ELSEVIER

An improved predictive correlation for the induction time of CaCO$_3$ scale formation during flow in porous media

E. Stamatakis [a,b,c,*], A. Stubos [b], J. Palyvos [a], C. Chatzichristos [c], J. Muller [c]

[a] *School of Chemical Engineering, National Technical University of Athens (NTUA), Greece*
[b] *National Centre for Scientific Research Demokritos (NCSRD), 15310 Agia Paraskevi, Attica, Greece*
[c] *Institute for Energy Technology (IFE), P.O. Box 40, NO-2027 Kjeller, Norway*

Abstract

The induction time, t_{ind}, of calcium carbonate precipitation in porous rocks was experimentally measured under dynamic conditions at temperatures from 25 to 120 °C with the use of a radiotracer technique, where the gamma-emitting nuclide ^{47}Ca was used as a tracer in order to monitor the scale deposition at real time. Based upon nucleation theory and experimental observations, the following improved correlation is proposed:

$$\log t_{ind}(\text{min}) = 3.2 - \frac{3.0}{\text{SI}} - \frac{959.8}{T} + \frac{1849.9}{\text{SI}T}.$$

This equation predicts satisfactorily the induction time of calcium carbonate scale formation under specific dynamic (flow) conditions in the near-well region (T is the absolute temperature in K, and SI is the saturation index, SI $= \log$ SR, where SR is the saturation ratio).
© 2005 Elsevier Inc. All rights reserved.

Keywords: Induction time; Scale formation; Calcium carbonate; Porous media

1. Introduction

The formation of mineral scales from produced water/brines in oil/gas wells and pipelines constitutes an old but persistent problem for the oil industry. The sparingly soluble CaCO$_3$ may form when a solution is supersaturated, that is, when the product of the concentrations of the precipitating ions (Ca^{2+}, CO$_3^{2-}$) exceeds the solubility product K_{sp}, which is the equilibrium constant for a reaction, in which a solid ionic compound dissolves to give its constituent ions in solution.

The reasons for the creation of a supersaturated solution are related to a number of mechanisms [1]. However, many waters that have become oversaturated and scale-prone do not always produce scale. Supersaturated calcium carbonate

can be metastable in a solution for some time before precipitating. Thus, a period of time usually elapses between the attainment of supersaturation and the appearance of crystals. This time lag, generally referred to as the induction time, t_{ind}, is considerably influenced by the level of supersaturation, state of agitation, presence of impurities, viscosity, etc. [2].

As the induction time can be affected by many external factors, it cannot be regarded as a fundamental property of a system. Nor can it be fully relied upon to yield basic information on the process of nucleation. Nevertheless, despite its complexity and uncertain composition, the induction time has frequently been used as a measure of the nucleation event, under the simplifying assumption that it can be considered to be inversely proportional to the rate of nucleation, J [2]:

$$t_{ind} \propto J^{-1}. \tag{1}$$

* Corresponding author. Fax: +47-63811168.
  E-mail address: manos@ife.no (E. Stamatakis).

According to Mullin [2], the classical nucleation relationship, stemming from the work of Gibbs, Volmer, and others, may be written as

$$\log t_{ind} \propto \left[\frac{\gamma^3}{T^3 (\log SR)^2} \right], \tag{2}$$

where γ is the interfacial tension of the crystalline solid in contact with a solution of its dissolved phase (mJ/m^2), T is the absolute temperature (°K), and SR is the saturation ratio, defined as

$$SR = \frac{a_{Ca^{2+}} a_{CO_3^{2-}}}{K_{SP}^0} = \frac{m_{Ca^{2+}} m_{CO_3^{2-}}}{K_{SP}}, \tag{3}$$

where α_i, m_i are the activity and the molarity of ion i, respectively, and K_{sp}^0 and K_{sp} the thermodynamic and stoichiometric solubility product, respectively.

