The containment of oil spills in unconsolidated granular porous media using xanthan/Cr(III) and xanthan/Al(III) gels

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Abstract

The gelation in situ of aqueous solutions of the biopolymer xanthan gum may be a method for temporarily containing oil spills in soil whilst the remediation procedure is planned and accomplished. The gelling reaction has been carried out using as crosslinking agents either Cr(III) or Al(III) cations. By using Cr(III) the gelation time, which has been measured for a range of xanthan and/or Cr(III) concentrations, is of the order of the hour. On the contrary, the gelation by means of Al(III) cations takes place at quite low pH and is instantaneous. Therefore, depending on the crosslinker adopted, rather different techniques must be used for generating the gel structure in situ. The gels have proven to be suitable for the containment of water and of many hydrocarbons without loosing their strength even for a long period of time. The rheological properties of xanthan aqueous solutions evidence a shear-thinning behaviour that is most favourable for the application. Theoretical considerations have permitted the establishment of the mobility conditions of xanthan solutions in porous media before the gelation, and the estimation of a suitable injection pressure. The experiments for investigating the mobility of xanthan solutions in porous media, and for simulating the containment of an oil spill, have been done using packed beds of uniformly sized spherical glass beads, in glass columns. The glass assembly made it possible to visualize the evolution of the phenomena of interest.
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1. Introduction

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 treatment of oil producing reservoirs contemplated for secondary or enhanced oil recovery operation.

The study presented in this paper follows the research line anticipated by Rocha et al. [1]. It is aimed at using the gelled polymer technology for a different field of application. When

a quantity of an oily phase is spilled on/in the soil, depending on the type of porous medium, it may remain entrapped in the porous material or move downwards, even though slowly, and eventually reach the aquifer. Techniques for soil remediation are well understood, however they require a long time to be planned and completed. Therefore, when the oil is mobile there is the actual risk of contaminating the aquifer. In such cases it may be convenient to devise emergency procedures for the containment of the oil plug while the remediation of the contaminated area is organized and eventually accomplished. Injecting a gelling polymer in the soil, underneath the oil spill, may be a quick technique for stopping the descent of the oil.

As described in the review paper by Vossoughi [2], a variety of polymers and crosslinkers have been tested and proved suitable for enhanced oil recovery operations. Research papers on specific gel systems have been published by several authors, among them Zhuang et al. [3] have

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Nomenclature

Bold characters denote vectors

Al(III)	concentration of Al^{3+} cations (ppm)
Cr(III)	concentration of Cr^{3+} cations (ppm)
c	acid molar concentration ($kmol/m^3$)
D_{ac}	diffusivity of acid in the gel (m^2/s)
D_p	diameter of a particle (m)
g	gravity (m/s^2)
k	intrinsic permeability (m^2)
I	ease of injection; injection rate/injection pressure (m^3/Pa s) (m^3/bar s, in Table 3)
L	height of acid solution in the vial (see Fig. 5) (m)
M_{ac}	molecular weight of acid (kg/kmol)
m	consistency factor of *power law* fluid ($Pa\,s^n$)
n	power law index
p	pressure (Pa)
$\mathcal{P}$	equivalent pressure $= p - \rho g z$ (Pa)
Re	Reynolds number $= D_p \rho v_o / \mu (1 - \varepsilon)$
r	radial distance in spherical coordinates, m
r_1	radius of the injection port (m)
r_2	radius of the spherical blob (m)
S	cross sectional area of vial (m^2)
t_g	gelation time (h or days)
v	superficial velocity (Darcy's velocity) (m/s)
$v_{LN\,min}$	minimum v_{LN} for lower-Newtonian behavior (m/s)
$v_{\rho g}$	superficial velocity under gravity (m/s)
Xn	xanthan gum concentration in aqueous solution (ppm)
z	vertical axis pointing as gravity (m)

Greek symbols and operators

α	acid/Xn pseudo stoichiometric coefficient, kg of acid consumed per kg of xanthan gelled;
ε	porosity
Γ	shear rate (s^{-1})
λ	distance of the moving boundary from the interface acid/gel (m)
μ	apparent viscosity (Pa s)
μ_{eff}	effective viscosity (see Eq. (3)) ($kg\,m^{-n}\,s^{n-2}$)
ρ	density of fluid (kg/m^3)
∇	"nabla" operator (m^{-1})
$|\nabla\mathcal{P}|_{min}$	pressure gradient @ $v_{LN\,min}$, Pa/m (bar/m in Table 3 and in Fig. 8)

Subscript

LN	lower-Newtonian region
UN	upper-Newtonian region
PL	power law region

studied the sulfomethylated resorcinol-formaldehyde system; Hunt et al. report in [4] on the gelation kinetics of polyacrylammide–Cr(III) system, Hejri et al. [5] and McCool et al. [6] have investigated the xanthan/chromium(III) system. For the case we are dealing with, however, (e.g., the containment of an oil spill), no gel should be used which by its chemical components and/or by its decomposition products could be toxic to humans, or ecotoxic with specific reference to the aquifer to be protected. For example we did not consider the most used polyacrylamide gels (moderately toxic), which may release acrylamide that is a highly toxic chemical. Instead we focused on xanthan gum that is 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. In addition it is biodegradable. Xanthan gum dissolves readily in water with stirring and gels with metal ions; among them Cr(III) [5,6]. Xanthan gels have long lasting capabilities of maintaining their property to reduce porosity of porous media. The xanthan polymer solution (before crosslinking) has the advantageous rheological property of shear thinning [7,8]. Therefore, it shows low apparent viscosity at high shear stress (making easy the injection through tubes) but has a very high apparent viscosity at low shear rate, thus impeding the permeation by gravity through the porous media in the mean time that the gelation process takes place.

In this paper we report on laboratory experiments on xanthan gel formation using two different crosslinkers; i.e., Cr(III) and Al(III) cations. The Xn/Cr(III) system has been already investigated. As reported in [6] it is characterised by gel times (of the order of the hour) which depend on the concentration of both xanthan and Cr(III). However, because different xanthan gum products can display different behaviours [7], we conducted a set of experiments for determining the gelation time of our specific xanthan/Cr(III) solutions, for various biopolymer and Cr(III) concentrations.

