Role of Diffusion and Shut - Off Time in Well Treatment Technology

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ABSTRACT

An analysis of ion diffusion in polymer/silicate gels is detailed. The diffusion coefficient, break-through time and retention of chromium ions was determined as a function of gel composition and geometry and temperature. The activation energy of diffusion was also calculated.

Concerning the profile correction techniques based on sequential injection of treating fluids it was concluded that the *in-situ* gelation of different chemicals is a diffusion controlled process. Thus, the shut-off time can be minimized by using such cross-linking agents which do not adsorb in gels and have high chemical driving force in the mass transport system. Further, the chemical composition of gels significantly influences the diffusion mass transport. Consequently, the shut-off time can be reduced by changing the gel composition in favour of the non-adsorbent type components. On the basis of the experimental findings it seems necessary to re-evaluate the chemical design of surface technology.

INTRODUCTION

Application of hydrated gels for profile correction opened up new vistas in hydrocarbon industry. During the past decades a great variety of gel-forming chemicals has been tested successfully under field conditions and the developed placement technologies showed also broad diversity. One of the most frequently used methods is based on sequential injection of solutions containing macromolecular materials and cross-linking agents. In this case it is firmly thought that the main element of the *in-situ* gelation is the hydrodynamic dispersion leading to direct chemical reactions and that process is aided only by sorption, mechanical entrapment and precipitation of chemicals or partially gelled domains. Supposing the chemical reactions to be very fast in the system the shut-off time of treated wells is not considered so far as important factor influencing the efficiency of gelation mechanism. Probably, that fact may explain the discouraging statistical data showing less than 50 % success rate all over the world.

The preliminary laboratory studies definitively proved that first a relatively thin gel layer forms at the interface of the sequentially injected solutions and then its thickening is controlled exclusively by the diffusion of cross-linking agents through this semi-permeable diaphragm. In this context the shut-off (relaxation) time applied is fundamental and becomes a crucial factor shaping the blocking efficiency. Recognizing these facts the objectives of the present study were as follows

- detailed analysis of the cumulative ion transport in gels having different geometry,
- determination of the diffusion coefficient, break-through time and ion retention in gels as a function of gel composition and
- determination of temperature dependency and the chemical driving force of the diffusion phenomena.

Finally, the experimental results will be evaluated with respect to the shut-off time and optimization of the surface technology.

EXPERIMENTAL

The diffusion transport was studied in a complex gel containing hydrolyzed polyacrylamide and sodium silicate. The polymer was cross-linked by Al^{3+} , while the silicate was gelled using Ca^{2+} ions and pH regulation, respectively. Earlier that gel system was successfully used for near well-bore treatment of oil producing wells in Hungary and for rehabilitation of damaged gas wells in Germany [1-3]. The silicon dioxide content of the gel varied between 0 and 75 g/l, while the polymer was present in concentration range of 0-2.5 g/l. The polymers were high molecular weight, partially hydrolyzed polyacrylamides.

The laboratory measurements were carried out in a conventional dual cell ap-

paratus placing the gel into the connecting glass tube. The size of gel membrane was the following:

diameter:	30 mm
thickness:	20 mm

The gel diaphragm was fixed in the glass joint by O-rings. One of the cells contained the solution of multivalent cations, while the other cell was filled up with the same amount of distilled water. The model measurements were performed by chromium ions added mostly as chromium(III) chloride and chromium(VI) dichromate in 100 mM/l concentration. A special hydrostatic by-pass was connected to both vessels in order to minimise the convective mass transport. The diffusion transport was calculated by the ion concentrations taking 1 ml sample simultaneously from both cells. The cation concentration of samples was determined by flame AAS method.

A software developed for calculation of the total mass balance made possible to determine the diffusion coefficient, break-through time and specific ion retention in gels. Since GHERKE and CUSSLER [4] have definitely pointed out that the migration of solutes in swollen hydrogels follow the *Fick's laws*, that relationships were applied for evaluation of the experimental results. The break-through time was obtained a linear extrapolation of the upward section of the Σn vs. *time* curves, while the specific retention was calculated by the difference in the break-through times found for adsorbing (Cr^{3+}) and non-adsorbing (Cr^{6+}) species, respectively.

