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Mineral Scale Formation
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The influence of pH on barite nucleation and growth

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Introduction

Barite ($BaSO_4$) scale formation is a problem in many industrial processes, especially in oilfields where mixing sea water with reservoir water can result in solid layers of barite scale that can completely block pipes.

Organic compounds (e.g. organophosphonates) have been used as inhibitors for barite precipitation. The effectiveness of these compounds is pH-dependent, usually more effective at high pH where they are highly deprotonated.

Thus we need to determine the influence of pH on barite nucleation and growth before the performance of organic additives as barite scale inhibitors can be assessed.

Experimental procedure

Growth experiments.

In situ AFM growth experiments were performed at room temperature in a fluid cell of a Digital Instruments (Veeco Instruments, GmbH) Multimode AFM, working in contact mode.

Optically clear barite single crystals were cleaved immediately before each experiment to expose an (001) surface and growth solutions were injected into the fluid cell at intervals of about 90s before each AFM scan.

Nucleation experiments.

Barite nucleation was studied from the evolution of turbidity and conductivity of supersaturated $BaSO_4$ solutions obtained by mixing $BaCl_2$ and Na_2SO_4 solutions at various pH.

Turbidimetry experiments : UV-Vis Spectrophotometry was used to determine the onset of nucleation. The precipitates formed were studied using FESEM.

Conductivity experiments: 1×10^{-3} M $BaCl_2$ solution was added continuously at a rate of 3.6 ml/min into 100 mL of a 5×10^{-4} M Na_2SO_4 solution. Conductivity and pH were continuously monitored. These experiments allow determination of the onset of nucleation as well as the supersaturation reached at that point.

Effect of pH on barite growth : AFM study

Growth rates and nucleation density increased with increasing pH of the growth solutions (and constant SI).

In solutions with alkaline pH, immediate nucleation was observed after injection and the first growth layer was covered in less than 100s. There was no growth after the first layer (i.e. self-inhibiting layer **(1)**).

