



Rheological behavior of xanthan gum solution related to shear thinning fluid delivery for subsurface remediation

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HIGHLIGHTS

- Remedial amendment and salt significantly lowered the xanthan viscosity.
- The viscosity of xanthan solutions decreases nonlinearly with salt concentration.
- Empirical relationships were developed between K and n for a power law fitting the xanthan thinning behavior.
- Xanthan degrades in days with the presence of site sediments.
- Xanthan first breaks down to smaller segments during degradation.

ARTICLE INFO

Article history:

Received 24 April 2012

Received in revised form 25 October 2012

Accepted 10 November 2012

Available online xxx

Keywords:

Xanthan gum

Rheology

Shear thinning

Degradation

Remediation

ABSTRACT

Xanthan gum solutions are shear thinning fluids which can be used as delivery media to improve the distribution of remedial amendments injected into heterogeneous subsurface environments. The rheological behavior of the shear thinning solution needs to be known to develop an appropriate design for field injection. In this study, the rheological properties of xanthan gum solutions were obtained under various chemical and environmental conditions relevant to delivery of remedial amendments to groundwater. Higher xanthan concentration raised the absolute solution viscosity and increased the degree of shear thinning. Addition of remedial amendments (e.g., phosphate, sodium lactate, ethyl lactate) caused the dynamic viscosity of xanthan solutions to decrease, but they maintained shear-thinning properties. Use of mono- and divalent salts (e.g., Na^+ , Ca^{2+}) to increase the solution ionic strength also decreased the dynamic viscosity of xanthan and the degree of shear thinning, although the effect reversed at high xanthan concentrations. A power law analysis showed that the consistency index is a linear function of the xanthan concentration. The degree of shear thinning, however, is best described using a logarithmic function. Mechanisms to describe the observed empiricism have been discussed. In the absence of sediments, xanthan solutions maintained their viscosity for months. However, the solutions lost their viscosity over a period of days to weeks when in contact with site sediment. Loss of viscosity is attributed to physical and biodegradation processes.

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1. Introduction

Contamination in heterogeneous subsurface materials poses difficulties for in situ remediation. Delivery of remediation amendments using traditional means targets the most permeable zones but typically results in a less-effective treatment for lower permeability zones. In many cases, treatment of the low permeable zones is not sufficient to meet remediation goals due to the back diffusion of contaminants from the low permeability zones. Because almost all aquifers contain some degree of heterogeneity, methods to improve in situ remediation of lower permeability zones

are needed. More specifically, the application of technologies that deliver remedial amendments into contaminated lower permeability zones is needed to improve remediation efficiency.

The flow of shear thinning fluids, usually aqueous polymer solutions, in porous media has the ability to enhance the uniformity of the injection fluid movement and reduce viscous fingering in a heterogeneous system. Shear thinning may facilitate the penetration of injected fluids into lower permeability zones [1–6]. The shear thinning fluid viscosity is a function of the shear rate, with higher shear causing lower viscosity. The shear rate is typically higher in lower permeability zones than it is in higher permeability zones and the reduced relative viscosity facilitates movement of the injected solution into the low permeability zones. The improvement in injection uniformity is a function of the shear thinning fluid rheological properties and the permeability contrast between the higher and lower permeability zones [5,6].

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Shear thinning fluids have been investigated in laboratory and field studies to facilitate remedial amendment delivery for subsurface remediation [5–10] and as stabilizer for particulate suspensions used in remediation [9–14]. Surfactant, phosphate, chemical oxidants, and zero-valent iron particles were remedial amendments used in these experimental studies or in field demonstrations. Shear thinning fluids were also used to suspend manganese dioxide particles produced from oxidation of permanganate in aqueous phase [15]. These laboratory and field studies suggest that shear thinning fluids have the potential to enhance solute and particle amendment delivery in heterogeneous systems. It is hypothesized that rheological behavior changes significantly as a result of environmental factors. An understanding of the relationships between these factors and the shear thinning fluid rheological behavior will improve the ability to design solutions for delivery of remedial amendments in the field. However, systematic rheological studies of shear thinning fluids needed to provide a design basis for injection solution formulation have not been reported.

We provide a systematic study on the rheological properties of the aqueous solutions of xanthan gum, a commonly used bio-polymer to form shear thinning fluids, and investigated the influence of environmental factors on its rheological properties. Xanthan is an extracellular polysaccharide produced by bacterium *Xanthomonas campestris*, with high molecular weight ($>2 \times 10^6$) and high water solubility [16]. It has a wide range of industrial applications, including viscosity modification and stabilization in food products (i.e., salad dressing, yogurt, and ice cream), drug delivery, personal care products (i.e., lotions, creams, body washes), and injection fluid additives in enhanced oil recovery.