RESULTS AND DISCUSSION

1. Cumulative mass transport of ions

The general features of ion diffusion in gels are illustrated in Fig. 1. Depending on the ionic form and the valency, the cumu-

lative mass transport through the gel diaphragm can be characterized by

- different slopes,
- different break-through times and
- linearly increasing tendency

as a function of time. According to *Fick's* first law, the slope is directly proportional to the diffusion coefficient the higher the slope, the greater the diffusion constant. After break-through of ions the proportionality found for Σn vs. *time* relationships seems to be logical on account of the negligible change in the concentration gradient. In this respect the application of a sensitive analytical indication technique (AAS method) proved to be an excellent idea. The break-through times and the diffusion coefficients obtained for chromate and chromium ions (Fig. 2.) apparently reflect the fact that the anion with higher diffusivity penetrates faster into the gel phase than the cation having lower diffusion coefficient does. The data listed in Table 1. can be well correlated with the hydrated ionic radii, which actually determine the ion mobility in aqueous media.

Fig. 1. Cumulative mass transport of Cr⁶⁺ and Cr³⁺ ions in polymer/silicate gels

Comparing the diffusion coefficients with values reported in literature [5], it is

obvious that the chromium ions tested in this programme show lower diffusivity in

Table 1
Diffusion characteristics of Cr⁶⁺ and Cr³⁺ ions
in polymer/silicate gels

Parameter	CrO ₄ ²⁻ (K ₂ CrO ₄)	Cr ³⁺ (CrCl ₃)
Diffusion coefficient, m ² s ⁻¹	1.1.10 ⁻⁹	0.58.10 ⁻⁹
Break-through time, h	12.3	60.8
Ionic radius, nm	0.4	0.9
Specific retention, M m ⁻³	0	29.0

gels than in aqueous bulk phase. The diffusion coefficients differ by about one order of magnitude. Consequently, the gel barrier formed between the sequentially injected treating solutions restricts fundamentally not only the convective mass flow (hydrodynamic dispersion) in porous media, but it has also a measurable impact on the chemical mass transport of cross-linking ions.

A difference in diffusion parameters obtained for chromate and chromium ions was expected, but it can hardly be explained exclusively by the ionic radii. E.g. the relative change of break-through times is not proportional to the change of diffusion coefficients. In this case it must be supposed that the chemical mass transport is jointly determined by the diffusion and the adsorption of species tested. Converging conclusions were drawn by JAHNKE and RADKE [6], who stated that these processes are not only coinciding in highly adsorbing and swelling gels, but the surface diffusion may primarily control the migration of cations in such media.

The interaction of silicate surfaces with different metal ions was investigated in the past three decades by many authors. Summarising their results ILER [7] and FALCONE [8] pointed out that the silicate surfaces adsorb irreversibly a great variety of ions, but the bonding forces are still

poorly understood. Probably the following processes are involved in ion sorption:

- enhanced hydrolysis of multivalent cations by surface hydroxyl groups,
- physical adsorption of cations by *van der Waals* forces and
- electrostatic attraction of positively charged cations.

In addition, the slightly alkaline media is favourable for *in-situ* formation of metal hydroxides, which often precipitate in gels decreasing further its permeability. That reaction is terminated when the free alkalis are entirely consumed by cations prone to form insoluble hydroxides.

The presence of anionic polyelectrolyte in gel adds further factors to complexity of phenomena. The ionic polymers are known as excellent complex-forming compounds with multivalent cations [9]. The *in-situ* cross-linking profile correction technique is just based on the irreversible ionic bonding between the chain-like macromolecular materials and the multivalent cations. As proved indirectly by the matrix effects of polymers in flame AAS, the interaction of polymers with certain cations is almost stoichiometric, viz. the sorption capacity of polymers is proportional to the degree of hydrolysis [10]. Since the cross-linking solution at the present time contains Al^{3+} ions in concentration sufficient only for partial saturation of carboxyl groups of polyacrylamides, this component of the gel might also be considered as an active cation sorber in the blocking phase.

According to the experimental finding the diffusing solutes can be subdivided into two basic groups: sorbing and non-sorbing species. The chromate, dichromate and perhaps lithium belong to the first group. Probably, we may generalize their properties so that the non-adsorbing species are usually anions and those cat-

ions which do not form insoluble hydroxides in neutral and alkaline media. The break-through time found for such ions is close to each other and is determined only by the diffusion coefficient or the ionic radius (Fig. 2).