There are circumstances, however, under which chromium cannot be considered for subsurface injection where the possibility exists for migration into freshwater aquifers. In such instance non-toxic cross-linking agents should be considered. We have focused the attention on aluminum which is a relatively safe and a naturally occurring element in soils. Dovan and Hutchins [9] have proved that Al(III) is a crosslinker for polyacrylamide. They report that the gelation takes place at low pH in a very short time. Therefore, the admixture polymer/Al(III) 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. We have extensively tested the gel system xanthan/Al(III) and have found that even for this system the gelation reaction takes place at low pH (acid must be added to the Xn/Al(III) solution), and is very rapid indeed. Therefore, in order to overcome this last inconvenience we have devised a rather different technique

for generating the gel structure in the porous structure when this gel system is adopted.

The rheological properties of our Xanthan stock solutions have been determined in order to obtain the applicable constitutive equation useful for studying the movement of these solutions in porous media. By a simple theoretical model the following have been calculated: (i) the necessary conditions for which the solution remains motionless in porous media, after the injection, before its gelation; (ii) the ease of injection of the solution.

Finally, a set of experiments have been carried out for testing the resistance of these gels to the chemical attack of a few hydrocarbons typically subject to spills in soil, and their aptitude to stop the drainage of these contaminants in porous media.

The results indicate, as anticipated by Rocha et al. [1], that gelled polymer technology might be a sound practical method for emergency actions, aimed at reducing the risk of aquifer contamination by oil spills, until the remediation of the contaminated area is eventually accomplished. Furthermore it has been verified that these gels are impermeable even to water, so that they could also be used, when possible, for the containment of contaminated waters.

2. Experimental section

2.1. Xanthan/Cr(III) gel system

2.1.1. Materials

The xanthan gum biopolymer was supplied as a powder by Aldrich (Lot 07207CO-073). Cr(III) ions were used as crosslinking agent. Three different salts were tested as source of Cr(III) cations: (i) chromium(III) sulfate hydrate $Cr_2(SO_4)_3 \cdot 15H_2O$; (ii) chromium(III) chloride hexahydrate $[Cr(H_2O)_4Cl_2]Cl \cdot 2H_2O$ (notice that chromium(III) chloride anhydrous would be practically insoluble) and (iii) chromium(III) acetate hydroxide $(CH_3CO_2)_7Cr_3(OH)_2$.

With regard to the toxicity of the crosslinker a few considerations are necessary. Among the ionic forms of chromium, the most toxic one is Cr(VI). According to the Italian law, the level of this compound must not exceed 2 or 15 ppm in soil (the lower value applies to residential areas, the upper to industrial sites) and 5 ppb in underground waters. Quite higher limits are considered for the much less toxic Cr(III). In fact for total chromium the limits are 150 or 800 ppm in soil and 50 ppb in underground waters. We are considering that the gelled polymer remains motionless in soil, for the containment of the oil spill, until the remediation of the contaminated area (including the removal of the gelled polymer) is planned and accomplished. Our experiments of gel formation with Cr(III) salts are limited to Cr(III) concentration in the range 50–200 ppm.

2.1.2. Gel formation and gelation time

Aqueous solutions of xanthan gum were prepared using distilled water. Xanthan gum dissolves readily in water with stirring. The water was coloured using trace amount of a pH indicator (bromocresol purple $C_{21}H_{16}Br_2O_5S$; it switches from yellow to blue in the pH range 5.2–6.8) This particular dye accomplishes a threefold task: (i) permits the visual observation of the gel during the containment experiments; (ii) verifies the control of the homogeneity of the solution and (iii) permits the visualization of the pH range of the solution (the exact value of the pH was ascertained, when necessary, by a Orion 420A pH-meter).

Chromium (1000 ppm Cr(III)) stock solutions were used for adding the desired amount of crosslinker to the xanthan solution. As reported by McCool et al. [6], the gelation time, and even the gel formation itself, are strongly dependent on the pH of the solution. Following the results of McCool et al. [6] we chose to prepare the solutions at pH ≈ 6. The pH of the solution after the addition of the chromium salt is below 6. Therefore, the initial pH was adjusted to the value 6 by the addition of NaOH solution.

Like other biopolymers, xanthan gum is biodegradable. Therefore, in order to prevent this phenomenon some formaldehyde is usually added to the polymer solution. Biodegradation could be much more evident in field applications rather than in laboratory. However, in order to simulate the solutions that would be used in field applications, we added formaldehyde to the xanthan solutions (before the addition of the crosslinker) for a final concentration of 1500 ppm. At any rate we did not observe any biodegradation of our gels even for times as long as 5 months and we conclude that formaldehyde would not necessarily be required for the application we are considering. With the desire to follow as closely as possible the recipe suggested by McCool et al. [6] we added potassium chloride to the solutions for a final concentration of 3% KCl. Helmreich et al. [7] suggest that the addition of NaCl leads to the double-helix structure of the xanthan gum making the polymer molecule rigid, because the anionic ligands (pyruvate) in the side chains find the best position relative to each other. The same effect should have KCl which behaves like NaCl. We prepared, however, for comparison, a few samples without KCl and did not observe any significant different behaviour of the gel system.

After the addition of the crosslinker, the solutions were introduced in vials (Alltech Italia, 28 mm × 95 mm) and set in a gently agitated thermostatic bath at the temperature chosen for the test. Following the bottle test suggested by McCool et al. [6] the gelation time was defined when the sample exhibited sufficient structure to remain as a single mass upon turning the vial upside down.

The gelation time of solutions at three different xanthan concentrations (2000, 4000 and 6000 ppm), three Cr(III) concentrations (50, 100 and 200 ppm) from chromium sulfate, and two temperatures (25 and 35 °C) are reported in Figs. 1 and 2 versus Cr(III) ion concentration. In Fig. 3 the salt source of Cr(III) is the chromium(III) chloride hexahydrate and the temperature is 25 °C.

