

Specificities of Scale Process Inside Wellbores in the Later Stage of Oil Field Development

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Abstract: The formation of barium sulfate scale in oil wells and in several industrial processes, in which water supersaturated with respect to this salt is used, is often a serious cause of energy losses. The spontaneous precipitation in aqueous solutions containing relatively high barium and sulfate concentrations was investigated in the present work. In our experiments the supersaturation of the solutions was chosen so that an induction period preceded the onset of precipitation. In all cases the induction time was found to be inversely proportional to the solution supersaturation and the rates of the subsequent precipitation were higher the higher the solution super-saturation. The stability domain of the barium sulfate system was not affected by the barium: sulfate molar ratio. The dependence of the induction time on the initial barium concentration was linear and irrespective of the molar ratio of barium/sulfate the same slope was obtained. The slope may be related to the size of the critical nucleus.

Key words: Scale • Barium sulfate • Induction period • Precipitation • Supersaturation

INTRODUCTION

One of the major problems in the oil industry is to improve the process of oil extraction in complicated geological and physical and technological conditions. This is due to the assumption of most of the high-yield oil fields of the country in late stage development and the growing proportion of hard to recover reserves to their total [1]. The processes of oil extraction while significantly complicated due to high water cut production wellbore, formation of organic and inorganic deposits.

An integral part of the development and exploration of oil fields is a water factor. As a result of flooding is the formation of scale. Accumulation of scale in the downhole equipment leads to reduced productivity, premature failure of the pumping equipment, current unscheduled and costly workover and as a consequence, a significant deterioration of the technical and economic indices of oil and gas companies [2].

In oilfield scale water is of primary importance, since scale will occur only if water is produced. Water is a good solvent for many materials and can carry large quantities of scaling minerals [3]. All natural waters contain dissolved components acquired through contact

with mineral phases in the natural environment. This gives rise to complex fluids, rich in ions, some of which are at the saturation limit for certain mineral phases [4].

The low solubility of barium sulfate in almost all solvents, as compared with other scale-forming minerals, make it a highly undesirable scale solid encountered in processes in which subsurface waters are used [5]. The salts of barium are the most difficult to remove from the scale. Barite (BaSO_4) precipitates already in the presence of low concentrations of sulfate ion [3].

MATERIALS AND METHODS

The formation of the solid phase from aqueous solution follows after the creation of supersaturation, nucleation and crystal growth. The time between the formation of a supersaturated solution and the appearance of the first visible changes in the physico-chemical properties of the solution, defined as the induction period. It is important to know the parameters and conditions of the formation of precipitation and its dependence on the supersaturation of the solution to successfully develop measures preventing scale formation. Moreover, it is interesting to know the

conditions under which spontaneous precipitation take place and subsequent deposition kinetics, which can vary significantly depending on the supersaturation of the solution. Knowledge of the kinetics of spontaneous precipitation is also necessary for the proper use of inhibitors. Thus, both processes as nucleation and crystal growth are very important and should be considered in more detail in order to be able to control the formation of insoluble salts in the operation of oil wells.

For each experiment fresh working solutions were prepared. Equimolar solutions of barium chloride and sulfuric acid were used in all experiments. The absorbance of the solutions was chosen as the physical parameter to be monitored in order to investigate the precipitation process. The experiments were made with a laser analyzer of micro-particles "Laska-1K." The instrument uses a laser diode that emits light with a wavelength $\lambda = 670$ nm (5 mW). As a result, we obtain the data intensity of light transmitted through the cuvette with a supersaturated solution, depending on the time. The onset of precipitation resulted in changes of the initially constant light intensity measured. The induction times were measured from the change of the slope of the absorbance vs. time, curves recorded.

The Main Part: Let us consider some theoretical aspects of the mechanism of scale. The first development within a saturated fluid is a formation of unstable clusters of atoms, a process called homogeneous nucleation. The atom clusters form small seed crystals triggered by local fluctuations in the equilibrium ion concentration in supersaturated solutions. The seed crystals subsequently grow by ions adsorbing onto imperfections on the crystal surfaces.

Crystal growth also tends to initiate on a preexisting fluid-boundary surface, a process called heterogeneous nucleation. Heterogeneous nucleation sites include surface defects such as pipe surface roughness or perforations in production liners, or even joints and seams in tubing and pipelines.

Note that the process is not truly homogeneous nucleation as the cuvette walls or dust particles may contribute. However, keeping the conditions the same (solution volume, solution preparation etc) we minimized these factors.

