

The containment of oil spills in porous media using xanthan/aluminum solutions, gelled by gaseous CO₂ or by AlCl₃ solutions

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Abstract

The gelation in situ of polymers may be a method for temporarily containing organic solvents and other petroleum derived products, which may enter the subsurface. In order to create gels that are neither toxic to humans nor to the ecosystem, we have investigated on the use of the biopolymer xanthan gum with aluminum as a crosslinking agent. Firstly we have considered xanthan/sodium aluminate solutions, which upon preparation are strongly basic and do not gel. The gelation takes place in acid solutions so that Al(III) ions are released, and is instantaneous. Therefore, a special technique must be used for generating the gel structure in situ. The un-gelled solution must be injected and an acid must be added afterwards. We have investigated on the gelling reaction induced by gaseous carbon dioxide, which is an acid gas. The insufflation of CO₂ above the solution generates a layer of gel whose thickness progressively increases as CO₂ diffuses in the polymer solution. Secondly we have investigated on the use of aluminum chloride as the source of Al(III) ions. Also in this case, due to the full availability of Al(III) ions, the gelling reaction would be instantaneous. Therefore, the solution of AlCl₃ must be added on the top of the xanthan solution after its injection. For both gelling systems we have studied both theoretically and experimentally the rate of formation of the gel layer which progressively thickens after the insufflation of CO₂ or after the addition of the AlCl₃ solution.

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1. Introduction

The in situ crosslinking of a water-soluble polymer is an effective technique for reducing the permeability of porous media. When a polymer solution is injected together with a crosslinking agent in a porous medium it reacts with the crosslinker to form a three-dimensional gel network, which reduces the effective permeability of the medium and plugs fractures. The permeability may be reduced by several orders of magnitude. The gelled polymer technology is traditionally applied for the secondary treatment of oil producing reservoirs. It, however, may be applied as well, in connection with underground-water pollution, for the temporary containment of organic solvents and other petroleum-derived products which may enter the subsurface, whilst the remediation procedure is planned and accomplished.

In a previous paper [1] we have investigated on the gelling property of xanthan gum: a biopolymer (polysaccharide) which is neither toxic to humans nor to the ecosystem. In fact it is used in foods, non-foods, and cosmetics as a stabilizer and emulsifying agent. Xanthan gels have long lasting capabilities of maintaining their property to reduce porosity of porous media. Xanthan gum dissolves readily in water with stirring and gels with metal ions; among them Cr(III) [1–3]. There are circumstances, however, under which chromium cannot be considered for subsurface injection where the possibility exists for migration into fresh-water aquifers. In such instance non-toxic crosslinking agents should be considered. In the paper [1] we have focused the attention on aluminum which is a relatively safe and a naturally occurring element in soils. In particular as a source of Al ions we used sodium aluminate which added to the Xn solution, due to hydrolysis reaction, imparts a basic value to pH. In alkaline solutions, however, there is a deficiency of Al ions so that the crosslinking does not take place. For this system the gelation reaction may occur at low pH (acid must be added to the xanthan/sodium aluminate solution), but it is very rapid indeed. This

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Nomenclature

c	aluminum chloride concentration (mol/cm ³)
c^0	initial concentration of AlCl ₃ in the solution (mol/cm ³)
c_T	total molar concentration in the liquid phase; $c_T \approx 55.6$ (mol/l)
D	diffusivity of carbon atom in the gel (cm ² /s)
D_{CO_2}	diffusivity of CO ₂ in water at $T = 25$ °C (cm ² /s)
D_S	diffusivity of AlCl ₃ in the gel at any time t (cm ² /s)
D_S°	diffusivity of AlCl ₃ in Xn solution (cm ² /s)
G'	shear storage modulus G' (Pa)
H_{CO_2}	Henry's constant (atm)
L	height of AlCl ₃ solution in the vial (see Fig. 6) (cm)
M	molecular weight of AlCl ₃ (g/mol)
pH_i	calculated value of pH at the interface upon addition of CO ₂
pH_0	initial pH of the xanthan/aluminate solution
P	pressure (atm)
t	time (s)
t^*	time at which the gel boundary stops (s)
Xn	xanthan gum concentration in aqueous solution (ppm)
y_{CO_2}	mole fraction of CO ₂ in the gas phase (=1 in our experiments)

Greek symbols

α	adjustable parameter for diffusivity, see Eq. (8)
β	AlCl ₃ /Xn pseudo stoichiometric coefficient (g of AlCl ₃ consumed per g of xanthan gelled)
γ	see Eq. (13)
λ	position of the gel/solution boundary (cm)
ρ	density of Xn solution (g/cm ³)
[·]	square brackets indicate concentrations (mol/l)

Subscript

i	at interface
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last feature would render impossible to inject the mixture “xanthan/sodium aluminate/acid” in the subsurface. We have proved that for making use of this gelling system the acid must be added after the injection with a procedure which has been set up in our laboratory and is described in paper [1]. In the investigation [1] the acid was a dilute solution of HCl. However, even though theoretically the acid is fixed in the gel structure, the possibility that undesired leaks could reach the aquifer is real. Therefore, in order to overcome this inconvenience we have studied, in the present paper, a gelling procedure which makes use of carbon dioxide as the acid which induces the crosslinking reaction. Namely, the mixture xanthan/sodium aluminate in its un-gelled state is injected below the spill to be contained. Then gaseous CO₂ is insufflated above the solution and diffuses through it, creating a layer of gel whose thickness increases with the diffusion time.

