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Kinetics of interaction of hardened oil-well cement slurries with acidic solutions from isothermal heat-conduction calorimetry

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Abstract

The kinetics of interaction of hydrochloric acid with oil-well cement slurries treated with the silane coupling agents, tetraethyl orthosilicate, 3-(trimethoxysilyl)-1-propanethiol and 3-(chloropropyl)-trimethoxysilane have been investigated isothermal heat-conduction calorimetry at 298.15 K. The Avrami kinetic model gives a better fit to the experimental data than the traditional Lagergren kinetics models. A pore diffusion model suggests acid diffusion only for the standard slurry. The results indicate that isothermal heat-conduction calorimetry is suitable to evaluate the protective role of silane coupling agents on hardened oil-well cement slurries.

Keywords: Hardened cement slurries; Silane coupling agents; Hydrochloric acid attack; Isothermal heat-conduction calorimetry; Kinetic modeling

1. Introduction

Hardened cement slurries are useful to preserve the integrity of oilwells and to fix their metallic parts. However, the deterioration of cement by acids represents a challenge in the materials field and requires further investigation. Several hardened oilwells have been observed to have intercommunication problems attributed to the occurrence of reactions between the hardened cement slurry in the annulus and the acid, which is used frequently in oilfield operations [1]. However, studies on the chemical nature of the acid attack are few and scattered. In this study, it is shown that adding silane coupling agents to fluid cement slurry mixes has significant effects on the chemical and thermal resistance of the hardened material [2–4]. The effectiveness of silanes is due to their reactivity with −OH groups on the surface of both cement and silica. The latter is a finely ground amorphous silicon oxide that is an essential ingredient. The quality and durability of silanized materials depends primarily on the nature of the attachment to the surface and possible changes of intrinsic mechanical properties after silanization [2–4].

Isothermal heat-conduction calorimetry has been used in the assessment of stability of drugs and explosives, in the characterisation of cement hydration [5], and to provide information on differences in surface chemistry and sorption characteristics of materials [6,7].

Our research group has recently published data on the synthesis, thermal characterization and interaction energies of hydrochloric acid with silane coupling agent treated oil-well slurries evaluated by isothermal calorimetry [8]. It was found that increasing temperature deacreased the time of action of the acid on the slurries. Our previous work also showed [8] that the standard slurry presented longer reaction times with HCl solutions than the silane-slurries described here. The interaction energies of the silane-slurries were higher than the standard slurry, which was attributed to the lower content of $Ca(OH)_2$ in relation to the standard slurry and the preferential binding of HCl to the surface-immobilized silane groups, which partially prevent the diffusion of the acid and the consequent destruction of the slurries in acidic medium [1].

The present work evaluates the interaction kinetics of hardened cement slurries with acid. The study is focused on

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determination of kinetic parameters of reaction of hydrochloric acid with cement slurries having as additives the silane coupling agents: 3-(trimethoxysilyl)-1-propanethiol (SH), 3-(chloropropyl)-trimethoxysilane (CL) and tetraethyl orthosilicate (SiL). The kinetic data were fitted by the traditional pseudo-first- and second-order Lagergren models, the pore diffusion model, and an alternative Avrami kinetic model. This investigation enables a better comprehension of the important long-term processes of acid attack on alternative hardened oil-well cement slurries.

2. Experimental

Reagent grades 3-(trimethoxysilyl)-1-propanethiol (SH), 3-(chloropropyl)-trimethoxysilane (CL) and tetraethyl orthosilicate (SiL) (all from Merck) were used without further purification. The cement was a special cement (Class A) from Cimesa (Laranjeiras-SE, Brazil) and silica (325 mesh) was from Schlumberger Oilfield Services (Nossa Senhora do Socorro/Sergipe, Brazil).

Standard slurry and slurries with the silane coupling agents were prepared as previously described [8]. The slurries are hereafter denominated as slurry-SH, slurry-CL and slurry-SiL for simplicity.

Calorimetric measurements were performed at 298.15 K in a SETARAM C80 mixing calorimeter. Calorimetric output is of thermal power (d*q*/d*t*; mW) as a function of time (*t*; min) and consequently the integral of these data over time is equal to *Q* (J). Performance and more details have been described elsewhere [8].