Fig. 2. Cumulative mass transport of Cr^{6+} and Li^+ ions in polymer/silicate gels

The Cr^{3+} ion being prone to form insoluble hydroxide ranks among the highly adsorbing cations. In this case the break-through time is nearly five times longer than the value obtained for non-sorbing species, while the diffusion coefficient is only slightly decreasing on account of the existing difference in the ionic radii. As shown in Fig. 1, both the break-through time and the diffusion coefficient depends on the type of anions attached to the cation, but this electrokinetic effect is negligible compared to the behaviour of non-adsorbing species. Other multivalent cations, like Ni^{2+} , Co^{2+} , Fe^{3+} , Mn^{2+} , etc. behave similarly as Cr^{3+} cation and their diffusion coefficient, break-through time and specific retention is in range obtained for Cr^{3+} compounds. The experimental observations imply that any ionic cross-linker should be used in higher valency form (e.g. Cr^{6+} instead of Cr^{3+}) because its mass transport is much greater in gels and as a result shorter shut-off time might be used in field operation.

2. Effect of gel geometry

The diffusion studies were extended to the effect of the size of gel diaphragm. The experimental results obtained for the diffusion coefficient, break-through time and specific ion retention are shown in Figs 3-5. As expected the diffusion coefficient is practically independent of gel thickness (Fig. 3). However, the effective volume of gel is increasing with the thickness. Accordingly, the increasing amount of sorbing media should result in a proportional increase in both the break-through time and the specific cation retention. As proved by data in Figs 4. and 5. nearly linear relationship exists between the break-through time and specific retention and the thickness of gel phase.

Fig. 3. Dependence of the diffusion coefficient on thickness of gel (Cr^{3+})

That experimental finding firmly proves that propagation of the gelling (cross-linking) reaction drastically slows down as the thickness of gel phase at the contact interface of solutions is increasing. As a result, the total blocking in porous media needs much more time than expected by the reaction rate, viz. the process becomes basically diffusion controlled on account of the lower diffusion coefficient in gel and the gradually reducing chemical driving force (concentration gradient).

Fig. 4. Dependence of the break-through time on thickness of gel (Cr^{3+})

Fig. 5. Dependence of the specific ion retention on thickness of gel (Cr^{3+})

3. Effect of SiO_2 content of gel on ion diffusion

An important objective of the present studies was the analysis of the impact of chemicals on diffusion phenomena and hence, on the setting time of gel. As a first step the effect of silicium dioxide content of the gel on diffusion characteristics will be demonstrated. It is interesting, but not surprising that the silicate content influences similarly the diffusion characteristics as the thickness of diaphragm does. The only exception is that with increasing SiO_2 content the diffusion coefficient slightly decreases in concentration range tested

(Fig. 6). Within and acceptable standard deviation both the break-through time and the specific retention seems to be linearly depending on SiO_2 content (Figs 7. and 8.). The latter results unambiguously suggest that the silicate takes a prominent part in cation retention if the polymer content is constant in the system.

Fig. 6. Dependence of the diffusion coefficient on SiO_2 content of gel (Cr^{3+})

Fig. 7. Dependence of the break-through time on SiO_2 content of gel (Cr^{3+})

4. Effect of polymer content of gel on ion diffusion

Apparently, the effect of polymer on diffusion coefficient is very close to that caused by the SiO_2 concentration. The diffusion coefficient practically decreases linearly with the polymer concentration as shown in Fig. 9. This fact can easily be ex-

Fig. 8. Dependence of the specific ion retention on SiO_2 content of gel (Cr^{3+})

plained by increased solid content of the gel and modification of the tortuosity. Here, it should be mentioned that the polymer/silicate gels up to 10 bar/m pressure gradient (mechanical stability, gel strength) behaves like a porous media. Namely, the forced convective liquid transport in gel can satisfactorily be described by the Darcy formula [11]. Hence, it is an obvious hypothesis that the extremely low permeability ($< 0.1 \text{ mD}$) may be traced back jointly to the high capillary forces and the tortuosity.

Fig. 9. Dependence of the diffusion coefficient on polymer content of gel (Cr^{3+})

A surprising observation is, however, that the break-through time and the specific ion retention alike show slightly decreasing tendency with the polymer con-

centration (Figs 10. and 11.). Though an opposite tendency was expected by the well known interaction of ionized polymers and multivalent cations, this experimental finding suggest an existence of competitive and simultaneous physico chemical processes. Probably, the negative tendencies in the break-through time and the specific ion retention can be attributed to favoured polymer adsorption on silica surface. Since the adsorption of macromolecules needs large area per molecule, the ion adsorption capacity of gel significantly reduces in presence of polymers. Thus, the ruling factor in polymer/silicate gels is the coverage of silicates or its free surface available for multivalent cations.