The main objective of this contribution is to quantify and analyze the influence of polymer concentration, solution ionic strength (*I*), amendment type, and amendment concentration on solution rheology for several water qualities. In addition, the polymer solution viscosity degradation and the corresponding chemical oxygen demand (COD) change were obtained in systems with the presence of site sediments. The results provide useful information regarding the xanthan solution rheological behavior as a function of environmental conditions, fluid composition (including remediation amendments), and temporal degradation over time in contact with sediments.

2. Materials and methods

2.1. Materials

Xanthan gum (Kelzan XC) powder (Kelco Oil Field Group, Houston, TX) was used to form shear thinning fluids. The powder was used as received without further purification.

Amendments tested in this study include commonly used bioremediation nutrients for degradation of chlorinated compounds, and phosphate, which can facilitate uranium immobilization [17]. Sodium lactate and ethyl lactate (JWR Bioremediation, LLC, Lenexa, KS) were used as representative bioremediation substrates amendments. Sodium mono-phosphate (NaH_2PO_4 ; Aldrich Chemical Company, Milwaukee, WI) was chosen as the phosphate amendment.

Calcium chloride (CaCl_2) and sodium chloride (NaCl) were the salts used to test the influence of salinity on the rheology of the polymer solutions. Accusand sand (grade #70) and natural subsurface sediment from the Hanford formation in the U.S. Department of Energy Hanford Site in Washington State were used in selected experiments. The Hanford formation sediments consisted of 30% sand (>0.050 mm and <2 mm) and 70% gravel (>2 mm and <8 mm). Sediments from a contamination site in the Offutt Air Force Base

Table 1
Summary of experiments.

Tests	Purposes	Experimental approach
Set 1	Test the influence of ionic strength, polymer concentration, and remedial amendment on dynamic viscosity.	Polymer, salt, amendments were added to polymer solutions in batch studies. Rheology was measured.
Set 2	Test the influence of sediment (subset 2A) and polymer concentration (subset 2B) on viscosity degradation.	Sediment was added to polymer solution in test vials or bottles with the solid/liquid ratio of 1/10 and 1/13.3. Rheology was measured over time.
Set 3	Test polymer degradation in contact with sediment.	Polymer solutions were injected into packed columns. Solutions were drained from the sediment at predetermined times for rheology and Chemical Oxygen Demand (COD) measurements.
Set 4	Qualitatively verify polymer viscosity degradation in intermediate-scale flow cell systems.	Polymer solutions were injected into sediment in 2-D flow cells. The stability of polymer solutions was monitored by visual observation.

at Omaha, Nebraska were used in the polymer degradation experiments.

2.2. Methods and measurements

Four sets of tests were conducted in this study to achieve the objectives. The tests and experimental approaches are summarized in Table 1.

2.2.1. Polymer concentration, ionic strength, and amendment influence tests (Set 1)

To prepare the shear thinning fluids, xanthan powder was added to water that was being stirred with a magnetic stir bar, or was mixed with water using a blender. Only one mixing method was used in a set of tests. Polymer concentrations between 300 mg/L (0.03%) and 5000 mg/L (0.5%) were used to test the influence of polymer concentration on rheology. When complete dissolution was achieved, cations and chemical amendments at different concentrations were added to the solution batches to test their influence on rheology. Samples were taken at predetermined times for rheology measurement. Deionized (DI) water, tap water (TW) from the city water of Richland, Washington, and groundwater (GW) from the Offutt site were used for polymer solution preparation to test the influence of different source of water.

2.2.2. Polymer degradation–batch system tests (Set 2)

Two subsets of tests were conducted. Set 2A was used to study the influence of sediment on viscosity degradation of xanthan solutions. 800 mg/L xanthan solution in TW was prepared and three solution-sediment combinations were made: xanthan solution with no sediment, with Accusand (Unimin, IL), and with Hanford sediment. 50 mL of polymer solution was used in each batch setup, and 5 g of sediment was added to the system at the start of test as needed. The batches were placed on a rotator to ensure continuous mixing and a homogeneous sediment distribution in the system. Set 2B was conducted to test the influence of polymer concentration on viscosity degradation in the presence of site sediment, using solutions at 600, 800, 1200, 1600, and 2000 mg/L. 1000 mL of each solution was contained in a bottle and 75 g of Hanford Site sediment enclosed in bags made of 100 μm filtration screens was added to each bottle. A bottle with 1000 mL of 800 mg/L xanthan gum solution without sediment was set up as a control. The batches were placed in a 17 °C water bath. The solution-sediment bag systems were stirred once a day. Samples

were taken for rheology measurement at 0.25 h, 168 h (1 week), 336 h (2 weeks), and 504 h (3 weeks). The sediment in the xanthan solution was allowed to settle to separate the sediment grains from the solution before rheology measurement.