Inspection of Figs. 1–3 shows that the gelation time decreases as the crosslinker concentration increases and tends
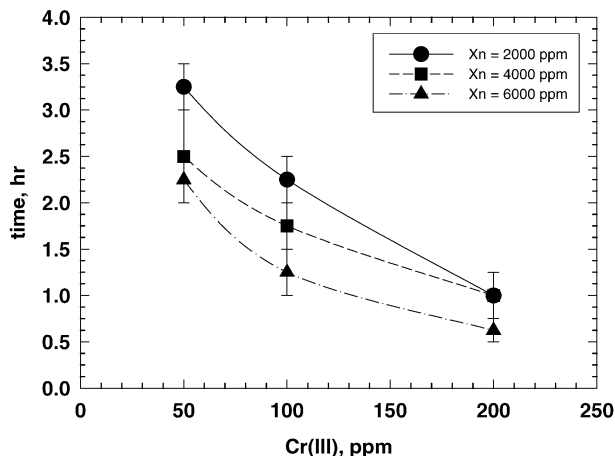
Fig. 1. Gelation time vs. Cr(III) cation concentration @ 25 °C. The source of Cr(III) is chromium(III) sulfate hydrate.
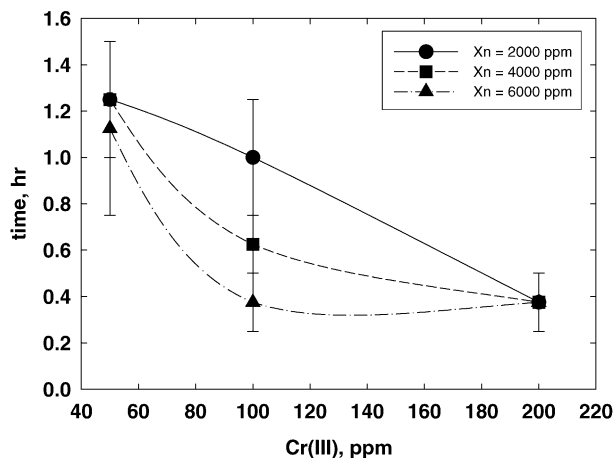

Fig. 2. Gelation time vs. Cr(III) cation concentration @ 35 °C. The source of Cr(III) is chromium(III) sulfate hydrate.
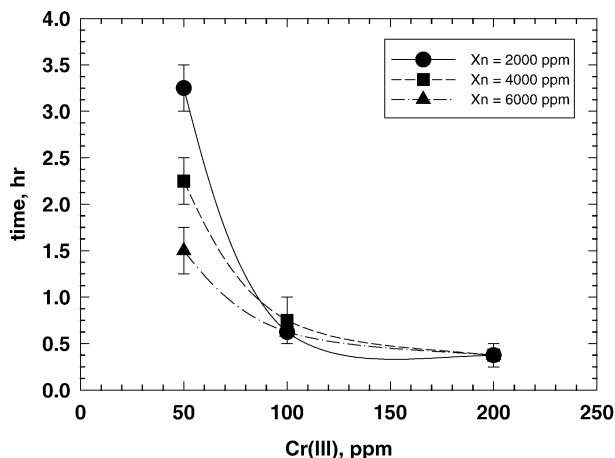

Fig. 3. Gelation time vs. Cr(III) cation concentration @ 25 °C. The source of Cr(III) is chromium(III) chloride hexahydrate.
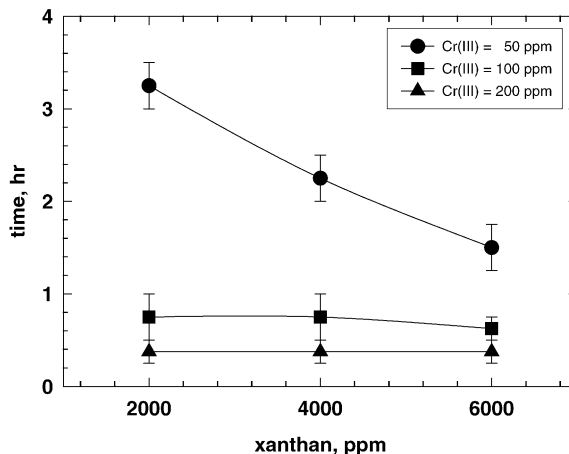

Fig. 4. Gelation time vs. xanthan concentration @ 25 °C. The source of Cr(III) is chromium(III) chloride hexahydrate.

to approach a constant value. In many cases the gelation time, after an initial drop, remains about constant for Cr(III) concentration above 100 ppm. The gel strength improves increasing the Cr(III) concentration even though the gelation time remains about the same. Furthermore, comparing the results of Fig. 1 with those of Fig. 3 it appears that the gelation time is not significantly influenced whether the source of Cr(III) cations is the sulfate or the chloride (with this salt, however, the gelation time is slightly shorter). The data of Fig. 3 has been used to show more clearly, in Fig. 4, that for Cr(III) above 100 ppm the gelation time does not depend on xanthan concentration, in the range 2000–6000 ppm.

A completely different time scale is valid when chromium(III) acetate hydroxide salt is used as crosslinker source. Using this salt the following gelation times t_g were measured @ 35 °C and xanthan concentration = 2000 ppm:

- Cr(III) = 50 ppm, t_g = 10 days;
- Cr(III) = 100 ppm, t_g = 6 days;
- Cr(III) = 200 ppm, t_g = 6 days.

At 25 °C the gel forms after 14 days at Cr(III) concentration of 200 ppm only.

Further details on the experimental procedure for preparing the gels, and on the experimental results are reported in the Chem. Eng. Thesis by Carotenuto and Roviello [10].