The driving force for the precipitation is the growth affinity, which is defined as a function of the difference in chemical potential between the crystallizing substance in the crystal and in the supersaturated solution [6]:

$$\beta = \frac{-\Delta\mu}{RT} = 2. \ln P. \quad (1)$$

In eqn. (1) R is the gas constant, T the absolute temperature and S the supersaturation ratio:

$$P = \left(\frac{(Ba^{2+})(SO_4^{2-})}{K_s} \right)^{0.5} \quad (2)$$

In eqn. (2) parentheses denote activities of the enclosed ions and K_s is the thermodynamic solubility product.

The stability of the barium sulfate solutions was found to depend strongly on the driving force. Supersaturated solutions, in which precipitation does not take place spontaneously for practically infinite time, may be prepared for $\beta < 4$.

To describe the kinetics of the process we used the curves of the change in optical density with time after mixing of two fluids at a certain salinity, one of which contains barium in the other - the sulfate ions with different concentrations. The curves can be divided into two types: with and without an induction period expressed induction period. Curves with a pronounced induction period were observed only when mixed with water at equimolar ratio and the relative supersaturation of at least 30 or with excess of one of the counter ion at a relative supersaturation of at least 3.

By mixing water at a relative supersaturation of more than 30, the case of the most common disorders of production casing, at equimolar ratio or with excess of one of the counter ion at a relative supersaturation of more than 3 induction period was several minutes.

As can be seen from Fig. 1, all curves can be divided into three areas. The first area - 0 to the point of extreme - the transmission drops to a minimum, an intensive formation of nuclei and growth of nuclei formed on the surface and in the bulk, there may be a horizontal section - an induction period.

The second area - from the minimum to a border - crystal growth continues, but the weight has reached a critical mass - a process of precipitations (sedimentation), under the influence of gravity, the formation of new crystallization centers practically ceases.

The third area - the crystal growth has stopped, reached a state of equilibrium "crystal-solution", brightening solution occurs due to deposition.

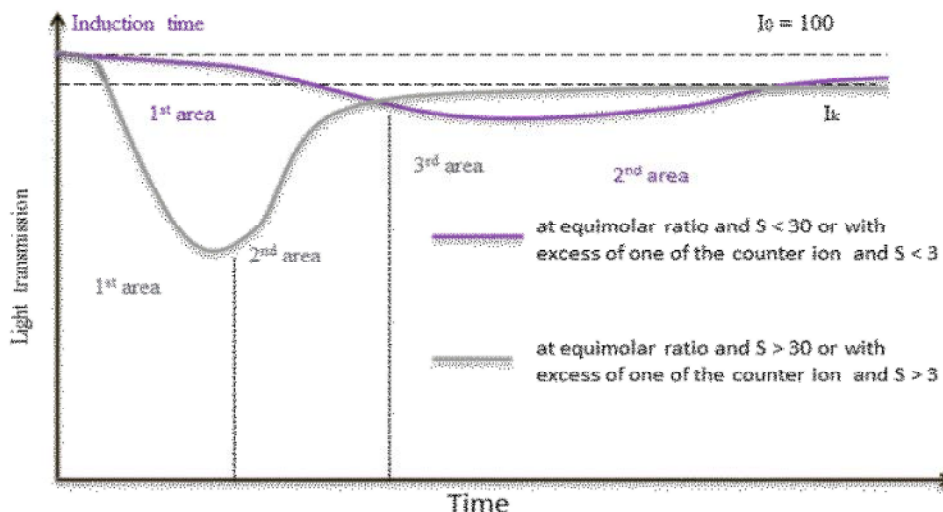


Fig. 1: Dependence of the light transmission at mixing liquids containing barium and sulphate ions

The final value of light transmission is slightly smaller than the primary, $I_e < I_i$. This is due to deposition of crystals on the surface of the measuring cell. From the ratio I_e/I_i can be estimated rate of sediment, which is fixed on the walls (approximately 5-10%).

The nature of the precipitate depends on the ratio of the velocities of two processes: nucleation rates - primary nucleation and the growth rate of the size of the nucleus. Precipitate would be macrocrystalline - small number of large particles - if the rate of nucleation of crystals is small compared with the growth rate of crystals, the reverse ratio of the velocities obtained by fine-dispersed precipitate, consisting of a large number of small particles. Speed of both processes depends on the relative supersaturation of the solution, defined by expression [7]:

$$Sr = \frac{c - c_0}{c_0} \quad (3)$$

In eqn. (3) C - concentration of solute in a supersaturated solution in a given moment of time, C_0 - solubility of the substance when the equilibrium between solid phase and solution at a given temperature.