2.2.3. Polymer degradation and COD-packed column tests (Set 3)

Sediment packed columns were used to study the polymer degradation and solution COD change in settings with field solution/sediment ratio. 1500 mg/L xanthan solution prepared in TW was injected into columns packed with sediments from the Offutt site. Columns with a length of 12.5 cm and a 5.0 cm internal diameter were used. Solutions were drained or pushed out with nitrogen gas at 10 min, 168 h (1 week), 504 h (3 weeks), and 1512 h (9 weeks) for sampling. Each sample consisted of 6 mL, of which 4 mL was used for a rheology measurement and 2 mL for COD determination.

2.2.4. 2-D Flow cell experiments (Set 4)

Two intermediate-scale two-dimensional (2-D) flow cell experiments, FC-1 and FC-2, were conducted to improve the understanding of xanthan solution rheological behavior in contact with sediments under continuous flow conditions. The FC-1 test was conducted with Accusand (20/30 mesh), and the FC-2 test was performed using a Hanford site sediment mixture. Both experiments were conducted in a 0.5-m-long, 0.4-m-tall, and 0.05-m-wide flow cell.

The flow cell was packed under saturated conditions to avoid entrapping of air bubbles. The average porosity and dry bulk density values for the site sediment mixture were 0.32 and 1.82 g/cm³, respectively. The xanthan solution was not dyed and water was dyed blue in FC-1, while the polymer solution was dyed with a red food dye at 100 mg/L concentration but water was not colored for FC-2. The influence of the dye on the rheology is negligible [6]. Denoting the left-bottom corner of the flow cell as (x —horizontal direction, z —vertical direction) = (0 cm, 0 cm), the polymer solutions were injected at (x, z) = (20 cm, 20 cm) at a concentration of 5000 mg/L with a rate of 50 mL/min for six minutes. Water flow with a rate of 0.20 cm/min. was applied to the left hand side of the flow cell. The water level in the constant-head chamber was kept at $z = 0.4$ m. Water flow was kept constant during the xanthan solution injection, and was continued through the whole testing period. In FC-1, water without dye was injected through the flow cell after 2 weeks flushing with blue-dyed water to observe changes inside the xanthan blob. Pictures were taken throughout the experiments.

2.2.5. Rheology and COD measurement

A rotational rheometer Physica MCR 101 (Anton Paar USA Inc., Ashland, VA) was used for the rheology measurements. The shear rate measurement range was between 0.1 s⁻¹ and 200 s⁻¹. A built-in temperature control chamber enabled the setting of desired temperatures for measurements. All the samples were measured at 25 ± 0.1 °C. The COD was determined using Standard Methods 5520 C [18]. Samples and standards were placed in screw-top ampules, and heated in the presence of K₂Cr₂O₇, H₂SO₄ (50%), and Ag₂SO₄ for two hours at 150 °C. After cooling, samples, blanks and standards are titrated with ferrous ammonium sulfate in the presence of Ferroin indicator to determine the amount of excess dichromate. The amount of dichromate consumed by the sample is used to calculate the total amount of oxygen that could be consumed by organic and oxidizable inorganic substances in the sample.

3. Results and discussion

The impacts of polymer concentration, solution ionic strength and composition, amendment type and concentration, and contact

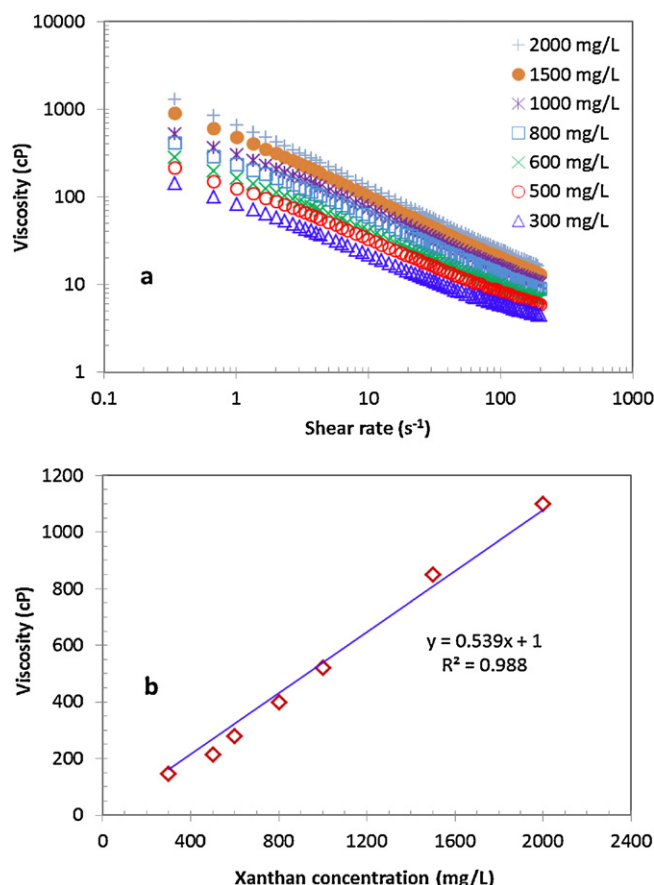


Fig. 1. (a) Viscosity as a function of shear rate, and (b) Viscosity at low shear rate (0.3 s⁻¹) for several xanthan concentrations. All solutions were made in de-ionized water.

with sediments on the properties of the solution are presented below.