Furthermore, we have investigated on the gelling behaviour of the system xanthan/AlCl₃. Aluminum chloride, upon dissolving in water, may be considered completely dissociated so that there is a full availability of Al(III) ions which induces an instantaneous gelling reaction. Therefore, in order to make use of this gelling system, the aluminum chloride solution must be added after the xanthan solution has been injected. Then also in this case the AlCl₃ slowly diffuses in the Xn solution creating a layer of gel, whose thickness increases with the diffusion time. However, the experiments have shown that as the diffusion and the crosslinking reaction proceed the gel becomes so strong that the diffusion of AlCl₃ practically stops and the thickness of the gel does not increase anymore.

The rate of gel formation for both systems is theoretically and experimentally investigated.

2. Ionic equilibria in aluminate aqueous solutions

As discussed by Stumm and Morgan [4], when an aluminum salt is dissolved in water, the aluminum species present in the solution, starting from a pH above 9.6, gradually shift, as the pH is lowered, as follows: $[Al(OH)_4]^- \rightarrow Al(OH)_3 \rightarrow [Al(OH)_2]^+ \rightarrow [Al(OH)]^{2+} \rightarrow Al^{3+}$.

Using the equilibrium constants reported in [4] we have drawn the distribution diagram (Fig. 1) of the above ionic species (expressed as mol/l) as functions of pH in an aqueous solution at 25 °C. This graph provides an overall picture of the equilibria involved. Because we have ascertained that a considerable gel formation takes place at $pH < 4$, we deduce by inspection of Fig. 1 that the most active ionic species in forming the gel is Al^{3+} .

The crosslinking activity increases as the pH is lowered. For xanthan polymer we have found that the crosslinking activity is practically nil at pH larger than 9.6.

With reference to the sodium aluminate, which is the salt used in our experiments (see Section 3.1), it must be remarked that upon dissolving the equilibrium state, depicted in Fig. 1,

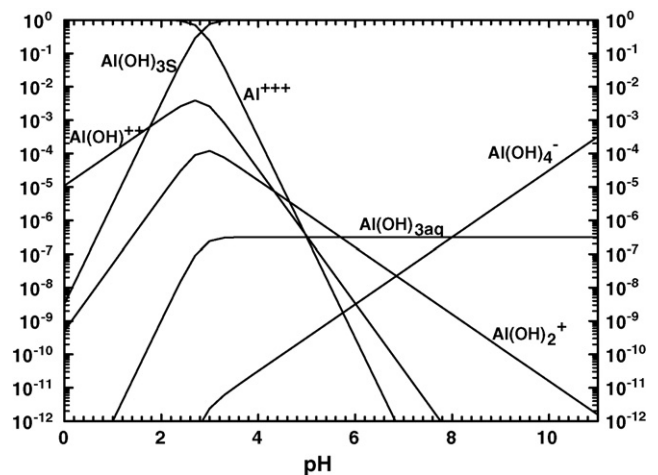


Fig. 1. Equilibrium distribution diagram of Al species in water: fraction of $Al(OH)_3(s)$ present as different ionic and dissolved species as a function of pH.

is not reached instantaneously. In fact even preparing a solution of aluminate 4000 ppm (as Al(III)), which is several orders of magnitude more concentrated than that permissible according to Fig. 1, the solution when prepared appears clear with no precipitate in it, indicating that all the aluminate is in a metastable dissolved state. As reported by Mellor [5], sodium aluminate solutions undergo a fairly rapid hydrolysis although no precipitation occurs in 96 h. The first product of the hydrolysis is alumina hydrosol, which then changes into the gel form, and then changes to crystalline aluminum hydroxide. Namely, whatever its chemical form is, it remains in the solution for long time in a metastable state. In order to investigate the kinetics for reaching the equilibrium state, we have prepared three solutions (300, 600, and 4000 ppm) as Al(III) and have analysed them by ICP (Perkin-Elmer, spectrometer model: Optima 2110, with autosampler model: AS-93plus) for the dissolved aluminum at increasing times. Right before the analysis the solutions were filtered and the pH measured. The measured concentration of Al as a dissolved species versus the time elapsed since the preparation of the solutions indeed confirms the indication of Mellor [5]. The first precipitate in the test solutions does not appear before 96 h.