It is established that an increase in the relative supersaturation of crystal nucleation rate increases exponentially and the rate of crystal growth - in direct proportion. At low relative supersaturation mainly takes place the growth of crystals. With increasing supersaturation of the solution (a decrease in solubility of the deposited material), the process of nucleation is practically suppresses the growth of crystals, formed by

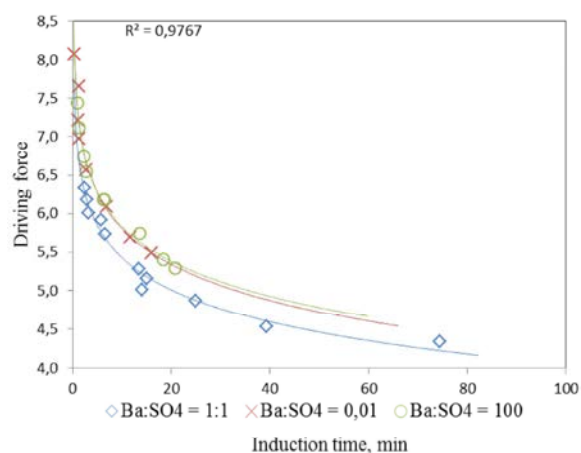


Fig. 2: Dependence of the driving force for the precipitation from the induction period

finely dispersed precipitate, as in the case of deposition of substances with low solubility product amorphous precipitates and colloids, consisting of dispersed particles in the solution precipitated the substance, are formed [8, 9]. Colloidal particles carry a positive or negative charge, which can be caused by adsorption of cations or anions on the surface of colloidal particles.

It is interesting to note, that the induction times were found to depend exclusively on the solution supersaturation. The stoichiometry of the salt constituent ions, Ba^{2+} and SO_4^{2-} had no effect on the induction time. As shown in Fig. 2, supersaturated solutions with ratios from 0,01 to 100 yielded induction times lying on the same curve.

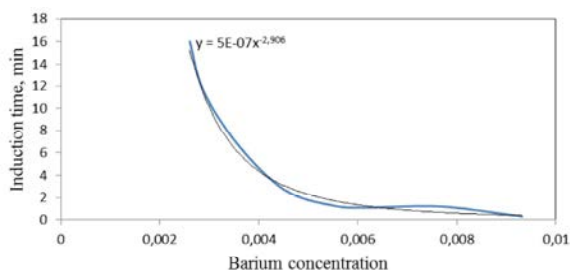


Fig. 3: Dependence of the induction time from the initial concentration of barium

Using the values of the induction period for different values of initial supersaturation, we can define the free surface energy of the resulting nucleus. This makes possible to determine the size of the critical nucleus:

$$r = \frac{2\sigma \cdot V_m}{RT \cdot \ln S_{ab}} \quad (4)$$

In eqn. (4) σ - specific free surface energy, V_m - molar volume, S_{ab} - the absolute degree of supersaturation:

$$S_{ab} = \frac{c}{c_o} \quad (5)$$

The dependence of the induction times measured on the initial concentration of barium ions, which in turn determined the solution supersaturation, according to the Christiansen-Nielsen formulation is [10]:

$$\tau = k \cdot [Ba^{2+}]_0^{1-p} \quad (6)$$

In eqn. (6) p is the number of ions in the critical cluster and k is a proportionality. According to eqn. (6), Fig. 3, gave a value of $p = 4$ for the number of ions participating in the critical nucleus.

CONCLUSION

Research has shown that the supersaturation of the solution affects the induction period. In all cases the induction time was found to be inversely proportional to the solution supersaturation and the rates of the subsequent precipitation were higher the higher the solution super-saturation. The deposition can occur on two of the most common way: a pronounced induction period and without the explicit induction period. The

stability domain of the barium sulfate system was not affected by the barium/sulfate molar ratio. The dependence of the induction time on the initial barium concentration was linear and irrespective of the molar ratio of barium: sulfate the same slope was obtained. Depending on the induction time of the barium ion content was determined by the size of critical nucleus.

Conclusions: The results are important and can give the ability to control the formation of insoluble scale in the operation of oil wells, such as barium sulfate.

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