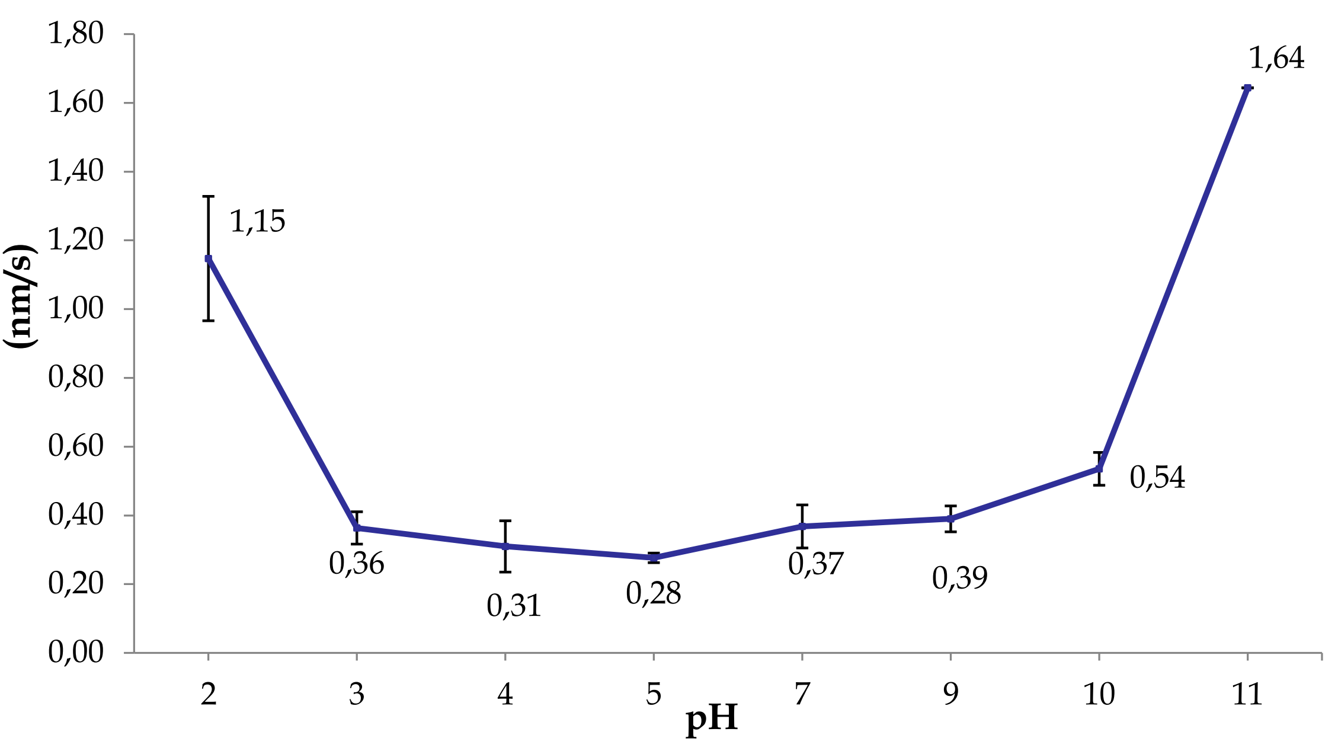

Fig 1. Growth rate in the [001] direction as function of pH.

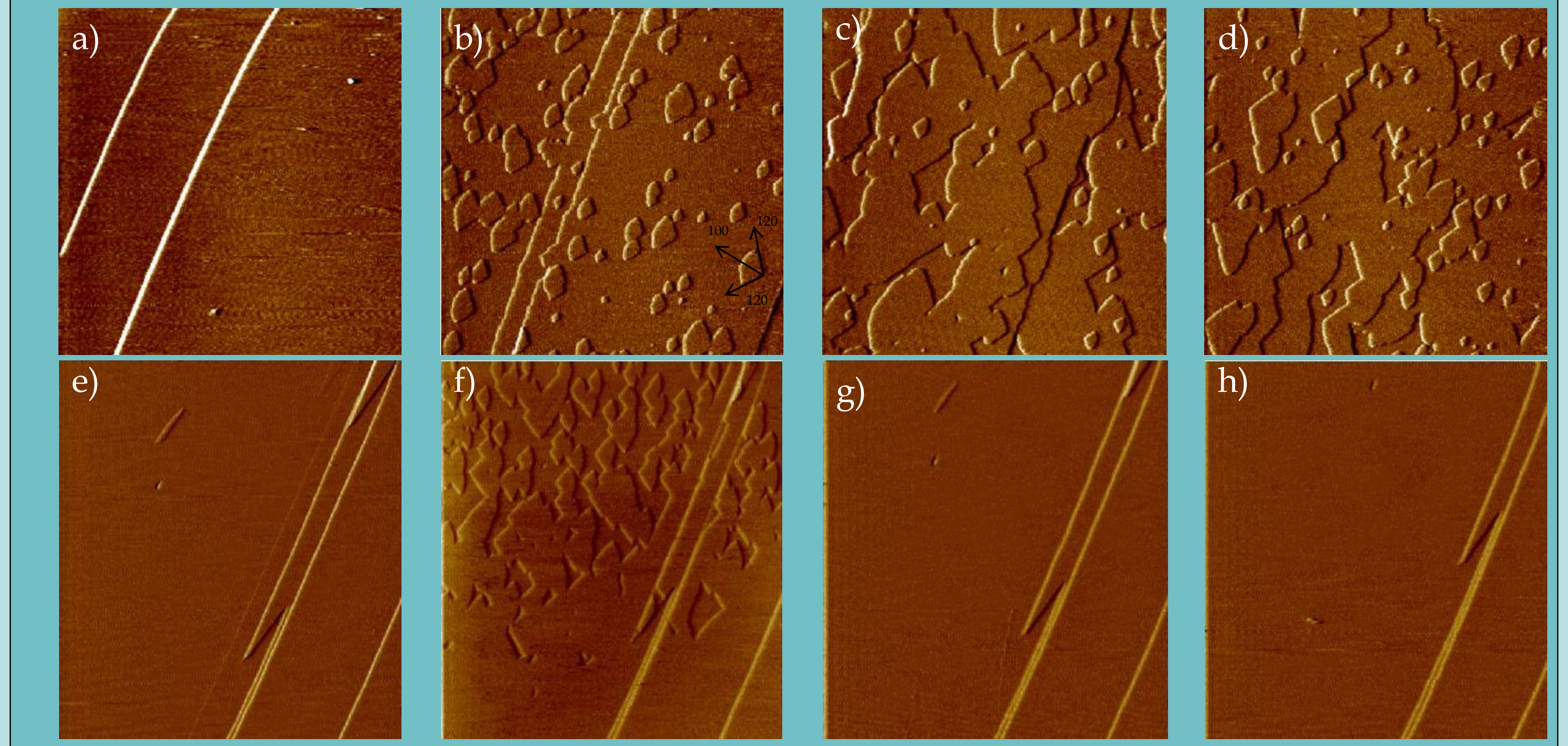

Fig.2. AFM deflection images of growth of (001) $BaSO_4$ surface at SI= 0.92 and (a-d) pH = 7 and (e-h) pH=12. Size of the image is 5 µm.