2.2. Xanthan/Al(III) gel system

Under most circumstances, chromium in any form is not a preferred chemical for subsurface injection where the possibility exists for migration into freshwater aquifer. In such instance alternative cross-linking agents should be considered. Aluminum is a relatively safe and a naturally occurring element in soils. In fact, the Italian law does not specify any limit to its concentration in soils but indicates a limit of 200 ppb in underground water. Dovan and Hutchins [9] have proven that aluminum is suitable for crosslinking polyacrylamide. Preliminary tests in our laboratory have proven

that aluminum is suitable for crosslinking xanthan gum. We used sodium aluminate as source of aluminum ionic species. Sodium aluminate in aqueous solution may produce different ionic species depending on the pH of the solution. As discussed in [9], upon dissolution of an aluminum salt the aluminum species present in the solution, starting from a pH above 9.6, gradually shift as follows, as the pH is lowered:

$$[Al(OH)_4]^- \rightarrow Al(OH)_3 \rightarrow [Al(OH)_2]^+$$
$$\rightarrow [Al(OH)]^{2+} \rightarrow Al^{3+}$$
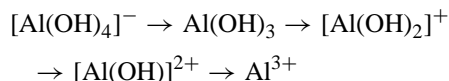
Above a pH of 9.6 $[Al(OH)_4]^-$ is the predominant ionic species; below a pH of 4, Al is almost entirely present as the single species Al^{3+}. The crosslinking activity increases as the pH is lowered. For xanthan polymer we have found that the crosslinking activity is practically nil for pH greater than 9.6. This holds true also for polyacrylamide [9]. The reactivity occurs when cationic species are present, and it is maximum for a pH lower than 4, when the cation Al^{3+} predominates in the solution. Therefore, the addition of sodium aluminate to a xanthan solution with a pH above 9.6 does not induce a gelation of the polymer. In order to obtain a gel, the pH must be lowered by the addition of an acid. But, when an acid is added to the xanthan/aluminate solution so that the pH drops below 4, the gelation takes place about instantly. Therefore for the purpose of using this gel system for the containment of an oil spill, the acid must be added after the Xn/Al basic solution (pH > 9.6) has been injected underneath the oil spill. We have investigated the gel formation in the most reactive condition, i.e., at pH lower than 4 when the predominant ionic species is Al^{3+}, and have conducted laboratory experiments for simulating the gelation process in order to obtain quantitative data to be used in field application.

2.2.1. Materials and experimental procedure

Stock solutions of sodium aluminate anhydrous (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, and the pH was adjusted to 10 by the addition of a 0.1 M NaOH solution. At this pH the solution shows an intense blue/indigo colour. 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. No gelling reaction takes place at the high pH of the solution. The mixture was then poured in a vial to fill about two-thirds of its volume and a given quantity of acid solution was added on the top of the xanthan solution. This is the time zero of the experiment. Upon the addition of the acid, a layer of gel instantly forms at the interface polymer/acid, which blocks any mixing of the two solutions. Namely the lowering of the pH causes the formation of Al^{3+} cations which induce an instantaneous gelling reaction. The gel is perfectly distinguishable as it shows up with a brilliant
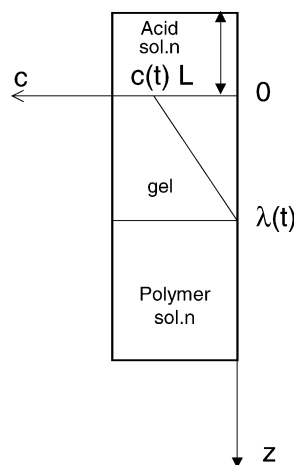

Fig. 5. Sketch of gel formation as a moving boundary process.

yellow colour, which contrasts with the blue of the un-gelled polymer, thus indicating that the acid remains blocked in the gel structure. Afterwards the acid 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. 5. The position of the moving boundary and the concentration of the acid in the solution above the gel were recorded versus time. We have conducted experiments on gel formation using either hydrochloric acid or acetic acid. However, even though the gelling reaction took place with acetic acid too, the gel strength was poorer (nevertheless applicable for reducing the effective permeability of a porous medium) than that obtainable with HCl. Therefore, in this paper we focus the attention mainly on the system Xn/Al(III)/HCl. Further details on the experimental procedure for preparing the gels as well as the results regarding the system Xn/Al(III)/CH₃COOH are reported in the thesis by Gaglione and Guida [11]. Operating conditions for the experimental runs are reported in Table 1. At least three replicates for each run were carried out. As an example the experimental data points $\lambda(t)$ versus the acid concentration $c(t)$, and λ versus time, for the three replicates of run no. 6, are reported in Fig. 6.

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

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

$$\frac{d\lambda}{dt} = \frac{M_{ac}D_{ac}}{10^{-6}Xn\rho\alpha}\frac{c(t)}{\lambda} \tag{1}$$

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

$$\frac{dc}{dt} = -\frac{D_{ac}}{L\lambda(t)}c \tag{2}$$

Table 1
Operating conditions adopted for the experimental runs of the Xn/Al(III) gel system

Run no.	Xanthan (ppm)	Al(III) (ppm)	c^0 (mol/ml)	L (cm)	α (grHCl/gr Xn)	λ_{max} (cm)	D_{ac} (cm²/s)	t_{max} (s)
1	4000	300	5.49×10^{-5}	0.588	0.17	1.718	3.56×10^{-5}	3.98×10^4
2	4000	300	5.49×10^{-5}	0.686	0.18	1.955	3.61×10^{-5}	5.21×10^4
3	4000	300	5.49×10^{-5}	0.784	0.18	2.207	3.47×10^{-5}	6.99×10^4
4	4000	300	5.49×10^{-5}	0.980	0.189	2.595	3.61×10^{-5}	9.88×10^4
5	6000	300	5.01×10^{-5}	0.784	0.176	1.357	3.40×10^{-5}	4.39×10^4
6	6000	300	5.49×10^{-5}	0.980	0.196	1.672	3.55×10^{-5}	6.47×10^4
7	4000	200	5.01×10^{-5}	0.686	0.173	1.807	4.10×10^{-5}	4.24×10^4
8	4000	200	5.49×10^{-5}	0.784	0.203	1.936	4.35×10^{-5}	4.89×10^4

The initial conditions are:

I.C. : $t = 0,\ c = c^0,\ \lambda = 0$ (3)