3.1. Polymer concentration

The shear thinning behavior of the xanthan in DI water solutions is shown in Fig. 1a. The viscosity at high shear rate (200 s⁻¹) was more than one order of magnitude lower than that at low shear rate (0.3 s⁻¹). At low shear rate the solution viscosity increased linearly with the increase of xanthan concentration within the range from 300 mg/L to 2000 mg/L (Fig. 1b).

The static viscosity and shear-thinning behavior of xanthan solutions are related but not proportional to the xanthan concentration over a wide range. Choppe et al. [19] reported an exponential relationship of the solution viscosity with the xanthan concentration when it was higher than 2000 mg/L. They observed deviation from the exponential relationship when the concentration was lower than 2000 mg/L, where the relationship was not defined. This study revealed that a linear relationship existed at lower concentrations when no salt was added to the solution. Garcia-Ochoa et al. [16] reported an exponential viscosity vs. xanthan concentration relationship for the concentration range from 1000 mg/L to 2000 mg/L when 1000 mg/L of NaCl was added to the solutions. This study and previously published data show a complicated correlation between xanthan concentration and viscosity. While there have been no quantitative studies on the mechanisms causing the observed viscosity-concentration relationship, the increase of viscosity with increasing xanthan concentration has been attributed to intermolecular interaction or entanglement that increases the effective macromolecule dimensions and molecular weight [20].

Although the shear-thinning curves in Fig. 1a looked similar to each other for all the solutions, the degree of shear thinning for a solution changed as a function of the xanthan concentration. For a shear thinning fluid, the shear rate dependence of viscosity can be well described by the power law equation [21]:

$$\eta(\dot{\gamma}) = K\dot{\gamma}^{-n} \quad (1)$$

where $\eta(\dot{\gamma})$ is the viscosity, $\dot{\gamma}$ is the shear rate, K is the consistency index (i.e., the solution viscosity at $\dot{\gamma} = 1.0 \text{ s}^{-1}$), and n is the flow behavior index. When $n = 0$, Newtonian flow behavior occurs. For larger n values, the shear thinning nature of the solution is more pronounced. The shear thinning curves in Fig. 1a were fitted to Eq. (1) using power law regression. The fitted K and n values, as well as the coefficient of determination, R^2 , are listed in Table 2. The results indicate an increased consistency and degree of shear thinning, i.e., potential of shear thinning, with increasing xanthan concentration. An analysis of the results in Table 2 is presented in Section 3.3.

3.2. Solution ionic strength and composition

Xanthan rheology was influenced by solution ionic strength and specific ions in solution. The influence of sodium and calcium ions on the rheology of 600 mg/L xanthan solutions is shown in Fig. 2a and b, respectively. When cations were initially added to the ion-free xanthan solution, the viscosity decrease was significant, and further addition of ions to the system resulted in less impact on viscosity. For Na^+ , when concentration increased from 0 mg/L to 25 mg/L, the viscosity at a shear rate of 0.3 s^{-1} decreased from 282 cP to 80 cP (72% decrease). However, an additional concentration increase from 25 mg/L to 50 mg/L only resulted in a viscosity decrease from 80 cP to 64 cP (5.7% decrease). The figures show that the impacts of NaCl and CaCl_2 solutions on rheology behavior over a large range of shear rates are similar. The similarity between the two salts is also obvious for the relation between ionic strength and viscosity at low shear rate (Fig. 2c), indicating that for ionic strengths in the tested range greater than $\sim 1.5 \text{ mmol/L}$, the low-shear rate viscosity is not negatively affected. The influence of Na^+ and Ca^{2+} on xanthan solutions at 300, 500, 800, and 1000 mg/L polymer concentrations were also tested and similar influence patterns were observed (data not shown).

Eq. (1) was fitted to the curves shown in Fig. 2a and b. The fitted K and n values and the coefficient of determination, R^2 , are listed in Table 3. The decrease in n values with increasing concentration or ionic strength clearly indicates the reduction in the degree of shear thinning. The consistency index of the solutions also decreases with ionic strength, which might be a concern for field applications. The data presented in Table 3 is further analyzed in Section 3.3.

At high xanthan concentrations, addition of cations to the solution did not lower its viscosity but instead increased the solution viscosity and the degree of shear thinning. For the 5000 mg/L xanthan solution, the addition of 200, 500, and 1000 mg/L Ca^{2+} increased the viscosity considerably from 6920 cP to 25,600 cP, 29,900 cP, and 33,000 cP, respectively (Fig. 3). In the solution with 1000 mg/L Ca^{2+} , the viscosity increase was more than 475% compared with that of solution without Ca^{2+} . By fitting Eq. (1) to the shear thinning curves of the solutions with no salt and with 1000 mg/L Ca^{2+} (Fig. 3), it was shown that the addition of salt not only caused an increase in the consistency index, but also increased the degree of shear thinning of the solution as indicated by the fitted n values (0.85 vs. 0.72). Pastor et al. [20] and Wyatt et al. [22] also observed the increase in xanthan solution viscosity with salt addition when the polymer concentration was higher than 2000 mg/L.