Effect of pH on nucleation

1) Induction time. Time elapsed between the moment at which supersaturation is created and that at which a "critical nucleus" is found.

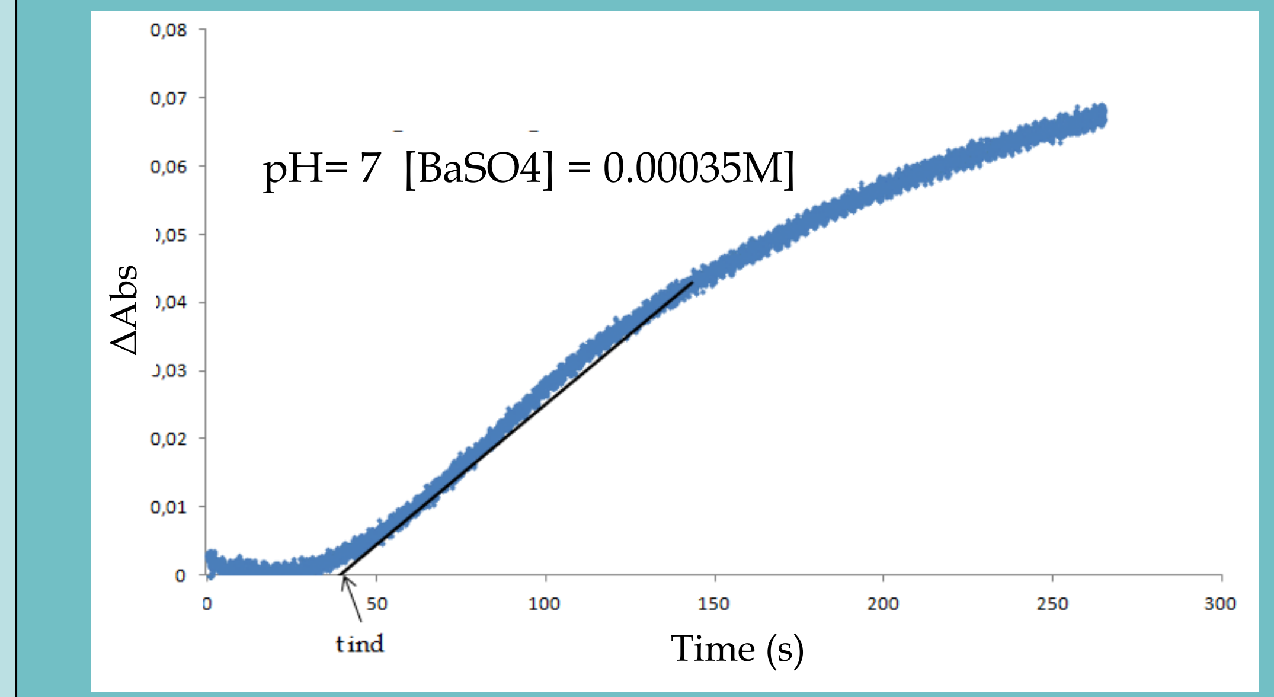

Fig. 3. Typical evolution of turbidimetry (expressed as absorbance) during precipitation experiments .