Samples of hardened cement slurries were used in powder form (100–150 mesh; surface areas were about 5.0 m^2/g, from BET methodology). Approximately 100 mg were put into the lower part of the calorimeter cell. A volume (3.0 cm^3) of 0.10 mol/L HCl solution was added into the upper part of the calorimeter cell. Water was used in blank tests to find the wetting effect of water alone. After stabilization of the calorimeter, a movable rod is maneuvered from outside the calorimeter to puncture a thick PTFE membrane and enable the slurry–solution interaction to start. Each individual experiment yields a calorimeter signal (power versus time), whose area was integrated over each 3 min of contact time. The integrations were made by the software SETSOFT (SETARAM). Integrations were continued until the interaction finished, where the base line was the same value as before the interaction was started by breaking PTFE membrane, as described earlier [8]. The integrations were made by the "horizontal way drawn from first point" methodology, which enables partial integrations for predetermined reaction times.

The time of 3 min for the partial integrations was chosen, since the final isotherms present at least 13 experimental points. No loss of information was detected in the early stages of the acid/slurry interactions. In all calorimetric measures only the experiments in which differences did not surpass 5% were considered as "replicate runs". In general, average of duplicate runs were used in the calculations.

The calorimetric data were used to obtain interaction isotherms and to apply the kinetic models. The building of interaction isotherms is also very common in isothermal incremental titration calorimetry [9,10]. The time-related cumulative heats were obtained from the general expression:

$$Q_t = Q_{\mathrm{r},t} - Q_{\mathrm{w},t} \tag{1}$$

where Q_t is the cumulative heat at a contact time *t*, $Q_{\mathrm{r},t}$ and $Q_{\mathrm{w},t}$ are the cumulative thermal effects originating from reaction and wetting effect (water), respectively.

3. Results and discussion

3.1. Kinetic studies

Fig. 1 shows cumulative heat (Q_t) as a function of contact time. Traditionally, the kinetics of interaction at solid/solution interfaces is described by the expressions originally given by Lagergren. A simple kinetic analysis is the pseudo-first-order equation in the form [11,12]:

$$\frac{\mathrm{d}Q_t}{\mathrm{d}t} = k_1(Q_\mathrm{e} - Q_t) \tag{2}$$

where k_1 is the rate constant and Q_e denotes the interaction heat (J) at equilibrium per gram of slurry. For calculation purposes, all Q_e values were the last cumulative points for each curve of Fig. 1, where equilibrium is assumed to be reached [9,10]. After integration and applying the initial conditions $Q_t = 0$ at $t = 0$ and $Q_t = Q_\mathrm{e}$ at $t = t_\mathrm{e}$ Eq. (2) becomes:

$$\ln(Q_\mathrm{e} - Q_t) = \ln(Q_\mathrm{e}) - k_1 t \tag{3}$$

In addition, a pseudo-second-order equation based on adsorption equilibrium capacity may be expressed in the form:

$$\frac{\mathrm{d}Q_t}{\mathrm{d}t} = k_2(Q_\mathrm{e} - Q_t)^2 \tag{4}$$

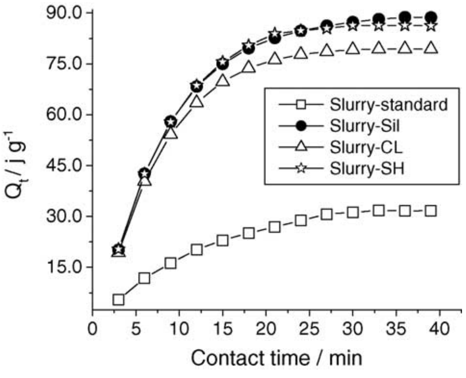

Fig. 1. Cumulative heat curves of the hardened slurries as a function of contact time, at 298.15 K.

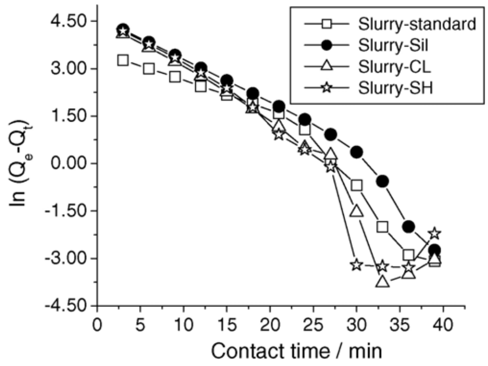

Fig. 2. Cumulative heat curves (exothermic values) of the hardened slurries as a function of contact time, at 298.15 K.