The results shown in Figs. 2 and 3 demonstrate that at low xanthan concentration, addition of salt lowered the solution viscosity, while at higher xanthan concentration, salt addition increased the viscosity. This kind of information is useful for field applications,

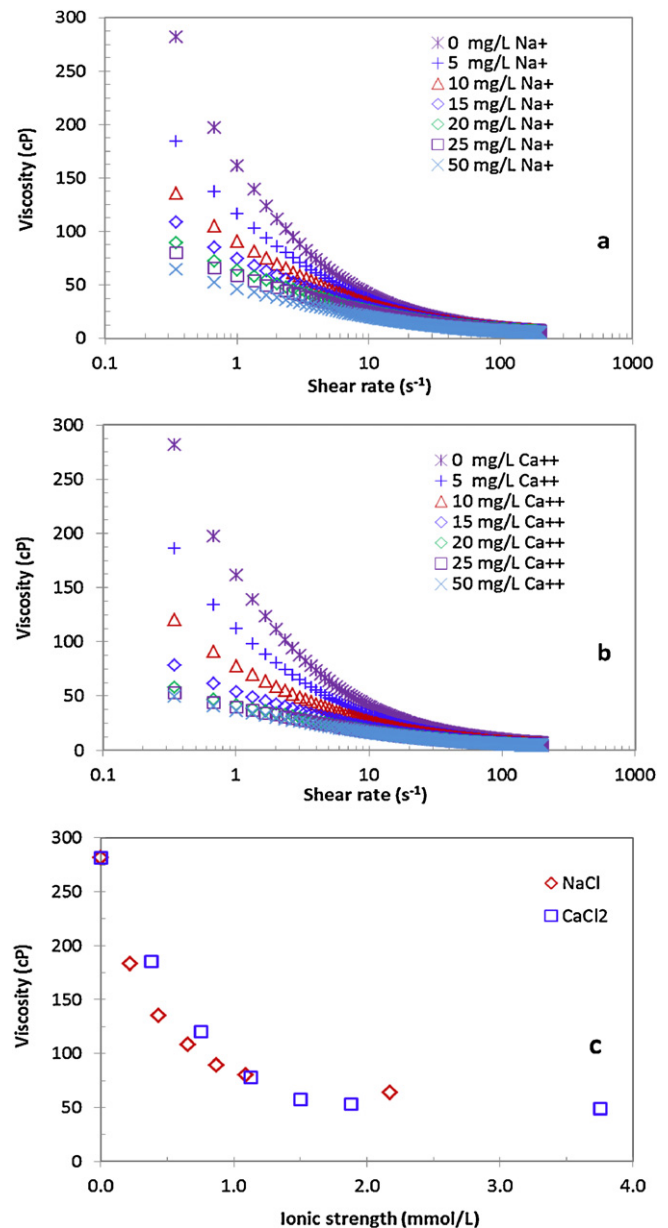


Fig. 2. Influence of Na^+ and Ca^{2+} ions on 600 mg/L xanthan solution rheology: (a) shear thinning curve for solutions with Na^+ ; (b) shear thinning curves for solutions with Ca^{2+} ; (c) viscosity of solutions with different ionic strength at $\dot{\gamma} = 0.3 \text{ s}^{-1}$.

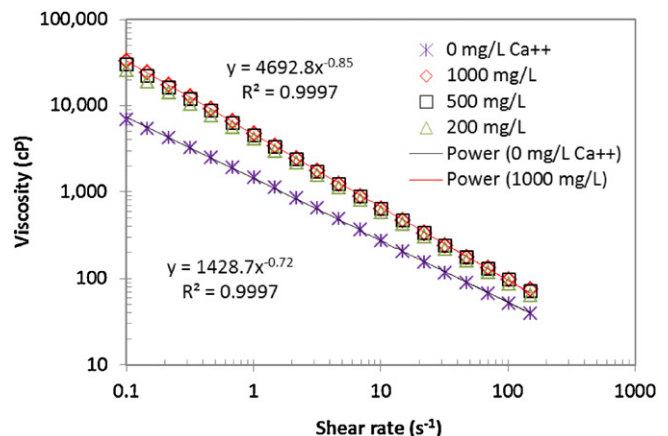


Fig. 3. Influence of Ca^{2+} on 5000 mg/L xanthan gum solution rheology.

Table 2Influence of xanthan concentration on shear thinning fluid rheology: Fitted K and n values according to Eq. (1) including the R^2 values.