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

$$\lambda \frac{d\lambda}{dt} = \frac{D_{ac}}{L}(\lambda_{max} - \lambda)$$ (4)

where

$$\lambda_{max} = \frac{L M_{ac} c^0}{10^{-6} Xn \rho \alpha}$$ (5)

Eq. (4) may be integrated to give:

$$t = -\frac{L}{D_{ac}}\left[\lambda + \lambda_{max} \ln\left(1 - \frac{\lambda}{\lambda_{max}}\right)\right]$$ (6)

The slope $\Delta c/\Delta \lambda$ of diagrams $\lambda(t)$ versus $c(t)$, like that of Fig. 6 permit to determine the pseudo-stoichiometric coefficient α. It is indeed:

$$\alpha = \frac{M_{ac} L}{10^{-6} Xn \rho}\left(-\frac{\Delta c}{\Delta \lambda}\right)$$ (7)

The data points λ versus t of diagrams like that of Fig. 6 are fitted by Eq. (6) where the diffusivity D_{ac} is evaluated

Fig. 6. Run no. 6 of Table 1. Hydrochloric acid concentration vs. gel thickness and gel thickness vs. time. Xn = 6000 ppm, Al(III) = 300 ppm, $c^0 = 5.49 \times 10^{-5}$ mol/ml.

as an adjustable parameter. The detail of the calculations are reported in the thesis [11]. The results of a few runs are in Table 1. The pseudo-stoichiometric coefficient α as well as the diffusivity D_{ac} of the acid through the gel, are the key parameters for determining the acid requirement and the time necessary for generating a desired thickness of the gel layer in applications. Notice that the diffusivity is comparable to that of HCl in water (3.1×10^{-5} cm²/s @ 25 °C [12]).

2.3. Chemical resistance of the gel

In order to use the gelled polymer 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 the attack of possible contaminants. We limited the check to a few hydrocarbons which are subject of 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 the vials, on top of the gel. These samples were prepared many months ago and even today we do not observe any attack to the gel or a penetration of any of the above chemicals into the gel structure. We tested also the resistance to water and found that the gel is impermeable; therefore it may be used even for the containment of contaminated water.

3. Theory

3.1. Rheological properties of xanthan solutions

The determination of the rheological properties of xanthan solutions is a prerequisite for studying the motion of these solutions in a porous medium. The apparent viscosity versus shear rate curves (reported in Fig. 7), for xanthan solutions at three concentration levels, were determined by means of a rheometer (Bohlin Instruments CVO 120) using a cone-plate geometry (4° angle and 40 mm diameter). These curves clearly show that these solutions are "shear-thinning" with a power law region in the range (10^{-3} to 10^3 s^{-1}). The same rheological behavior is reported by Helmreich et al. [7]
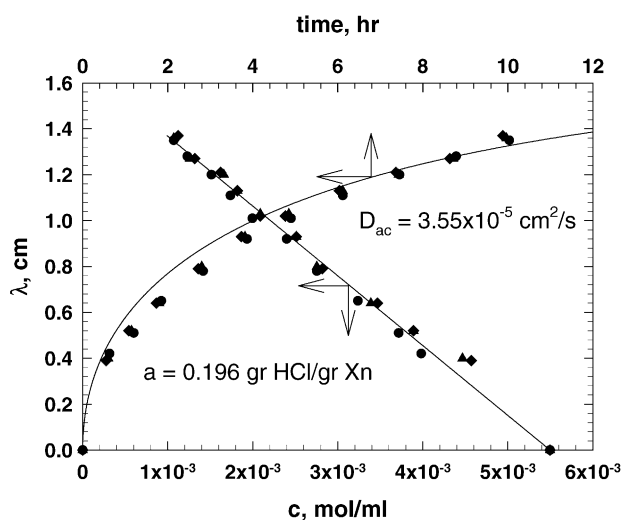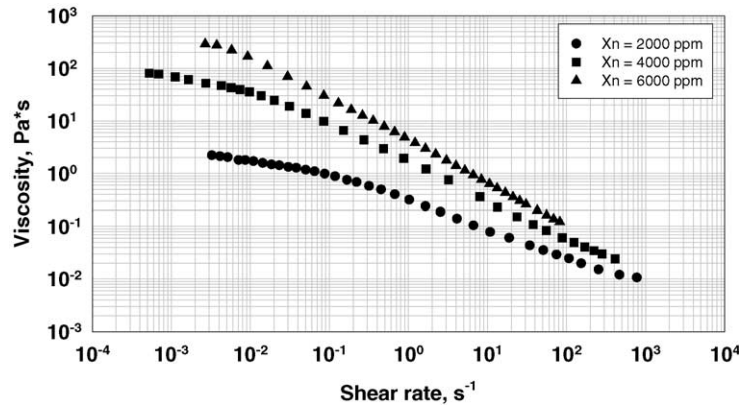
Fig. 7. Apparent viscosity vs. shear rate of xanthan aqueous solutions at three different concentrations. Consistency factors m, and power law indexes n (see Eq. (1); units in nomenclature) are: Xn = 2000 ppm, $m = 0.3$, $n = 0.46$; Xn = 4000 ppm, $m = 1.8$, $n = 0.26$; Xn = 6000 ppm, $m = 4.5$, $n = 0.175$.

and Zhang et al. [8]. However, it is advisable to determine everytime the constitutive equation of these solutions because different xanthan gum stocks can display quite different rheological parameters [7].

The approach to constant values of the viscosity at low and high shear rate ranges are referred to as upper- and lower-Newtonian regions, respectively. In the power law region the relationship between viscosity and shear rate is:

$$\mu(\Gamma) = m|\Gamma|^{n-1} \tag{8}$$

where m is the consistency factor and n the power index. The values of these two empirical parameters are reported in the caption for Fig. 7. The power law index decreases with increasing concentration of xanthan. The viscosity at the upper-Newtonian region is quite larger than that at the lower-Newtonian region. A more complex constitutive equation could describe more accurately the rheological behaviour of xanthan solutions; e.g., the four parameters equation [13]. However, for the purpose of this paper the use of the quite simple Eq. (8) is satisfactory.