It is reported however by Pascal [6] that sodium aluminate is decomposed by carbonic acid with precipitation of hydrated sodium oxide. In fact, bubbling CO_2 in the 4000 ppm solution produces the immediate formation of a white sediment. Upon filtration the solution shows a pH 10.33 and a total concentration of Al dissolved species (as measured by means of a photometer DrLange LASA 20) equal to $1.97 \text{ mg/l} = 7.3 \times 10^{-5} \text{ mol/l}$. This value agrees with that predicted by the distribution diagram in Fig. 1. The predominant ionic species present being $[\text{Al}(\text{OH})_4]^-$.

3. Runs $\text{Xn}/\text{NaAlO}_2/\text{CO}_2$

3.1. Materials and experimental procedure

The xanthan gum biopolymer was supplied as a powder by Sigma–Aldrich (Lot 07207CO-073). The sodium aluminate, anhydrous, was produced by Riedel-deHaën and supplied by Sigma–Aldrich. The label indicates a composition as: Al (as Al_2O_3) 50–56%; Na (as Na_2O) 40–45%; Fe (as Fe_2O_3) max 0.05%, which mainly corresponds, according to Pascal [6], to the aluminate: $4\text{Na}_2\text{O} \cdot 3\text{Al}_2\text{O}_3$.

Stock solutions of sodium aluminate (2000 ppm as Al(III)), and of xanthan polymer (8000 ppm) in distilled water were prepared. A quantity of xanthan stock solution, for a final desired concentration in a given volume, was coloured with trace amount of the pH indicator “Bromocresol Purple”, which switches from yellow to blue-violet in the pH range 5.2–6.8. Then the amount of sodium aluminate stock solution for the desired final concentration was added to the xanthan solution. Finally the mixture was brought to the final volume by the addition of distilled water. Before starting the run, the initial pH of the solution (pH_0) was measured (pH meter Orion model 420A). The corresponding $[\text{OH}^-]_0$ was about equal to $[\text{Na}^+]_0$ indicating that the alkalinity was essentially due to the hydrolysis of the sodium aluminate. At

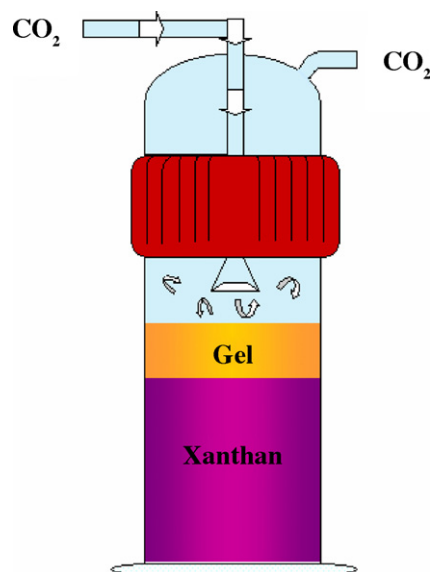


Fig. 2. Test cylinder for the runs $\text{Xn}/\text{NaAlO}_2/\text{CO}_2$. Three cylinders were arranged in series for obtaining three replicates of each run.

the initial basic value of pH the solution shows an intense blue-violet colour. No gelling reaction takes place at the high pH of the solution. The mixture was then poured in three glass cylinders 3.8 cm i.d. (in which the gelling process takes place), to fill about two-thirds of their volume. The inlet/outlet ports for the CO_2 gas are assembled on the glass stopper as shown in Fig. 2. The three cylinders were connected in series for obtaining three replicates of each run. A gas humidifier was connected to the first cylinder and a bubbler (for controlling the CO_2 flow) to the outlet of the last cylinder. Then a flow of carbon dioxide was started. This is the time zero of the experiment. Upon the addition of CO_2 , a layer of gel forms at the polymer/gas interface. Namely the lowering of the pH causes the formation of Al cations which induce the gelling reaction. The gel is distinguishable as it shows up with yellow colour, which contrasts with the blue-violet of the un-gelled polymer. Afterwards the CO_2 diffuses through the gel layer towards the un-gelled solution and the thickness of the gel progressively increases. It must be pointed out that in the presence of CO_2 the formation of hydrated sodium oxide precipitate is observable in the gel. The position $\lambda(t)$ of the moving boundary where the pH indicator changes colour (i.e. $\text{pH} \approx 6.8$) was recorded versus time. The operating conditions of the experimental runs are reported in Table 1. The diagrams of $\lambda(t)$ versus

Table 1
Runs $\text{Xn}/\text{NaAlO}_2/\text{CO}_2$

Run no.	Xanthan (ppm)	Al(III) (ppm)	pH_0	pH_i^a	α
1	3000	50	10.18	4.14	0.30
2	3000	100	10.57	4.40	0.20
3	3000	300	11.06	4.86	0.40
4	6000	50	10.76	4.57	0.36
5	6000	100	11.03	4.83	0.35
6	6000	300	11.10	4.90	0.48
7	6000	600	11.19	4.99	0.24
8	6000	900	11.46	5.28	0.17

^a pH_i is a calculated value.