Xanthan conc. (mg/L)	300	500	600	800	1000	1500	2000
K	71.80	119.09	162.29	242.43	316.36	481.57	652.63
n	0.54	0.58	0.61	0.64	0.65	0.69	0.71
R^2	0.991	0.996	0.996	0.999	0.999	0.998	0.998

Table 3Influence of salinity on shear thinning rheology of 600 mg/L xanthan solutions: Fitted K and n values according to Eq. (1), including R^2 values.

Influence of NaCl							
Na ⁺ conc. (mg/L)	0	5	10	15	20	25	50
I (mmol/L)	0.00	0.22	0.43	0.65	0.87	1.09	2.17
K	162.29	131.58	106.57	88.81	76.02	69.85	54.45
n	0.61	0.57	0.53	0.51	0.49	0.47	0.45
R^2	0.996	0.998	0.997	0.997	0.997	0.996	0.996
Influence of CaCl ₂							
Ca ²⁺ conc. (mg/L)	0	5	10	15	20	25	50
I (mmol/L)	0.00	0.38	0.75	1.13	1.50	1.88	3.75
K	162.29	117.90	86.83	62.57	49.62	46.85	43.55
n	0.61	0.57	0.53	0.49	0.46	0.45	0.44
R^2	0.996	0.996	0.996	0.996	0.995	0.995	0.995

although the relatively high viscosities of the higher xanthan concentrations might preclude usage in actual injection scenarios. It should be noted that Wyatt et al. [22] showed that a critical xanthan concentration of ~2000 mg/L can be defined for concentration regions where added salt neither lowers nor increases the viscosity.

The effects of salt concentration on shear thinning viscosity can be explained in terms of molecule confirmation states. It is believed that a xanthan molecule exhibits two different conformational states: ordered and disordered [23,24]. In the ordered conformation, the side chains are folded in and associated with the backbone, forming helix molecular conformation. In the disordered conformation, also referred as extended configuration, the side chains project away from the backbone and the molecule occupies a larger hydrodynamic volume. The disordered conformation occurs in salt free solution, where strong Columbic repulsions between like charges along the polyelectrolyte backbone stretch and elongate individual chains. At low xanthan concentration (<2000 mg/L), addition of salt neutralizes the ionic charge of xanthan molecules. As a result, the elongated molecules are therefore transformed into helix molecular conformation, which occupy smaller hydrodynamic volume. Therefore, addition of salt reduces the solution viscosity.

When the polymer concentration is larger than the critical concentration, the interaction among the intermolecular bonds increases, and its effect on solution viscosity is relatively more important than the effect caused by the change in hydrodynamic volume of molecules [20]. It has been hypothesized that, with salt addition, local charge inversion and subsequent chain expansion between polymer molecules entanglements increases the viscosity. It has been further hypothesized that ion bridging occurs where either an inter- or intra-molecular ionic “crosslink” is formed. Under these conditions, the salt induced bridging between polymer chains would introduce a stiffer network, resulting in increased viscosity [25].

As stated above, even relatively low concentrations of mono- and di-valent cations may considerably impact xanthan rheology. The influence of water composition on rheology is important because for field applications, either tap water (TW) or pumped groundwater (GW), both containing cations, are cost-effective water sources. For that purpose, the rheology of xanthan gum solutions made with TW and GW from the Offutt site was studied and compared with that of solutions prepared with DI water. As is shown in Fig. 4, both TW and GW considerably lowered the solution

viscosity and the impact of both waters was greater when the polymer concentration was lower. For example, the viscosity of the TW xanthan solution was 36.0%, 23.0%, and 8.9% of the 800 mg/L, 600 mg/L, and 300 mg/L equivalent xanthan solution in DI water, respectively (Fig. 4a). The Offutt site GW lowered the viscosity of the