For the application we are contemplating, the first important property that xanthan solutions should exhibit is that of remaining in place, motionless, after injection in the porous medium, during the gelation time. A shear thinning behaviour with a large viscosity at low shear rate is a feature that helps in fulfilling this prerequisite.

Having determined the viscosity behavior versus shear rate (Eq. (8)) it is possible to ascertain, by means of simple calculations, how well the above important property is fulfilled by xanthan solutions. Naturally, many advanced researches are reported in the literature on the flow of non-Newtonian fluids in porous media [14–18]. In most studies, the simple power law (or more generally the Herschel–Bulkley) fluid model is employed. For the sake of simplicity, however, it is satisfactory to use the Darcy's law for a "power law" fluid in a bed of unconsolidated particles

as reported in [19]. Namely:

$$v_{PL}^n = -\frac{k}{\mu_{eff}}\nabla\mathcal{P} \tag{9}$$

where k is the intrinsic permeability of the medium as determined for Newtonian flow and:

$$\mu_{eff} = m\left[\frac{2(25/12)^n(3 + (1/n))^n 3^{n+1}}{150}\right]\frac{D_p^{1-n}\varepsilon^{2(1-n)}}{(1-\varepsilon)^{1-n}} \tag{10}$$

Notice that μ_{eff} does not have the units of viscosity. The intrinsic permeability of an unconsolidated granular porous medium and for $Re < 10$ may be calculated as [19]:

$$k = \frac{D_p^2\varepsilon^3}{150(1-\varepsilon)^2} \tag{11}$$

The constraints to Eq. (9) are $v_{UN} \le v_{PL} \le v_{LN}$. Where v_{LN} and v_{UN} are the Darcy's velocity for Newtonian behaviour at the lower- and upper-Newtonian regions, respectively. Whenever the velocity falls outside the above range, the fluid must be considered Newtonian with a viscosity equal to that of the upper- or lower-Newtonian region as applicable.

Using the above set of equations we have calculated the Darcy's velocity v_{PL} for xanthan solutions at three different concentration levels, and for different particle size, versus $\nabla\mathcal{P}$. An example of these calculations is reported in Fig. 8. The actual velocity pattern is the line A–B–C–D. Naturally a more sophisticated constitutive equation (e.g. a 4 parameters [13]) would have smoothed the two discontinuities at the points B and C). Inspection of Fig. 8 shows that for $\nabla\mathcal{P} < 10^{-1}$ bar/m, the flow of the solution in the porous bed is Newtonian with a velocity v_{UN}, while for $\nabla\mathcal{P} > 2$ bar/m the velocity is v_{LN}. Fig. 8 permits us to make an estimate, even though a rough one, of the velocity of xanthan solution in the porous medium after the injection. In this instance the xanthan solution is in slow laminar flow under gravity: $|\nabla P| = |\rho\mathbf{g}| = 0.097$ bar/m. At this gradient we read a velocity of 2.3×10^{-8} m/s (8.3×10^{-3} cm/h), which practically means that the solution remains motionless, after the injec-
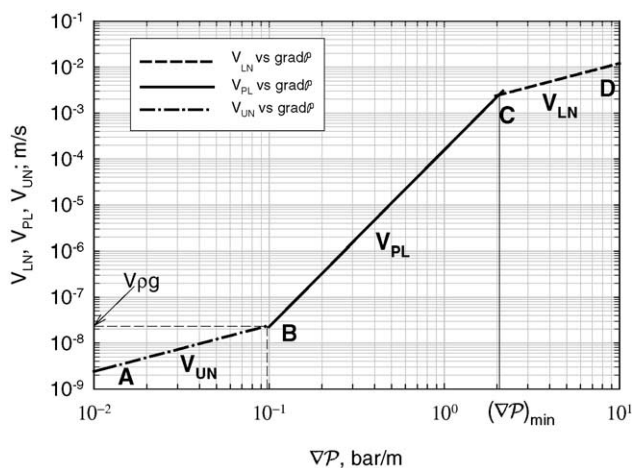
Fig. 8. Darcy's velocity of xanthan aqueous solution vs. pressure gradient in a bed of unconsolidated particles. $Xn = 4000$ ppm, $D_p = 0.5$ mm.

tion during the gelation time, in a bed packed with 0.5 mm particles. The velocity under gravity (indicated with the symbol $v_{\rho g}$) has been calculated for other cases of interest and is reported in Table 2. In all instances it is $Re < 10$ (except for $Xn = 2000$ ppm and $D_p = 5$ mm, for which it is $Re = 35$ and $v_{\rho g}$ is in the lower-Newtonian region). Inspection of this table shows that for practical applications the xanthan solution remains practically immobile after the injection during the gelation time. In fact considering as an example a xanthan concentration of 4000 ppm @ 25 °C and a Cr(III) (from sulfate) concentration of 200 ppm, we read from Fig. 1 that the gelation time is of the order of 1 h. The corresponding values of $v_{\rho g}$ of Table 2 indicate that for particles up to 2 mm the solution may be considered "motionless"; for 3 mm particles the maximum distance travelled during the gelation time would be 108 cm.

3.2. Experimental validation and containment experiments

We made an experimental validation of the above theoretical findings by observing the movement of xanthan solutions in glass columns packed with glass beads of various sizes. The columns (42 mm inside diameter, 550 mm height) had a steel net 10 cm above the bottom to support the beads. Below the net, at the sidewall, a vent was present for equilibrating the air pressure. The column was filled with humid beads of uniform diameter, and 5.5 ml of coloured xanthan solution

(without crosslinker) were slowly injected by a syringe, 5 cm below the top of the bed. We observed the position of the solution for at least 4 h. The experiments showed that whenever the calculated $v_{\rho g}$ is less than 1 cm/h the solution is truly immobile. Actually, the values of $v_{\rho g}$ in Table 2 must be considered fairly conservative. For cases in which a movement of the solution was observable (at larger bead diameters) we measured velocities even slower (for a factor between 1/3 and 1/4) than $v_{\rho g}$. For example, for xanthan at 4000 ppm and 2 mm beads we measured a velocity of about 3 cm/h versus a theoretical $v_{\rho g} = 12.6$ cm/h. It may be that the retention capillary forces at the interface, which have not been accounted for in the calculations, play a role even though xanthan solutions are completely miscible with the water that wets the beads. In fact "motionless" solutions injected 5 months ago are still in the same position. Further details on the results of these experiments are reported in the theses [10,11].

