

New pressure flow cell to monitor BaSO₄ precipitation using synchrotron *in situ* angle-dispersive X-ray diffraction

Alison Hennessy,^{a*} Gordon Graham,^a Jerry Hastings,^b D. Peter Siddons^b and Zhong Zhong^b

^aDepartment of Petroleum Engineering, Heriot-Watt University, Edinburgh EH14 4AS, UK, and ^bNLSL, Brookhaven National Laboratory, Upton, NY, USA.
E-mail: alison.hennessy@pet.hw.ac.uk

A flow cell has been commissioned to monitor *in situ* precipitation reactions under non-ambient conditions. The majority of high-pressure systems use anvils and presses to obtain high pressures around a small reaction area; however, this prototype is unique in that solutions may be examined as they flow through the cell under pressure. The cell is made of single-crystal silicon, which is capable of withstanding the high pressures created by liquid flow within the cell. With the capability of reaching pressures of up to 4×10^7 Pa, the cell is ideal for work on geological and oilfield systems. Here it is used to examine the formation of barium sulfate scale *in situ* under non-ambient conditions using angle-dispersive XRD on beamline X17b1 at the NLSL.

Keywords: high pressure; synchrotron *in situ* X-ray diffraction; scale; BaSO₄.

1. Introduction

Crystallization processes are extremely sensitive to external conditions such as pressure, temperature and pH. Many high- and low-temperature devices for *in situ* diffraction have been commissioned in recent years, including a flow cell used to monitor oilfield wax crystallization (Hennessy, 2001). However, most pressured systems consist of diamond anvil presses on solid samples. The cell described here allows the application of pressure prior to precipitation. Diffraction data are collected as the crystallites form and pass through the beam as a suspension in the mother liquor. The commissioning of the cell, which has been pressure tested to 4×10^7 Pa, is described here. As a test experiment, we monitored BaSO₄ precipitation from mixing of BaCl₂ and Na₂SO₄.

The study of barium sulfate formation and prevention has been an active area of crystal research for many years. This is partly due to its high industrial relevance, especially in the oil industry. Sulfate scales form when waters in the rock formation, which are high in barium, calcium and magnesium, interact with sulfate-rich seawater, which is injected into the rock matrix to maintain pressure. The resulting scales are almost insoluble and very difficult to remove. Traditionally, chemical inhibitor packages are used to prevent and inhibit the scale formation. It is not fully understood how the inhibitors work; however, it is known that the concentration and nature of the divalent cations in the water influence the mechanism. Calcium ions were found to enhance phosphonate-inhibitor efficiency, while magnesium ions poisoned them (Boak *et al.*, 1999).

Previous work has shown that calcium incorporation invariably occurred in the barium sulfate lattice; the amount of incorporation was determined by the mixing ratio of seawater to formation water and the absence or presence of impurities (Hennessy & Graham, 2002). Although magnesium ions were not themselves incorporated

in the lattice, they increased the levels of calcium incorporation when both ions were present in the reaction mixture. This also occurred in the case of two common scale inhibitors. Since calcium is a smaller ion than barium, this caused a reduction in the unit-cell parameters, as predicted by Vegard's law (Vegard, 1921). These changes were monitored using X-ray diffraction. It was proposed that the inhibitors and magnesium work within the reacting solution to allow more calcium into the barium sulfate crystal, possibly by delaying the reaction between barium and sulfate ions. Increased calcium levels undoubtedly compromise the stability of the barium sulfate lattice. It is known that phosphonate inhibitors form a complex with barium, calcium and magnesium. This complex is strongest between inhibitor and calcium, and it was proposed that this is why the presence of calcium in the reacting mixture enhances the efficiency of the inhibitor. The increased solubility of the barium sulfate leads to higher levels of calcium incorporation in the lattice. This increased level of calcium in the bulk may be extrapolated to the crystal surface, where the calcium content is much higher than usual. This increases the likelihood of inhibitor surface interactions, as the inhibitor interacts more strongly with the calcium than it would have done with barium.

While these findings were very interesting, they were all obtained under ambient conditions, and it is clear that there is a need to carry out the tests under the high-pressure conditions prevalent in oilfield reservoirs. This cell was designed so that changes in the crystal structure could be examined under non-ambient conditions, with the aim of increasing the understanding of the inhibition process.