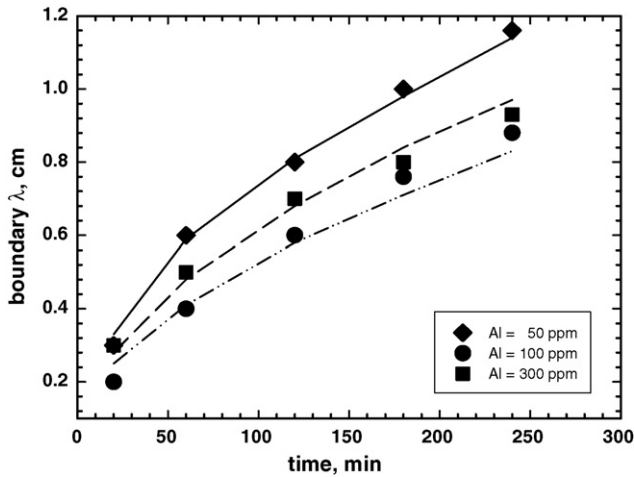


Fig. 3. Gel thickness vs. time for Xn/NaAlO₂/CO₂ for Xn = 3000 ppm and three different NaAlO₂ concentrations, expressed as Al(III).

t are reported in Figs. 3 and 4, the curves are the model equation to be discussed below. The gel strength was characterized by measuring the shear storage modulus *G'* and the viscosity by means of an oscillatory controlled stress rheometer (SR-200 Rheometric Scientific Inc.; parallel plate 25 mm; 1 mm gap). *G'* is a measure of the solid like behaviour of a gel. The diagrams obtained from the instrument for the CO₂ runs showed a *G'* value in the range: 10 < *G'* < 20 Pa at a frequency in the range 10⁻² to 10 rad/s. Namely the strength of the gel is somewhat weak. The gel strength is poorer than that obtainable with HCl [1] or with AlCl₃ (to be discussed in Section 4). The gel, however, is strong enough to reduce the effective permeability of a porous medium for containing pollutants in the soil.

3.2. Interpretation of experimental results

The CO₂ concentration in the liquid phase at the interface, in equilibrium with the gaseous phase is given by the Henry's

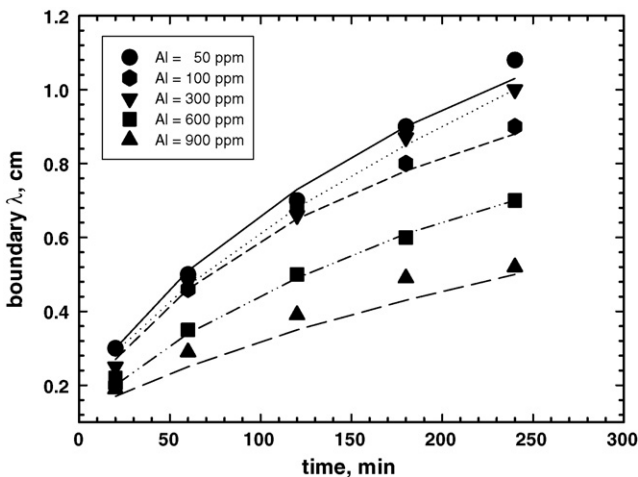


Fig. 4. Gel thickness vs. time for Xn/NaAlO₂/CO₂ for Xn = 6000 ppm and five different NaAlO₂ concentrations, expressed as Al(III).

equation, i.e.:

$$[\text{CO}_2]_0 = \frac{P_{\text{yCO}_2} c_{\text{T}}}{H_{\text{CO}_2}} \quad (1)$$

The liquid phase is alkaline because of the presence of sodium hydroxide, due to the hydrolysis of NaAlO₂. Therefore, at the interface, upon absorption, CO₂ undergoes ionic reactions leading to the formation of CO₃²⁻ and HCO₃⁻. The equilibrium concentrations of the ionic species at the interface are calculated by means of the equilibrium equation (2) and (3):

$$\frac{[\text{HCO}_3^-]_i}{[\text{CO}_2]_i [\text{OH}^-]_i} = K_1 = 4.5 \times 10^7 \text{ mol/l} \quad (2)$$

$$\frac{[\text{HCO}_3^-]_i [\text{OH}^-]_i}{[\text{CO}_3^{2-}]_i} = K_2 = 2.38 \times 10^{-4} \text{ mol/l} \quad (3)$$

coupled with the charge balance and the mass balance on carbon atom, Eqs. (4) and (5) respectively:

$$2[\text{CO}_3^{2-}]_i + [\text{HCO}_3^-]_i + [\text{OH}^-]_i = [\text{OH}^-]_0 \quad (4)$$

$$[\text{CO}_3^{2-}]_i + [\text{HCO}_3^-]_i + [\text{CO}_2]_i = [\text{CO}_2]_0 \quad (5)$$