The experiments of oil containment were essentially based on visual observation. Therefore, the porous medium was a bed of glass beads. First of all we checked how uniformly the gel embeds into a porous structure and how strongly it sticks the particles together. A typical test was done by injecting, by means of a syringe with a long needle, deeply inside a bed of 0.5 mm glass beads in a large container, 5 ml of a freshly prepared xanthan/Cr(III) solution ($Xn = 2000$ ppm, Cr(III) = 200 ppm from sulfate). Then after the gelation time the dry particles surrounding the zone where the gel was present were removed and a compact blob, about spherical, of gel and beads was dug out. Notice that the almost perfect spherical shape of the blob is due to the isotropic nature of the porous medium. Knowing the volume of the blobs, the porosity of the bed, the volume of the solution injected, and the shrinkage (very small indeed) of the gel, it was calculated that the gel completely filled the porosity in all cases. Furthermore, all blobs showed that the beads were firmly stuck together in a sort of elastic ball.

The first experiments for checking the containment aptitude of the xanthan/Cr(III) gel system were carried out in glass columns (already described). A column containing humid beads of uniform diameter and 10 ml of coloured xanthan/Cr(III) solution, whose composition was such as to remain motionless in the bed, was set as a disk about 7 cm below the top of the bed. After the gelation time, an identical column, equally packed was set beside the first column to track the movement of the oil in the absence of gel. Then the same quantity of coloured hexadecane was spilled on the top of the two beds and the descent of the oil was observed. In

Table 2
Flow characteristics for three xanthan solutions and various bead diameters

Medium			Xanthan 2000 ppm		Xanthan 4000 ppm		Xanthan 6000 ppm	
D_p (mm)	ε	k (m²)	$v_{\rho g}$ (m/s)	$v_{LN\,min}$ (m/s)	$v_{\rho g}$ (m/s)	$v_{LN\,min}$ (m/s)	$v_{\rho g}$ (m/s)	$v_{LN\,min}$ (m/s)
0.5	0.38	2.38×10^{-10}	10^{-5}	3.3×10^{-3}	2.3×10^{-8}	2.5×10^{-3}	9.0×10^{-12}	5.5×10^{-4}
2.0	0.41	5.28×10^{-9}	2.4×10^{-3}	1.5×10^{-2}	3.5×10^{-5}	1.2×10^{-2}	1.8×10^{-7}	2.5×10^{-3}
3.0	0.42	1.32×10^{-8}	5.0×10^{-3}	2.6×10^{-2}	3.0×10^{-4}	2.0×10^{-2}	5.0×10^{-6}	4.3×10^{-3}
5.0	0.43	4.08×10^{-8}	4.0×10^{-2}	4.0×10^{-2}	4.6×10^{-3}	3.3×10^{-2}	2.0×10^{-4}	8.0×10^{-3}

all cases we observed a containment of hexadecane at the gel barrier. However, the containment was not absolute because a quantity, even though a very small one, of the oil slowly overpassed the gel infiltrating between the glass wall and the gel disk because the gel does not stick on the glass.

To overcome this inconvenient, we repeated the experiments in a large cylindrical vessel filled with 0.5 ml humid glass beds. We arranged in the vessel a xanthan/Cr(III) solution as to form a shallow bowl. We covered the bowl with beads and, after the gelation time pertaining to the solution, we poured on the surface of the beads a volume of oil such as to be contained in the bowl. In this experiment the thickness of the bed did not permit a visual observation. Therefore, after an extended period of time the glass beads were dug out, layer after layer, until the gel bowl was reached and it showed to contain the oil. Further details on containment experiments are reported in [10,11].

3.3. Ease of injection

An important property required for a convenient utilization of a gel system is a favourable ease of injection, which is defined as the injection flow rate divided by the injection pressure. In other words for a convenient application it is required that the ease of injection be as great as possible. For the xanthan gel system the low viscosity at the lower-Newtonian region favours this feature. Increasing the pressure gradient the shear rate increases and the apparent viscosity decreases and eventually the lower-Newtonian region is reached. It is of interest to make a quick estimate of the minimum pressure gradient above which the fluid is in the lower-Newtonian region. Naturally the best condition for injection is for pressure gradients not smaller than $|\nabla\mathcal{P}|_{\min}$. In fact, consider the ratio $v_{\mathrm{PL}}/\nabla\mathcal{P}$, which behaves like the ease of injection. From Eq. (9) it is:

$$\frac{v_{PL}}{\nabla\mathcal{P}} = \left(\frac{k}{\mu_{\mathrm{eff}}}\right)^{1/n} \nabla\mathcal{P}^{(1-n)/n} \tag{12}$$

This ratio increases ($n < 1$) with the pressure gradient in the power law region and reaches its maximum value at $|\nabla\mathcal{P}|_{\min}$ where it becomes constant ($n = 1$, $v_{\mathrm{PL}} \equiv v_{\mathrm{LN}}$, $\mu_{\mathrm{eff}} \equiv \mu_{\mathrm{LN}}$).

For the specific case reported in Fig. 8 $|\nabla\mathcal{P}|_{\min}$ is 2.1 bar/m, correspondingly the Darcy's velocity $v_{\mathrm{LN\,min}}$ is 2.5 $\times 10^{-3}$ m/s. The determinations for other cases are reported in Table 3.