2. High-pressure flow cell

The cell is a silicon capillary (length 1 cm, ID 1 mm, wall thickness 2.6 mm) flanked by two steel cones. The use of silicon as a cell material brought several benefits. It has a low atomic number, and therefore it is relatively transparent to X-rays, even with the thickness required to sustain the high pressures used. Since it is a single crystal, it does not generate diffraction rings, which would interfere with the experiment. It is inert, therefore it does not introduce additional reactions. Finally, it is inexpensive and quite readily machinable. The steel cones are made from a corrosion-resistant high-nickel alloy, Hastelloy, to prevent corrosion while flowing high-salinity brines through the cell. One of the cones contains a mixing chamber of approximately 1 cm³. Two Gilson pumps transport the respective solutions to the mixing chamber to form crystals at the desired pressure. These crystals are then transported into the silicon capillary and the direct path of the beam. Pressure transducers are used to monitor the inlet and outlet pressures of the cell in order to identify possible blockage of the silicon capillary. Pressure relief valves are connected into the feed lines in order to prevent overpressure. The suspensions are transported through a high-pressure settling and dilution vessel prior to fluid passage through a pressure regulator and finally to waste at ambient conditions. The settling and dilution vessel is required to prevent scale crystals from blocking the pressure-relief valve (F). A schematic diagram of the cell is shown in Fig. 1.

3. Experimental

The beamline contains a wiggler insertion device, which allows a high critical energy. A Siemens CCD detector allows effective two-dimensional data collection. The recent development of a sagittally focusing monochromator gives a high-intensity stable synchrotron beam with excellent resolution (Zhong *et al.*, 2001*a,b*).

In the commissioning study, 4.38 g l⁻¹ Na₂SO₄ and 4.16 g l⁻¹ BaSO₄ were mixed in a 35:65 ratio in order to determine whether the

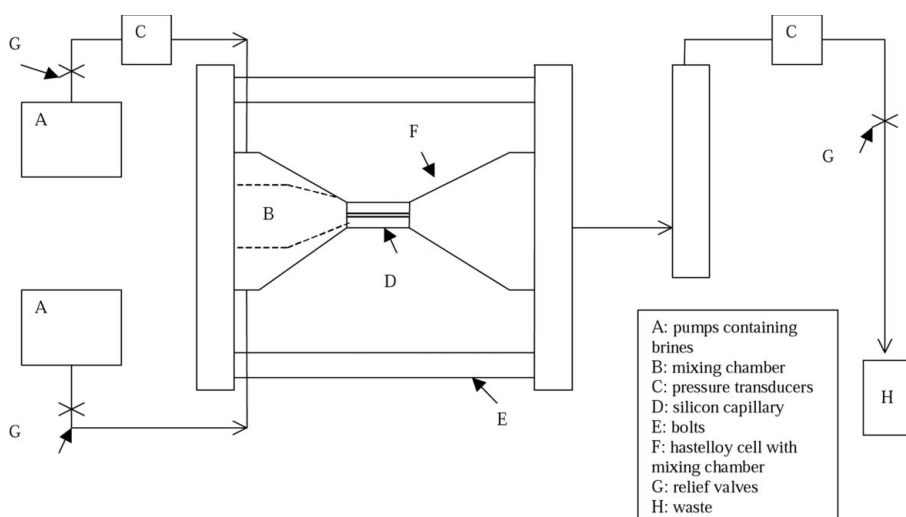


Figure 1
A schematic diagram of the high-pressure cell.

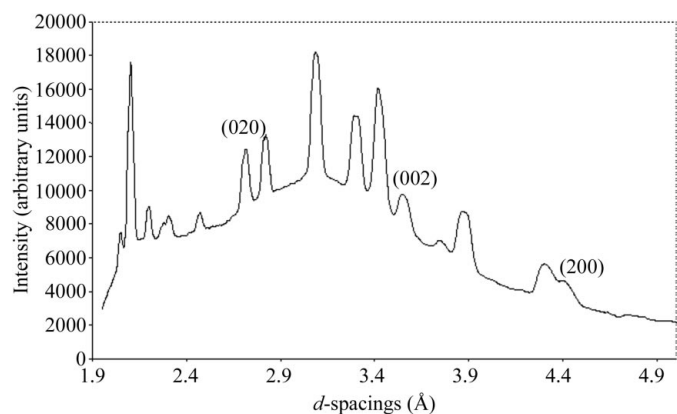


Figure 2
Angle-dispersive XRD data of realistic concentrations of BaSO₄.

experimental set-up could be used to detect representative oilfield scale formation. These concentrations were based on normal seawater sulfate concentrations and realistic sulfate-scaling formation barium concentrations, and therefore results obtained at these relatively low concentrations will have important applications. The mixing ratio yields the highest precipitation mass as predicted by *Scaleup* (Yuan & Todd, 1991).