[OH⁻]₀ is the hydroxyl ion concentration corresponding to the measured pH₀. It is [OH⁻]₀ ≈ [Na⁺]₀ which is the initial concentration of sodium ions considering the NaAlO₂ loaded in the xanthan solution. Al ions are not considered in Eq. (4) as we assume they are linked to xanthan molecules to form the gel. The solution of the above equations permits calculation of the pH ≡ pH_i of the solution at the interface at *t* = 0.

3.3. Transient diffusion in the gel

Let us assume that the diffusivities of CO₂, HCO₃⁻ and CO₃²⁻ are about the same, then we can consider the diffusion of the three species altogether, i.e. we consider the diffusion of the carbon atom. Say *C* = [CO₂] + [HCO₃⁻] + [CO₃²⁻]; at any *z* position and at any time *t* the transient diffusion of carbon atom in the layer of xanthan solution is described by Eq. (6):

$$C(t, z) = C_i \text{erfc} \left(\frac{z}{\sqrt{4Dt}} \right) \quad (6)$$

As the acid gas CO₂ advances in the solution, the pH decreases. The pH of the solution at any *t* and *z* may be calculated by means of the set of equations:

$$[\text{CO}_2] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}] = C(t, z) \quad (7)$$

coupled with the charge balance (4) and the ionic equilibrium equations (2) and (3). *D* in Eq. (6) is the diffusivity in the gel. Missing any information on its value, we set:

$$D = \alpha D_{\text{CO}_2} \quad (8)$$

where *D*_{CO₂} is the diffusivity of CO₂ in water and α is an adjustable parameter to be determined fitting the experimental data.

Following this procedure, we have built diagrams of the increase of pH along *z* versus time for the runs of Table 1. As an example we report in Fig. 5 the diagrams regarding run 1.

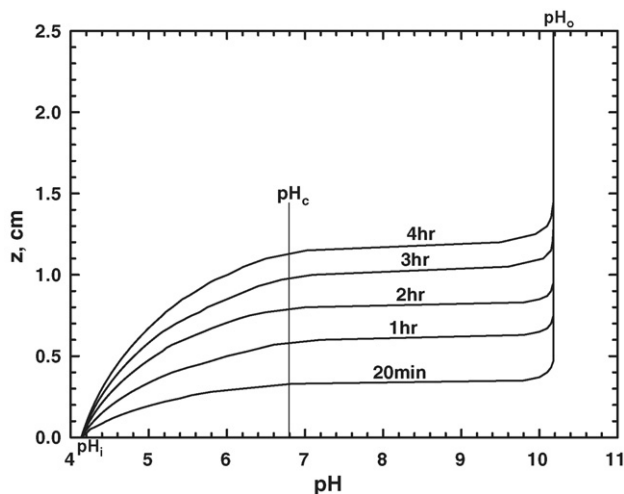


Fig. 5. Advancement of gel thickness vs. pH. Xn = 3000 ppm; Al = 50 ppm (as Al(III)). The moving boundary position is at pH 6.8.

As described in Section 3.1 we have measured the advancement versus time of the boundary where the pH indicator “Bromocresol Purple” switches from blue-violet to yellow at pH 6.8. This value of pH is indicated in Fig. 5 with the symbol pH_c . Therefore, for all runs we have calculated the position λ of the boundary (at pH_c) versus t , obtaining the model curves drawn in Figs. 3 and 4. The fitting procedure of the theoretical curves to the experimental data let us determine the best value of the adjustable parameter α (reported in Table 1). It must be noted that due to the smooth change of pH, also the gel strength changes smoothly around pH_c .

4. Runs Xn/AlCl₃

4.1. Materials and experimental procedure

AlCl₃·6H₂O was supplied by Aldrich. Upon dissolution in water the aluminum chloride being a salt, can be considered completely dissociated, i.e.:



The solution, due to the hydrolysis reactions is acid pH = 3.74 at 300 ppm Al(III). Therefore, according to the diagrams of Fig. 1, there is a full availability of Al(III) ions and there is the maximum crosslinking activity.