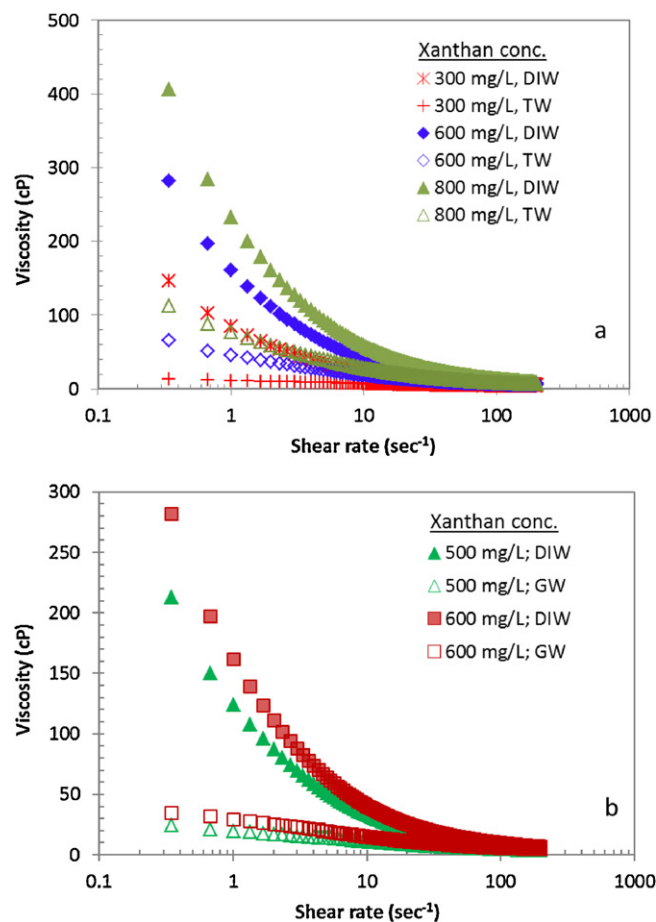


Fig. 4. Influence of water source on xanthan solution rheology: (a) DI water and TW; (b) DI water and Offutt GW.

Table 4Influence of water source on shear thinning fluid rheology: Fitted K and n values according to Eq. (1) including R^2 values.

Xanthan conc. (mg/L)	300		500		600			800	
	DIW	TW	DIW	GW	DIW	TW	GW	DIW	TW
K	71.80	12.82	119.09	23.64	162.29	53.21	35.25	242.43	88.67
n	0.54	0.30	0.58	0.35	0.61	0.47	0.40	0.64	0.52
R^2	0.991	0.983	0.996	0.992	0.996	0.995	0.993	0.999	0.997

DIW: de-ionized water; TW: tap water; GW: groundwater.

500 mg/L xanthan solution by 90% and that of the 600 mg/L solution by 88% (Fig. 4b). These observations imply that when a certain viscosity level is required in the field application to achieve improved delivery, an increased polymer concentration may be required to account for the influence of using TW or GW.

The shear thinning curves in Fig. 4 were also fitted with Eq. (1). The fitted K and n values and the coefficient of determination, R^2 , are listed in Table 4. The decrease in K values for solutions prepared with TW and GW compared with that for solutions in DIW indicate the loss of viscosity and are consistent with the findings for salt additions shown in Table 3. In addition, the lower n values demonstrate a reduction in the shear thinning potential. An analysis of the data in this table follows in the next section.

3.3. Analysis of the effects of xanthan concentration and ionic strength on xanthan rheology

The R^2 values of the Eq. (1) fitting to the various shear thinning curves shown in Figs. 2–4 indicate that the rheological behavior of the xanthan solutions is well described by the power law model (Tables 2–4). To investigate the relationship between both the xanthan concentration and the ionic strength on the fitted rheology parameter (K and n) values, the fitted values in Tables 2–4 were plotted against the xanthan concentration (Fig. 5a) and solution

ionic strength (Fig. 5b). Linear trend lines with high R^2 values could be fitted to the K vs. xanthan concentration data for the DI water and TW solutions, which were forced through intercept of (0, 1) to recognize that for a xanthan concentration of 0 mg/L, the DI water and the TW viscosity is approximately 1 cP (Fig. 5a). The consistency index, K , representing the solution viscosity at 1.0 s^{-1} shear rate, is smaller than the viscosity value at $\gamma = 0.3 \text{ s}^{-1}$ for the same DI water solutions, as shown in Fig. 1b. This observation is due to the shear thinning behavior of the solutions, i.e., the viscosity was lower at higher shear rate. The slopes of the fitted lines in Fig. 1b and Fig. 5a are 0.539 and 0.315, respectively. The higher slope at the lower shear rate (Fig. 1b) indicates that shear thinning is greater at higher xanthan concentrations. In other words, the viscosity drop from $\gamma = 0.3 \text{ s}^{-1}$ to $\gamma = 1.0 \text{ s}^{-1}$ is larger for solutions with a higher xanthan concentration. This observation was also indicated by the relationship of fitted n with xanthan concentration plotted in Fig. 5a. In Fig. 5a, the slope of the line fitted to DIW (0.315) is considerably higher than the slope of line fitted to TW (0.096), demonstrating again the impact on salt concentrations on rheology. This result, further explained in this section below, strongly indicates that interested users should independently determine the K –concentration relationship if a water source containing salt will be used. As is also shown in Fig. 5a, the n vs. xanthan concentration data were best fitted with logarithmic trend lines. The value of plots