2. Literature review for the prediction of CaCO$_3$ precipitation induction time

A first empirical approach to the estimation of the induction time of the precipitation process is described by Nielsen [3], and yields a relationship between the induction time, t_{ind}, and the initial concentration, c, of the supersaturated solution,

$$t_{ind} = kc^{1-p}, \tag{4}$$

where k is a constant and p is the number of molecules in a critical nucleus. It was pointed out that the induction time may range from microseconds to days, depending on the initial degree of solution supersaturation, SR. For a more direct correlation of the induction time to the SR, the following form was proposed later [4],

$$t_{ind} = kSR_0^{-n}, \tag{5}$$

where SR_0 denotes again the initial degree of solution supersaturation and n is a constant.

In 1969, Nielsen suggested that the induction time for precipitation under constant temperature could obey the relationship [5]:

$$\log t_{ind} = B(SI)^{-2} + C, \tag{6}$$

where SI is the saturation index ($SI = \log SR$), C is a constant, and B is a function of temperature and interfacial tension that takes the form

$$B = \frac{\beta \gamma^3 V_m^2 N_A f(\theta)}{(k_B T)^3}. \tag{7}$$

In Eq. (7), γ is the interfacial tension (or surface energy) of a crystalline solid in contact with a solution of the dissolved solid, β is a geometric shape factor ($4S^3/27V^2$, where S and V are the surface area and the volume of the nuclei; e.g., $\beta = 16\pi/3$ for a spherical nucleus), V_m is the molar volume (6.132×10^{-23} cm^3 for calcite), N_A is Avogadro's number,

T is the absolute temperature (K), k_B is the Boltzmann constant (1.38×10^{-23} J K^{-1}), and $f(\theta)$ is the correction factor for heterogeneous nucleation ($f(\theta) = 1$ for homogeneous nucleation, and $f(\theta) < 1$ for heterogeneous nucleation).

Equation (6) has been confirmed experimentally by Söhnel and Mullin [6,7] and by He and co-workers [8]. In addition, published experimental data show that the $\log t_{ind}$ vs $(\log SR)^{-2}$ relation at constant temperature is linear for a large number of substances, varying from the readily soluble, e.g., KH$_2$PO$_4$ [9], through the moderately soluble, e.g., ZnC$_2$O$_4$ [10], to the sparingly soluble, e.g., BaSO$_4$, SrSO$_4$, BaCrO$_4$ [5,11].

In 1972, an empirical relationship was suggested by Gunn and Murthy, introducing the effect of temperature upon the induction time [12],

$$\log \frac{1}{t_{ind}} = A - \frac{E_a}{2.303RT}, \tag{8}$$

where A is a constant and E_a is the activation energy for nucleation.

The relationship was confirmed by the work of Liu and Nancollas [13] and fitted well the data obtained from the work of He and co-researchers [8]. A year later, He and co-workers developed a semiempirical model, which can predict the induction time of BaSO$_4$ precipitation, based on the nucleation theory and their experimental observations [14]. It resulted in an expression of the form

$$\log t_{ind} = -2.235 + \frac{[1087.2 - 0.297T]^2}{T^2 SI}$$
$$- 0.123 \frac{[1087.2 - 0.297T]^3}{T^3 SI^2}. \tag{9}$$

Equation (9) was based on 102 data points, ranging from a few seconds to a day, with $r^2 = 0.99$.

More recently, He and co-workers [15], on the basis of the classic nucleation theory and the available experimental observations, proposed that, within a limited range of supersaturation and temperature, the logarithm of the induction period of CaCO$_3$ is proportional to $1/SI$ at a given temperature and proportional to $1/T$ at a given SI. They developed a predictive correlation for CaCO$_3$ precipitation,

$$\log t_{ind} = 4.22 - \frac{13.8}{SI} - \frac{1876.4}{T} + \frac{6259.6}{SIT}, \tag{10}$$

where the constants in Eq. (10) were obtained by nonlinear regression analysis of the experimental data of the induction time over a range of saturation indices (1.0–2.6) and temperatures (25–90 °C).

All the approaches presented above have been derived either experimentally, from static precipitation measurements, or theoretically, by assuming a homogeneous nucleation process. However, it is generally accepted that true homogeneous nucleation is not a common event. It is virtually impossible to achieve a solution completely free of foreign bodies or even free of surface roughness [2]. Furthermore, none of the aforementioned studies seems to take in to consideration the effects of flow on the induction time. Scaling