It could be instructive to attempt an estimate, even though a rough one, of the ease of injection at the minimum pressure (at the outlet of an injection tube) necessary for obtaining a Newtonian flow behaviour in the lower-Newtonian region. If the contribution of gravity is negligible in respect to the applied pressure, the polymer will fill the pore volume symmetrically (for an isotropic porous medium) as a spherical blob around the injection port. The continuity equation of an incompressible fluid in spherical coordinates is:

$$\frac{1}{r^2}\frac{\mathrm{d}}{\mathrm{d}r}(r^2 v_r) = 0 \tag{13}$$

then:

$$r^2 v_r = C_1 \tag{14}$$

For a Darcy's flow at the low-Newtonian region:

$$r^2 \frac{k}{\mu_{\mathrm{LN}}}\frac{\mathrm{d}p}{\mathrm{d}r} = -C_1 \tag{15}$$

Eq. (15) may be integrated to give:

$$p = C_1 \frac{\mu_{\mathrm{LN}}}{kr} + C_2 \tag{16}$$

The boundary conditions are:

$$r = r_1, \quad p = p_1 \tag{17}$$

and assuming that the solution is the wetting liquid, the pressure in the solution immediately adjacent to interface is [20]:

$$r = r_2, \quad p = p_2 - p_{\mathrm{c}} \tag{18}$$

where p_{c} is the capillary pressure and p_2 is the air pressure outside the moving front (e.g., 1 bar). Neglecting p_{c}, B.C. 18 becomes:

$$r = r_2, \quad p = p_2 = 10^5 \, \mathrm{Pa} \tag{19}$$

Introducing the boundary conditions 17 and 19 in Eq. (16), the integration constants C_1 and C_2 are calculated and from Eq. (14) we obtain the flow rate Q:

$$Q = 4\pi r^2 v_r = \frac{4\pi k}{\mu_{\mathrm{LN}}}\frac{p_1 - p_2}{r_2 - r_1}r_1 r_2 \tag{20}$$

where $p_1 - p_2$ is the gauge pressure at the injection port. The ease of injection is:

$$I = \frac{Q}{p_1 - p_2} = \frac{4\pi k}{\mu_{\mathrm{LN}}}\frac{r_1 r_2}{r_2 - r_1} \tag{21}$$

Table 3
Pressure gradient at $v_{\mathrm{LN\,min}}$ and ease of injection for three xanthan solutions and various bead diameters

Medium			Xanthan 2000 ppm		Xanthan 4000 ppm		Xanthan 6000 ppm	
D_{p} (mm)	ε	k (m^2)	$|\nabla\mathcal{P}|_{\min}$ (bar/m)	I^{a} (m^3/bar s)	$|\nabla\mathcal{P}|_{\min}$ (bar/m)	I^{a} (m^3/bar s)	$|\nabla\mathcal{P}|_{\min}$ (bar/m)	I^{a} (m^3/bar s)
0.5	0.38	2.38×10^{-10}	1.4	1.68×10^{-5}	2.1	8.42×10^{-4}	2.3	1.68×10^{-4}
2.0	0.41	5.28×10^{-9}	2.8×10^{-1}	3.71×10^{-2}	4.4×10^{-1}	1.94×10^{-2}	5.0×10^{-1}	3.74×10^{-3}
3.0	0.42	1.32×10^{-8}	1.8×10^{-1}	9.32×10^{-2}	1.9×10^{-1}	4.73×10^{-2}	3.3×10^{-1}	9.35×10^{-3}
5.0	0.43	4.08×10^{-8}	9.7×10^{-2}	2.89×10^{-1}	1.7×10^{-1}	1.44×10^{-1}	1.8×10^{-1}	2.94×10^{-2}

[a] Calculated for $r_1 = 5$ cm, $r_2 = 50$ cm.

It must be noted that Eq. (21) applies if:

$$\frac{p_1 - p_2}{r_2 - r_1} > |\nabla \mathcal{P}_{\min}| \qquad (22)$$

Notice that (for a fixed value of p_1) if condition 22 is verified when $r = r_2$, it is certainly verified for $r < r_2$; i.e., during the whole injection process. As an example the values of the ease of injection I for creating blobs of size $r_2 = 0.50$ m and $r_1 = 0.05$ m are reported in Table 2. The blob will be about spherical if $\rho\mathbf{g}$ is negligible with respect to $(p_1 - p_2)/(r_2 - r_1)$.

4. Conclusions

The gelled polymer technology, using xanthan gum aqueous solutions is suitable for the temporary containment in urgent situations of oil (and other hydrocarbons) 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 studied using either Cr(III) or Al(III) cations. The gelation time of Xn/Cr(III) system has been measured for different xanthan and Cr(III) concentrations and using three different salts as a source of the crosslinker ions. As a general rule, the gelation time is a decreasing function of crosslinker concentration and approaches a constant value above a given concentration level (for the case at hand about 100 ppm of Cr(III)). The order of magnitude of the gelation time is strongly influenced by the salt used as the source of the Cr(III) ions. In fact, using chromium(III) sulfate hydrate or chromium(III) chloride hexahydrate the gelation time is on the order of a few hours. On the contrary using chromium(III) acetate hydroxide the gelation time is on the order of weeks. The possibility of modulating the gelation time in a large range of values may prove useful in practical applications.

The gel formation with Al(III) occurs at low pH. Therefore, acid must be added to the solution Xn/Al(III) in order to promote the gelling reaction. However, upon the addition of the acid, the gel formation is instantaneous. Therefore, the technique for generating the gel structure in situ would require the injection of the Xn/Al(III) solution first, and then the addition of an acid solution. In this case the gel formation proceeds as a moving boundary process, The pseudo-stoichiometric coefficient HCl/Xn for the gelling reaction as well as the diffusivity of the acid through the gel have been determined. These quantities permit the estimation of the acid requirement and the time necessary for creating a desired thickness of the gel layer.

The shear-thinning rheological behaviour of xanthan solutions, which show a low viscosity at high shear-rate and a viscosity larger for at least two orders of magnitude at low shear-rate, could be very helpful for the application we are considering. A high viscosity at low shear rate permits that the solution remains in place, motionless, after the injection, until the gelation takes place. A low viscosity at high shear rate makes the injection in a porous medium easier.

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