In the presence of a significant concentration of Al³⁺ the gelation takes place in a very short time. Therefore, the mixture polymer/AlCl₃ does not have appropriate properties for in-depth injection in porous media. In fact the gel system can only be injected through a porous medium for a time period of usually less than about one-fourth of the gel time before a significant increase in the flow resistance is observed. Therefore, in order to overcome this last inconvenience we have devised a different technique for generating the gel structure in the porous structure when this gel system is adopted. Namely, for the purpose of using this gel system for the containment of an oil spill, the aluminum chloride solution must be added after the Xn solution has been injected underneath the oil spill. The experiments were

performed as follows: The xanthan solution coloured with few drops of a pH indicator (Bromocresol green which changes from yellow to blue at pH values in the range 3.8–5.4) was poured in a glass cylinder to fill about two-thirds of its volume, and a given quantity of AlCl₃ solution was added on the top of the xanthan solution. This is the time zero of the experiment. Upon the addition of the aluminum chloride, a layer of gel instantly forms at the interface polymer/AlCl₃, which blocks any mixing of the two solutions. Namely the presence of Al³⁺ cations induce an instantaneous gelling reaction. The gel is perfectly distinguishable as it shows with a yellow colour, which contrasts with the blue of the un-gelled polymer. Afterwards the AlCl₃ diffuses through the gel layer towards the un-gelled solution and the thickness of the gel progressively increases. Namely the system evolves as a moving boundary process as sketched in Fig. 6. The position of the boundary and the concentration of the AlCl₃ (as Al(III)), measured by means of a Cl⁻ electrode in the solution above the gel, were recorded versus time. The frequent measurement of Cl⁻ helped in destroying possible concentration gradients in the AlCl₃ solution. At least three replicates for each run were carried out. The materials and the operating conditions of the experimental runs are reported in Table 2. The experimental data points $\lambda(t)$ versus time, for the runs of Table 2, are reported in Fig. 7. The fitting curves are the model equation to be developed below.

4.2. Interpretation of experimental results

The experiment is mathematically described by the two following differential equations:

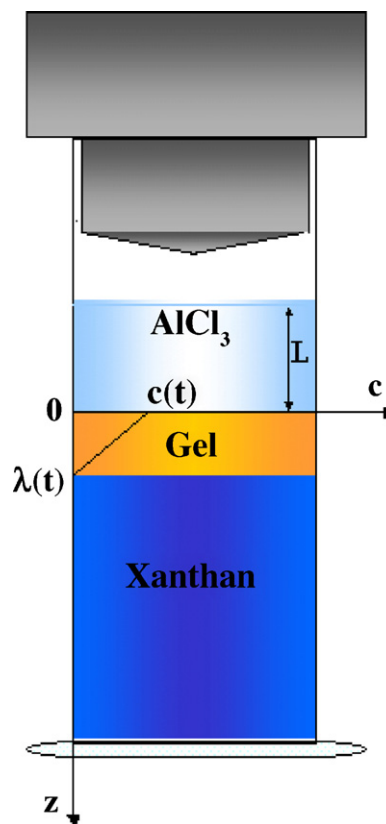


Fig. 6. Sketch of gel formation as a moving boundary process.

Table 2
Runs Xn/AlCl₃; Xn = 8000 ppm

Run no.	Al(III) (ppm)	c^0 (mol/cm ³)	c^* (mol/cm ³)	t^* (h)	λ^* (cm)	β (Eq. (17))	β (Exp. I)
1	25	9.32×10^{-7}	6.30×10^{-7}	10	0.6	0.017	0.013
2	50	1.86×10^{-6}	1.29×10^{-6}	10	0.7	0.027	0.019
3	100	3.73×10^{-6}	2.52×10^{-6}	10	1.0	0.040	0.020
4	300	1.11×10^{-5}	7.19×10^{-6}	10	1.2	0.109	0.043

(1) Transient diffusion of AlCl₃ through the gel. Assuming pseudo-steady-state condition the rate of advancement of the gel layer λ is

$$\frac{d\lambda}{dt} = \frac{MD_S}{10^{-6} X_n \rho \beta} \frac{c(t)}{\lambda} \quad (10)$$

β is a pseudo-stoichiometric coefficient, i.e. g of AlCl₃ consumed per g of Xn gelled.

(2) Transient mass balance of AlCl₃ on the volume of solution contained in the vial on the top of the gel. Given the low concentration of AlCl₃, we assume the volume of the salt solution on the top of the Xn solution to remain constant:

$$\frac{dc}{dt} = -\frac{D_S}{L\lambda(t)} c \quad (11)$$

The initial conditions are: $t=0, c=c^0, \lambda=0$.

The meaning of the symbols is reported in Nomenclature. The two equations may be combined to give

$$\lambda \frac{d\lambda}{dt} = \frac{D_S}{L} (\gamma - \lambda) \quad (12)$$

where

$$\gamma = \frac{LMc^0}{10^{-6} X_n \rho \beta} \quad (13)$$

The experiments showed that as the diffusion and the crosslinking reaction proceed the gel becomes so strong that the diffusion of AlCl₃ practically stops and λ does not increase anymore.

