

## City University of London: Conclusion

The nucleation, precipitation and aggregation processes when solid materials separate from their aqueous solutions can be affected by a number of factors. In these processes there will always be competition between growth of the solid material on suspended crystallites and on the walls of the container. When growth on the walls is favoured, deposition of chemical scale occurs. The work described in this thesis is concerned with some of the factors affecting nucleation, precipitation, aggregation and scale formation in systems of particular relevance to the offshore oil industry. The factors affecting the processes studied in this work are (1) the effects of applied electromagnetic fields on the deposition and scale-forming properties of calcium carbonate and (2) the effects of varying the significant ion concentrations and the ratios of mixing of solutions in the  $\text{BaSO}_4\text{-SrSO}_4\text{-CaCO}_3$  and  $\text{CaCO}_4\text{-CaCO}_3$  systems. In all of the systems the main method used to study both the rate of precipitation and crystallisation was based on the deposition of solid material in a small bore tube such that the time taken to reach a cut-off back pressure provided a measurement of the rate of deposition and the propensity to form scale. The results show that this method of measurement gives reproducible results. In the rate of deposition and propensity to scale experiments sufficient measurements were made to ensure that the data obtained were both reproducible and statistically significant.

The effects of an applied electromagnetic field on deposition of calcium carbonate from aqueous solutions were studied using a Hydromag DN15 electromagnetic unit. This unit subjects the flow of water through it to an applied magnetic field of about 2500 Gauss in a system that involves a change in polarity for 5 seconds every minute. Experiments were carried out on (1) calcium carbonate deposited chemically by the addition of a solution of sodium hydrogen carbonate to a solution containing calcium ions and (2) the deposition of calcium carbonate from hard waters in both laboratory experiments and industrially monitored trials. The results of propensity to scale measurements show that the magnetic treatment of calcium ion solutions significantly reduces the rate of deposition of calcium carbonate (when precipitated with sodium hydrogen carbonate solutions) compared to treatments in zero field conditions. This effect of applied fields was found to be significant over the range of flow rates tested for treating calcium ion solutions, with the Hydromag DN15 electromagnetic unit having an optimum flow rate of 6 l/min. The magnitude of the effect was also shown to be dependant on the sodium hydrogen carbonate concentration and the temperature at which the experiments were carried out. Replicate experiments show that the effects of applied fields on calcium ion solutions

are reproducible in all the propensity to scale experiments. Heat exchanger experiments have also demonstrated that magnetic treatment significantly reduces the quantity of scale formed. Laboratory experiments show a significant difference in the crystal and aggregate sizes which affect the nature of the scale formed. In particular the crystallites obtained following magnetic treatment are distinct and show little tendency to aggregate to form scale. In the zero field experiments, the fundamental particles obtained are much smaller but they readily aggregate to form large conglomerates made up of these aggregated particles.

These effects on calcium carbonate precipitation can be explained in terms of the direct interaction of the applied magnetic field at the highly charged surfaces of calcium carbonate nuclei or pre-nuclear clusters. The results on the calcium carbonate scaling system, along with other data show unequivocally that the magnetic treatment of fluids (i.e. the interaction of charged species in fluids and applied fields) is a general phenomenon. The results can be explained in terms of the direct field-charge interaction between applied magnetic fields and the important charged species in the system.

The effects of coexisting ions on the precipitation of all possible solid phases in the systems BaSO<sub>4</sub>-SrSO<sub>4</sub>-CaCO<sub>3</sub> and CaSO<sub>4</sub>-CaCO<sub>3</sub> were studied in model systems for formation water and sea water mixing in offshore oil production.

Propensity to scale data for the BaSO<sub>4</sub>-SrSO<sub>4</sub>-CaCO<sub>3</sub> system show that increasing each significant ion concentration in simulated formation and sea water separately, leaving the other ion concentrations unchanged, leads to different effects depending on the ion concentration increased. The ion concentrations which increase the rate of deposition of scale were those of the sulphate and barium ions. The rate of deposition of scale is decreased for increase in the concentration of sodium, magnesium and calcium ions, while increase in the potassium ion concentration did not affect the rate of deposition of scale. Increasing the strontium ion concentration in formation and sea water produced a significant decrease in the rate of deposition of scale below 70<sup>o</sup> C, but above 70<sup>o</sup> c a significant increase in scale deposition was found for high strontium ion concentrations in formation water. The results from mixing the most and least scale-forming formation and sea waters, as determined from the ion concentration experiments, vary depending on the combinations of each water used. The results for the ratio of mixing experiments showed that the most scale-forming ratio was between 60:40 and 70:30 for the standard formation and sea waters used. The least scale-forming ratio was found to be 10:90. Precipitation tests and scale

prediction model data were used to provide information on the quantity of each material deposited. The precipitation of calcium carbonate was found to increase when the formation water to sea water ratio was small and reached a maximum at 10:90. The precipitation of strontium sulphate was found to be a maximum between the ratios of 50:50 and 70:30 in the precipitation tests compared with a maximum at 70:30 from the scale prediction model data. Barium sulphate precipitation increased as the formation water to sea water ratio increased and reached a maximum at 90:10.

For the  $\text{CaCO}_4\text{-CaCO}_3$  system the effects of increasing each significant ion concentration in simulated formation and sea water separately, leaving the other ion concentrations unchanged, depend upon the particular ion increasing in concentration. The ion concentrations which increase the rate of scale are those of the calcium and sulphate ions, while increased in the sodium, magnesium and hydrogen carbonate ion levels decrease the rate of deposition of scale. Increase in the potassium ion concentration does not affect the rate of deposition of scale.

The data from this work on studied of the variation of the ion concentrations present in simulated formation and sea waters and the changes in the ratio of mixing of these waters results in changes in the rate of deposition of scale in the systems  $\text{BaSO}_4\text{-SrSO}_4\text{-CaCO}_3$  and  $\text{CaSO}_4\text{-CaCO}_3$ . The changes in the types and amount of scale-forming material deposited and in propensity to scale measurements are interpreted in terms of solubility effects, ionpair effects and kinetic effects.