Fig. 10. Dependence of the break-through time on polymer content of gel (Cr^{3+})

The effect of gel composition on diffusion ion transport can be summarized so that changing the structure and the sorption/retention capacity of gel the *in-situ* setting time might be controlled within wide limits. Accordingly, the shut-off time applied in well treatment technology is not invariant for the type of chemicals and the composition of the sequentially injected solutions.

5. Effect of temperature on ion diffusion

Theoretically, the diffusion coefficient depends exponentially on temperature

Fig. 11. Dependence of the break-through time on polymer content of gel (Cr^{3+})

and the *Arrhenius* equation correctly describes the relationship. The validity of the Arrhenius equation in special cases can be proved by logarithmic presentation, which may also serve for determination of the activation energy. Advantage of that treatment is that the activation energy of diffusion directly characterizes the driving force of gelation in diffusion controlled process. Thus, the actual values might be used for differentiation of multivalent cations or selection of the most appropriate cross-linking agent.

The experimental results shown in Figs 12. and 13. meet the expectations and the activation energies calculated by the slope of the lines in Fig. 13. are as follows:

$$\begin{aligned}\text{Cr}^{3+} &= -32 \text{ kJ/mol K} \\ \text{Cr}^{6+} &= -44 \text{ kJ/mol K}\end{aligned}$$

The practical message of these data is that the chemical driving force of gelation is much greater for chromate or bichromate ion than for chromium ion. Consequently, shorter shut-off time is required if the former ones are used as cross-linkers even though special reducing agents must be added in this case to the polymer or polymer/silicate solutions.

Fig. 12. Dependence of the diffusion coefficient on temperature

Fig. 13. Dependence of the logarithmic diffusion coefficient on reciprocal temperature

Further, it is surprising that the break-through times illustrated for both ions in Fig. 14. show different characteristics. On the one hand, the break-through time for non-adsorbing chromate ions seems to be slightly dependent on temperature and its fast migration in gel is characteristic through the whole temperature range. On the other hand, the break-through time found for chromium ions drops steeply at low temperature, but finally it approaches the values obtained for the chromate ions. That phenomena is explained by the fact that not only the diffusion rate increases with the temperature, but simultaneously and favourably the ion adsorption capacity of gel also radically decreases at elevated temperatures. Since the specific ion reten-

tion is proportional to the area between the curves, the amount of chromium ions retained by the gel also diminishes with the temperature (Fig. 15.).

Fig. 14. Dependence of the break-through time on temperature

Fig. 15. Dependence of the specific ion retention on temperature

CONCLUSIONS

The experimental results obtained by a detailed analysis of ion diffusion in polymer/silicate gels can be summarized as follows:

1. The diffusion coefficients calculated for multivalent cations in gels are smaller by an order of magnitude than the values characteristic for inorganic electrolytes in aqueous bulk phase.

2. The diffusion coefficient is inversely proportional to the silicate and the polymer content of gels, but it sharply increases with the temperature.

3. The diffusing solutes can be subdivided into two groups: adsorbing and non-adsorbing species. The anions containing metals and the monovalent cations are practically not retained by the polymer/silicate gel. The activation energy of diffusion calculated for adsorbing and non-adsorbing ions is roughly -32 and -44 kJ/mol K, respectively;

4. The polymer/silicate gels have high retention capacity for multivalent cations. Retention of multivalent cations can be explained mainly by ion adsorption. The ion retention increases with the silicate content, but it decreases with the polymer concentration and the temperature.

5. The break-through time linearly depends on the silicate content and the thickness of gel. Reciprocal relationship was found, however, for the polymer content and the temperature.

Concerning the profile correction techniques based on sequential injection of treating fluids the following conclusions could be drawn:

1. The *in-situ* gelation of macromolecular materials is a diffusion controlled process, therefore the shut-off time must be determined accordingly.

2. The shut-off time can be minimized by using such cross-linking agents which do not adsorb in gels and have the highest chemical driving force in the mass transport system.

3. The chemical composition of gels significantly influences the diffusion mass transport. Consequently, the shut-off time can be reduced by changing the gel composition in favour of the non-adsorbent type components.

On the basis of the experimental findings it seems necessary to re-evaluate the

chemical design of surface technology. The converging facts clearly support that the shut-off time must be extended to weeks or even months if we want to avoid the risk of insufficient gelation.

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