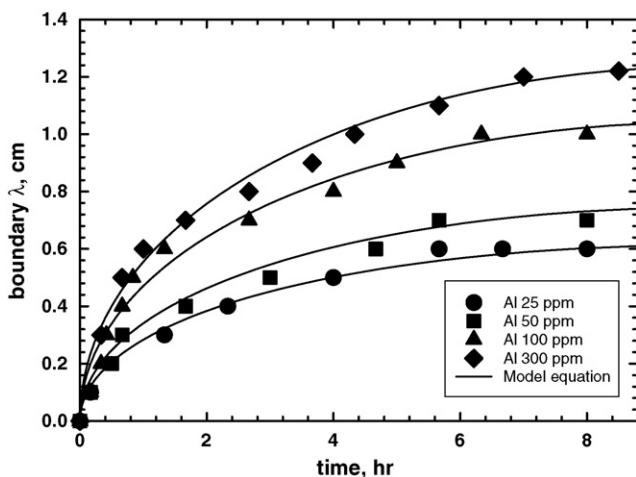


Fig. 7. Gel thickness vs. time for Xn/AlCl₃ for Xn = 8000 ppm.

In order to ascertain this peculiarity we measured by the rheometer the variation of the gel strength with time. The results are reported in Fig. 8 where it is shown the change of the shear storage modulus G' with time for a given couple of Xn/AlCl₃ concentrations. It may be noted that after 24 h the gel is solid like ($G' > 300$ Pa). Thus, indicating the formation of a very strong gel, so that the further diffusion of the crosslinker is about nil. Therefore, we must consider that the diffusivity in Eqs. (10)–(12) is a function of time. In order to make a reasonable hypothesis on this function, G' at 1 rad/s has been plotted versus time. This diagram, not reported here, shows that G' has a linear behaviour with time. Therefore, missing other information, a reasonable assumption is that the diffusivity also has a linear dependence with time, i.e.:

$$D_S = D_S^0 \left(1 - \frac{t}{t^*}\right) \quad (14)$$

where D_S^0 is the diffusion of AlCl₃ in the Xn solution (before gelation) and t^* is the time at which the gel boundary stops. We estimate the diffusivity of AlCl₃ in water to be 1.1×10^{-5} cm²/s. The integration of Eq. (12) with Eq. (14) gives

$$\frac{t^2}{t^*} - t - \frac{L}{D_S^0} \left[\lambda + \gamma \ln \left(1 - \frac{\lambda}{\gamma}\right) \right] = 0 \quad (15)$$

The applicable solution of this quadratic algebraic equation is

$$t = \frac{t^* - \sqrt{t^{*2} + \frac{4Lt^*}{D_S^0} \left[\lambda + \gamma \ln \left(1 - \frac{\lambda}{\gamma}\right) \right]}}{2} \quad (16)$$

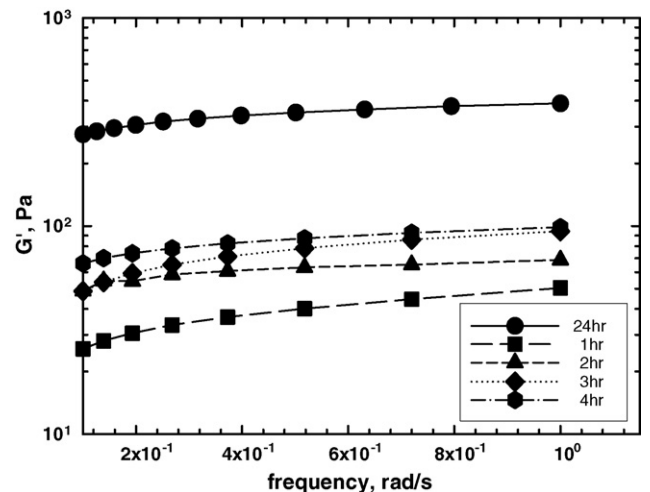


Fig. 8. Shear storage modulus G' of Xn/AlCl₃ gel as a function of frequency and time. Xn = 8000 ppm; Al(III) = 300 ppm.

The pseudo-stoichiometric coefficient β has been determined as an adjustable parameter. The continuous curves fitting the experimental data in Fig. 7 are the model equation (16).

In a deterministic approach the parameter β has been calculated by the equation:

$$\beta = \frac{ML}{10^{-6} X_n \rho} \frac{c^0 - c^*}{\lambda^*} \quad (17)$$

where c^* and λ^* are the concentration of AlCl_3 and the moving boundary position at t^* , respectively. The concentration c^* has been determined measuring Cl^- by means of a spectrophotometer (Shimadzu UV-1601). Both values of β are reported in Table 2. The discrepancy between the two values of β may be due to the fact that when the concentration of AlCl_3 is in large excess some of it penetrates into the gel but remains unreacted. This possibility is not accounted for in the model equations. Inspection of Table 2 shows that the ratio of the two values of β approaches unity as the AlCl_3 concentration is reduced. Finally we remark that our experiments showed that the minimum AlCl_3 concentration for obtaining a consistent gel is 25 ppm as Al(III) .

