and observed values for the slope of the line in Figure 2 gives credence to our empirical geometrical ray-model as well as supporting the hypothesis that radiation lost at the end of the fibre is predominantly due to radial emission, from the region of crystal growth, of initially guided modes according to our empirical geometric ray model.

Figures 4a and 4b compare the attenuation of the fibre with the change in the measured fibre core thickness ($\Delta D$) which is attributed to the progressive growth of the crystals residing on the surface of fibre core. The fibre diameter used in this suite of measurements was 200 m. Figure 4a graphically illustrates the link between crystal growth and attenuation at the point where the fibre is cleaned, in-situ at the end of the crystal growth experiment. The fibre diameter returns to its original value (200 m) and the attenuation returns back to zero.

Figure 4b illustrates the linear relationship between crystal height and radiation attenuation. The method of measuring the composite fibre-crystal diameter in Figure 4 gives only an estimate in crystal dimensions perpendicular to the core surface; however, the increase in crystal size is not limited to the perpendicular growth. It represents an average increase in crystal size in a 3 dimensional plane. Therefore, we infer that the area of core on which crystal adhesion takes place is expanding at a similar rate as the increase in crystal size perpendicular from the core. Following the empirical geometrical ray-model described earlier, more guided modes are refracted out of the core, resulting in an increase in attenuation.

Figures 5a and 5b show SEM micrographs, at two different magnifications, of calcium carbonate crystals on the fibre surface after 90 minutes of crystallization. Figure 5a shows the uniform distribution of crystals on the surface of the core. Figure 5b shows the 3 polymorphs of calcium carbonate which are, in order of thermodynamic stability, vaterite (spheroidal), aragonite (needle-like) and calcite (rhombohedral). Calcite is the most stable polymorph.
4. Conclusion

An intrinsic, exposed core, optical fibre sensor has been used for directly monitoring surface crystal growth in-situ. An empirical geometric ray-model, based on the refraction of guided modes out of the exposed fibre core into the crystals of higher refractive index supports observations of a negative, linear relationship ($R^2 = 0.98$, $n = 44$) between radial loss of radiation at sites of crystal growth and radiation transmitted along the fibre as guided modes. A positive, linear response ($R^2 = 0.99$, $n = 8$) observed between measured crystal thickness (on the surface of the fibre core) and attenuation of radiation guided within the fibre also demonstrates the potential of using the optical fibre as a fully-recoverable, quantitative sensor of crystal growth with a view to monitoring surface, as opposed to bulk-solution growth phenomena.

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