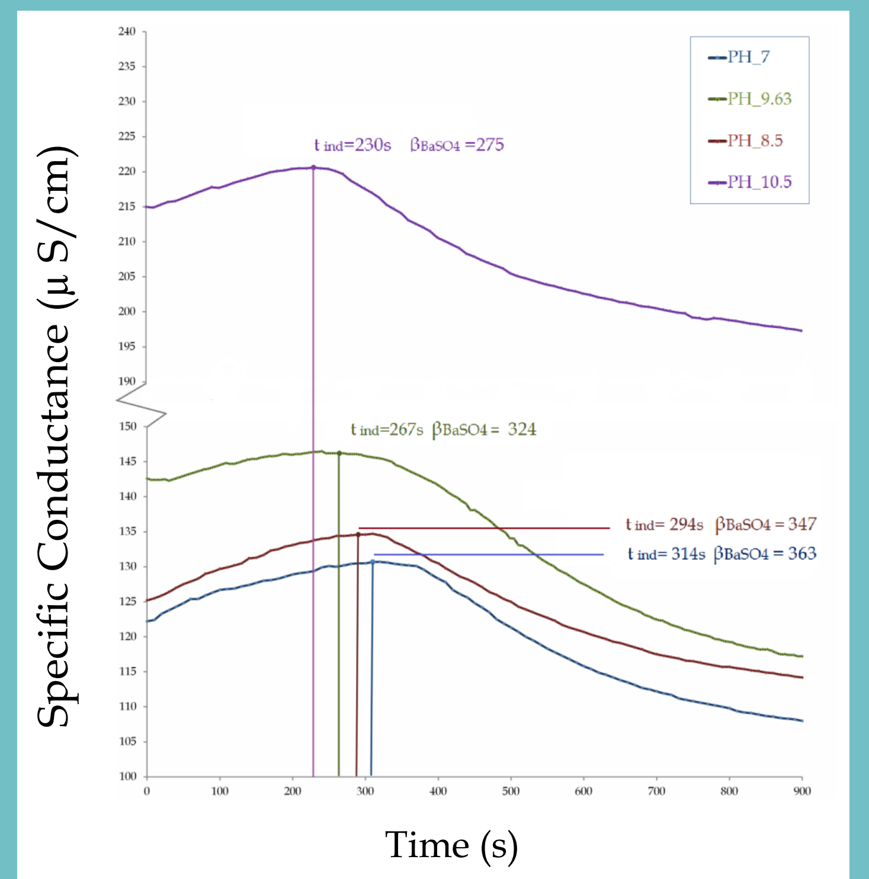

Fig. 4. Specific conductance (µS/cm) as function of time for different pH values.

2) Interfacial tension (γ)

Induction times determined from spectrophotometry measurements enable estimation of the interfacial tension at different pH **(2)**. Interfacial tension decreased between pH= 7 and pH=10.

pH	γ(mJ/m²)
7	22,80
8,5	21,31
10	17,88

Table 1. Interfacial tension values for different pH of the growth solution.

3) Changes in particle size and morphology

Barite particles evolved towards more equidimensional shapes and smaller sizes with increasing pH.

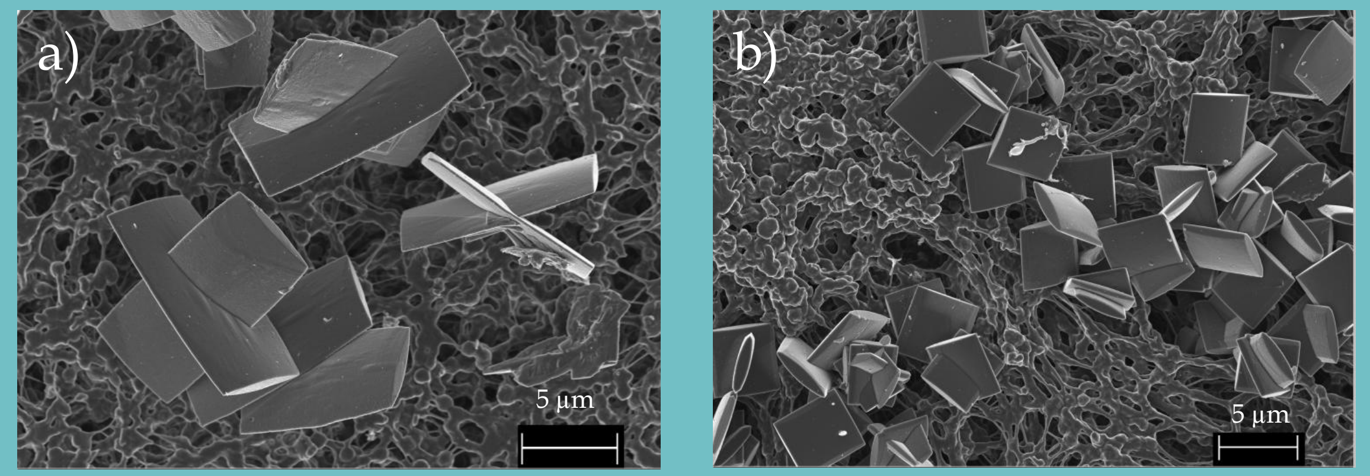

Fig. 5. FESEM images of $BaSO_4$ precipitates formed at (a) pH=7 and (b) pH=11 and SI=2.24.

Conclusions

The higher concentration of strongly hydrated OH^- ions in high pH solutions could reduce Ba^{2+} hydration in solution and help desolvation of barite surfaces **(3)**. This would eventually facilitate barite nucleation and growth, as suggested by our results. The reduction in interfacial tension and particle size found at high pH 10 is also consistent with the observed nucleation enhancement in those solutions.

References

(1) Astilleros J.M. (2002) *Geochimica et Cosmochimica Acta.*
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(3) Kowacz M. and Putnis A. (2008) *Geochimica et Cosmochimica Acta.*