An X-ray energy of 67 keV, a line pressure of 1.38×10^7 Pa and a flow rate of 6.5 ml min^{-1} were used throughout the study. The high energy of the incoming radiation reduced the range of the diffraction cone, which meant that the cell itself did not create a barrier to the diffracted beam. Scatter from the beam-defining slits was eliminated by placing lead around the silicon.

The data were calibrated with NIST standard Cr₂O₃ powder, and diffraction patterns were acquired. Spatial and flat-field corrections were made using the CCD detector's built-in functions for all data. Custom-made software was written in IDL to fit the centre of the diffraction rings and to calibrate the distance from the sample to the detector's phosphor. This software also performs integration along the portions of the diffraction rings that have high resolution (usually from -20° to $+20^\circ$ from the vertical direction, depending on the width and amount of sagittal focusing). Regions in the integration range that contained diffuse scattering, caused by the silicon single-crystal tube, were ignored.

4. Precipitation of BaSO₄ at realistic oilfield concentrations

Fig. 2 shows the diffractogram for a 20 min scan recorded during the mixing of the two brines. The scan comprises sharp crystalline peaks (caused by the barium sulfate) and a diffuse halo (caused by the solvent). After background subtraction, the peaks were fitted using *Peakfit4 for Windows* (AISN Software, 1995, 1991, 1990), a least-squares iterative peak-fitting package. Peak positions of 4.407, 2.716 and 3.559 Å were obtained for the (200), (020) and (002) reflections, respectively, representing unit-cell parameters of $a = 8.814$, $b = 5.434$ and $c = 7.180$ Å. These values are close to the published barite unit-cell parameters of $a = 8.884$, $b = 5.458$ and $c = 7.153$ Å (Colville & Staudhammer, 1967). Peak positions were easily ascertained and the present experimental set-up may be used to determine the effect of additives on BaSO₄ unit-cell parameters at realistic concentrations.

5. Conclusions

Angle-dispersive XRD was carried out using a new pressure flow cell, and BaSO₄ was used to commission the cell.

Precipitation of BaSO₄ was successfully monitored using realistic oilfield concentrations. Data collection took place *in situ*, and the diffraction peaks were easily identified above the diffuse halo. This cell, which has been pressure-tested up to 4×10^7 Pa, will be used to monitor the effects of additives and pressure on the unit-cell parameters of crystallizing systems. This has important industrial applications, as it will increase the understanding of scale-inhibitor mechanisms of action, leading to the development of improved inhibitor packages.

We gratefully acknowledge the EPSRC for funding this work and the sponsors of the Flow Assurance and Scale Team at Heriot-Watt University: Baker Petrolite, BioLab, BP, Champion, ChevronTexaco, Dynea, ExxonMobil, Halliburton, Ker McGee, Marathon, ONDEO Nalco, Norsk Hydro, Petrobras, Phillips, Rhodia, Saudi Aramco, Schlumberger, Shell, Statoil, TotalFinaElf and TR Oil Services. We thank Mr Walter Crawford for building the cell, Miss Claire Hobden for assisting with data collection, and Professor Anne Neville in the Department of Mechanical and Chemical Engineering at Heriot-Watt University for carrying out pressure calculations for the silicon tube.

References

AISN Software (1995, 1991, 1990). *Peakfit*. Version 4.0 AISN Software Inc., SPSS Science, Chicago, IL 60606-6307, USA.
 Boak, L. S., Graham, G. M. & Sorbie, K. S. (1999). *Proceedings of SPE Oilfield Chemistry Conference*. Houston, Texas, USA.
 Colville, A. A. & Staudhammer, K. (1967). *Am. Mineral.* **52**, 1877.
 Hennessy, A. J. B. (2001). PhD thesis, Heriot-Watt University, Scotland.
 Hennessy, A. J. B. & Graham, G. M. (2002). *J. Cryst. Growth.* **237/239**, 2153–2159.
 Vegard, L. (1921). *Z. Phys.* **5**, 17.
 Yuan, M. D. & Todd, A. C. (1991). *SPE J. Prod. Eng.* **63**, 237.
 Zhong, Z., Kao, C. C., Siddons, D. P. & Hastings, J. B. (2001a). *J. Appl. Cryst.* **34**, 504–509.
 Zhong, Z., Kao, C. C., Siddons, D. P. & Hastings, J. B. (2001b). *J. Appl. Cryst.* **34**, 646–653.