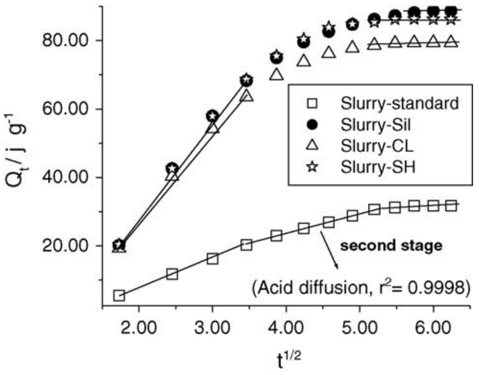

Fig. 4. Pore diffusion model plots for the slurries at 298.15 K.

Integrating Eq. (4) and applying the initial conditions, we have

$$\frac{1}{Q_\mathrm{e}-Q_t}=\frac{1}{Q_\mathrm{e}}+k_2t \tag{5}$$

or equivalently

$$\frac{t}{Q_t}=\frac{1}{k_2Q_\mathrm{e}^2}+\frac{1}{Q_\mathrm{e}}t \tag{6}$$

The validity of these models is traditionally checked by the linearity of plots of $\ln(Q_\mathrm{e}-Q_t)$ versus t, and (t/Q_t) versus t, respectively [11–13]. Figs. 2 and 3 show the kinetic Lagergren plots at 298.15 K. The best linear fit (r^2 values of at least 0.9885) was observed for the second-order kinetic model.

The two Lagergren equations cannot give interaction mechanisms, so another model tested to check the acid diffusion into the slurries. The pore diffusion model, described by Eq. (7), is used here and in most solid/solution interaction studies [16]:

$$Q_t=k_\mathrm{int}t^{1/2} \tag{7}$$

where k_int is the pore diffusion rate constant (J g^{-1} min$^{-1/2}$). Fig. 4 shows the pore diffusion plots for the slurries. These plots indicate that two or more stages are taking place. The first stage is the external surface sorption stage. The second stage is a more gradual sorption, where intraparticle pore diffusion is rate-controlling. However, this stage seems to occur only in the standard slurry. The silane coupling agents seem to prevent acid diffusion into the other cement slurries. The third portion is the final equilibrium stage where pore diffusion slows and stops.

An Avrami kinetic equation is also tested in this work. The use and validation of this equation have been reported in interaction studies of metals on thin chitosan membranes [11], chemically modified silica gel [12], and recently in adsorption of anionic dyes on chitosan microbeads [14].

The Avrami exponential function is shown in Eq. (8):

$$\alpha=1-\exp[-(k_\mathrm{av}t)]^n \tag{8}$$

where α is the fraction of heat produced at a contact time t, $\alpha=Q_t/Q_\mathrm{e}$, k_av is the Avrami kinetic constant, and n is another constant, related to the interaction mechanism [11,12,14]. The linearized form of this equation is presented in Eq. (9) [11,12,14]:

$$\ln(-\ln(1-\alpha))=n\ln k_\mathrm{av}+n\ln t \tag{9}$$

Fig. 5 shows the general behavior of the $\ln(-\ln(1-\alpha_i))$ versus $\ln(t)$ plots for each cement slurry studied. The slopes and intercepts provide the n and $\ln(k_\mathrm{av})$ values, respectively. From Fig. 5, one linear region (r^2 value of at least 0.9975) was found for the silane-modified slurries. However, for the standard slurry, two linear regions are suggested with two

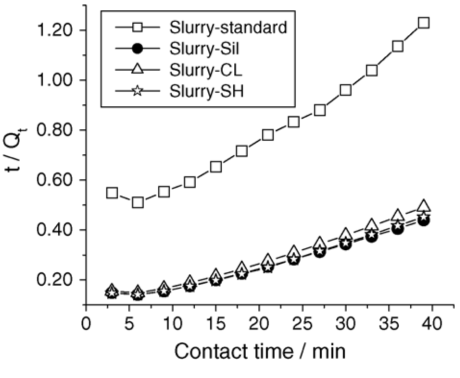

Fig. 3. Lagergren second-order plots for the slurries at 298.15 K.

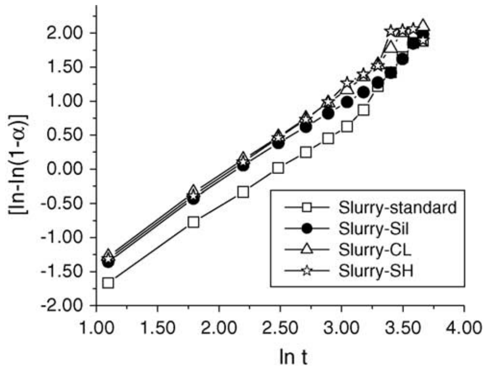

Fig. 5. Avrami plots for the slurries at 298.15 K.