5. Chemical resistance of the gel

The gelled polymer technology is currently used to limit the flow of water during oil extraction from wells. In order to use this technology as a technique for the temporary containment of spills in soil, while the definitive remedial action of the contaminated area is organized and eventually accomplished, it is mandatory to check that the xanthan gel resists attack by possible contaminants. In a previous paper [1] we checked this opportunity with a few hydrocarbons which are subject to possible spills; they are: hexadecane (as a typical heavy paraffin-oil), gasoline, fuel-oil, lubricating-oil (all of them lighter than water), and perchloroethylene (heavier than water). The check was done introducing a quantity of the chemical to be tested into vials, on top of the gel. These samples were left undisturbed for more than 6 months and we did not observe any attack to the gel or a penetration of any of the above chemicals into the gel structure. We also tested the resistance to water and found that the gel is impermeable; therefore it may be used even for the containment of contaminated water. In the present work, due to the fact that the gel xanthan/ Al(III) / CO_2 is the weakest among those tested, we repeated the above check even for this gel. The result showed that even this weak gel is resistant and impermeable to the above chemicals so that it is suitable for the considered application.

6. Conclusions

The gelled polymer technology, using xanthan gum aqueous solutions is suitable for the temporary containment of oily hydrocarbon spills in soil. Even contaminated waters could be contained. The gel has a long lasting capacity of containing these contaminants. The gel formation has been attained using aluminum ions as crosslinker. The source of these ions has been either sodium aluminate or aluminum chloride. The first salt in

mixture with the xanthan solution does not induce a gelling reaction inasmuch as, due to the high value of the pH of the solution, the concentration of Al(III) ions is very low. Therefore, in order to run the crosslinking reaction the pH of the solution must be lowered by the addition of an acid. We have proved that CO_2 is an acid strong enough to release Al ions so that the gelling reaction may proceed. The experiments have been performed using flowing gaseous CO_2 on the top of the Xn/NaAlO_2 solution and observing the advancement of the gel layer. The process is a moving boundary problem. Accordingly a theoretical model is provided for determining the rate of advancement of the gel layer.

The situation is completely different with aluminum chloride. In fact, upon dissolving in water, being AlCl_3 a salt, it can be considered completely dissociated. Therefore, there is a full availability of Al(III) ions and there is the maximum crosslinking activity. In this case, aluminum chloride cannot be mixed with the xanthan solution because an instantaneous gelling reaction takes place impeding the injection of the solution in the soil. In this case the aqueous Xn solution must be injected first. Then the aqueous solution of AlCl_3 is added on the top of the already injected Xn solution. Also in this case the gelling proceeds as a moving boundary as the AlCl_3 diffuses in the solution. With difference to the previous case, the gel that forms increases its strength with time becoming, after about 10 h, solid like so that the diffusion process stops. As a matter of fact we did not achieve gel layer thicknesses larger than about 1.2 cm. Also for this case a theoretical model of the process is provided for determining the rate of advancement of the gel layer.

It must be remarked that the gel strength (as measured by the shear storage modulus G') obtained with CO_2 is about an order of magnitude smaller than that obtainable with AlCl_3 . Nevertheless it is suitable for the containment of a spill as well.

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References

- [1] F. Gioia, M. Urciuolo, The containment of oil spills in unconsolidated granular porous media using xanthan/ Cr(III) and Xanthan/ Al(III) gels, *J. Hazard. Mater.* 116 (1/2) (2004) 83–93.
- [2] S. Hejri, F. Jousset, D.W. Green, C.S. McCool, G.P. Willhite, Permeability reduction by a xanthan/chromium(III) system in porous media, *SPE Reserv. Eng.* (1993) 299–304.
- [3] C.S. McCool, D.W. Green, G.P. Willhite, Fluid/rock interactions between xanthan/chromium(III) gel systems and dolomite core material, *SPE Prod. Facil.* 15 (3) (2000) 159–167.
- [4] W. Stumm, J.J. Morgan, *Aquatic Chemistry*, John Wiley & Sons Inc., New York, 1996, pp. 272–275.
- [5] J.W. Mellor, *A Comprehensive Treatise on Inorganic and Theoretical Chemistry*, vol. V, Longmans Green & Co., London, 1946, p. 285.
- [6] P. Pascal, *Nouveau Traité de Chimie Minérale*, vol. VI, Masson et Cie Editeurs, 1961, pp. 601–604.