Table 1
Kinetic parameters for the interactions of the slurries with acid solutions, at 298.15 K

Slurry	Second-order Lagergren model			Second stage pore diffusion model		Avrami model				
	k_2 ($\times 10^{-3}$ g J^{-1} min^{-1})	Q_e (J g^{-1})	ΔQ_t (%)	k_{int} (J g^{-1} min$^{-1/2}$)	ΔQ_t (%)	$k_{av,1}$ ($\times 10^{-1}$ min^{-1})	n_1	$k_{av,2}$ ($\times 10^{-1}$ min^{-1})	n_2	$\Delta\alpha$ (%)
Standard	1.02	31.4	6.4	5.88	4.00	0.83	1.20	0.65	2.14	0.27
Sil	0.88	91.0	12.8		P.F.	1.12	1.22			0.35
CL	1.20	89.1	P.F.		P.F.	1.23	1.31			0.29
SH	1.03	88.6	18.0		P.F.	1.22	1.32			0.20

P.F. = Poorly fitted kinetic model (higher than 20%) [5].

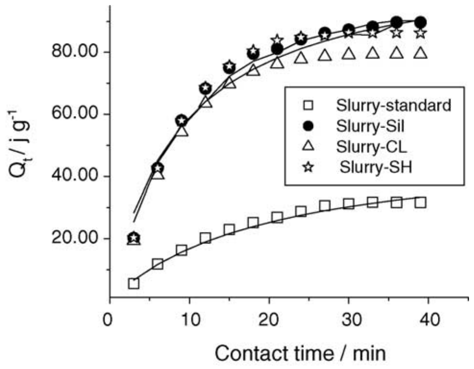

Fig. 6. Correlation curves for the interaction of the slurries with the acidic solution. Experimental data are reported as points and the calculated second-order Lagergren model as curves.

independent sets of values of n (n_1 and n_2) and k_{av} ($k_{av,1}$ and $k_{av,2}$). Figs. 6 and 7 show the fits of the Lagergren and Avrami model to the experimental data, respectively.

The kinetic data are given in Table 1. To quantitatively compare the applicability of each model, normalized standard deviations between the experimental and calculated values of Q_t and α, are obtained as follows [15]:

$$\Delta Q_t(\%) = 100 \times \sqrt{\frac{\sum [(Q_{t,\mathrm{exp}} - Q_{t,\mathrm{calc}})/Q_{t,\mathrm{exp}}]^2}{n-1}} \qquad (10)$$

$$\Delta\alpha(\%) = 100 \times \sqrt{\frac{\sum [(\alpha_{\mathrm{exp}} - \alpha_{\mathrm{calc}})/\alpha_{\mathrm{exp}}]^2}{n-1}} \qquad (11)$$

where n is the number of data points. Taking into account the numerical values of ΔQ_t and $\Delta\alpha$, for the Lagergren, pore diffusion and the Avrami models, it can be seen that the Avrami model fits the kinetic data satisfactorily.

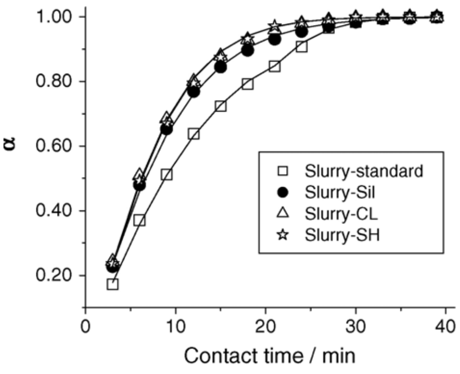

Fig. 7. Correlation curves for the interaction of the slurries with the acidic solution. Experimental data are reported as points and the calculated Avrami model as curves.

The Avrami model suggested that all silane-modified slurries presented only one interaction mechanism for all contact times evaluated, the external surface acid sorption. The interactions take place with similar rates, the $k_{av,1}$ values are very similar for all silanized slurries. The standard slurry presented a second interaction, after about 20 min of contact time, which is described by the $k_{av,2}$ and n_2 values. This last stage seems to occur due to acid diffusion into the internal parts of the standard slurry, as also indicated by the second stage pore diffusion model.

The use of continuous isothermal heat-conduction calorimetry proved to be efficient to evaluate the protective effect of the silane coupling agents on the oil-well cement slurries.

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