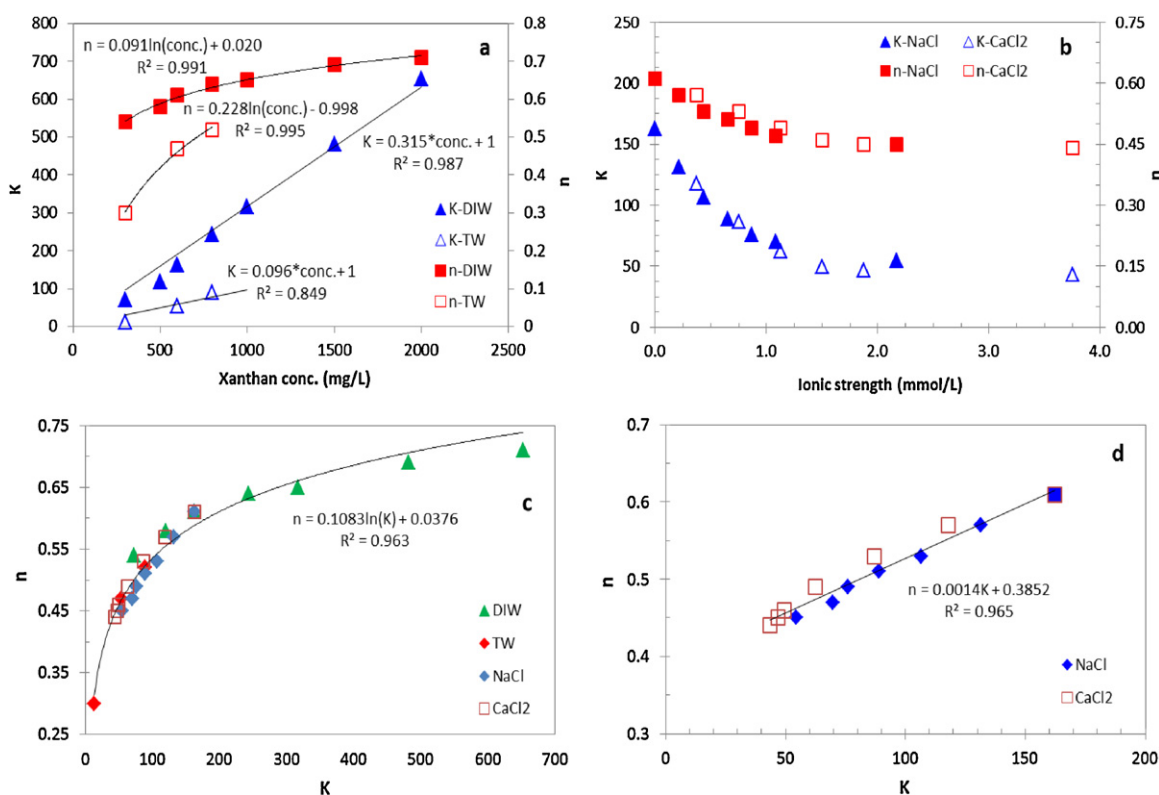


Fig. 5. Power law fitting parameters K and n vs. (a) xanthan concentration and (b) ionic strength. K vs. n relations for (c) xanthan solutions with various polymer concentration and salt solutions, and for (d) solutions with salt additions only. The xanthan concentration in Fig. 5b and d is 600 mg/L.

shown in Fig. 5a is that over a range of xanthan concentrations, fitted K and n value can be computed that can be directly used in field application designs.

The influence on viscosity and degree of shear thinning were negligible between the two salts for the same ionic strength (Fig. 5b). The impact of ionic strength was more pronounced at lower salt concentrations. At higher concentrations, the change in K and n diminished until an asymptotic value was obtained. The same trend was observed for K in Fig. 2, where the viscosities were measured at $\gamma = 0.3 \text{ s}^{-1}$, and supports the notion that above an ionic strength threshold, the rheology for a certain xanthan solution does not change anymore.

Fig. 5c and d shows examples of how relations between K and n values might be used. In Fig. 5c, all data in Tables 2–4 are lumped together and best fitted with a logarithmic curve. The high R^2 value indicates that this approach may be used to relate the parameters over a considerable range in polymer concentration and solution ionic strength. Such an empirical model or nomograph might be useful because only a K value is needed to effectively obtain the accompanying n value to fully parameterize Eq. (1). The K value might be obtained from Fig. 1b or experimentally obtained by determining the viscosity at $\gamma = 1.0 \text{ s}^{-1}$. Although a nomograph as shown in Fig. 5c might have a broad appeal and be useful for scoping investigations, higher quality linear relations might be obtained for specific solutions. An example is shown in Fig. 5d for just the NaCl and CaCl₂ salt additions.

Although the plots in Fig. 5 describe useful empirical relations for several xanthan solutions, it is important to investigate potential mechanisms behind these relationships. Xanthan solutions have high viscosity and exhibit a profound shear thinning behavior, even at low concentrations. Studies on the mechanisms behind the unique rheological behavior of these solutions started nearly four decades ago [16,19–22,26–40]. Although considerable progress has been made, a full understanding has not been achieved. In general, when the xanthan concentration increases, the polymer intermolecular interaction, entanglement, and aggregation increase [16,40], and therefore a solution has a larger K value, i.e., exhibits a higher viscosity. Examples of how these mechanisms manifest themselves can be seen in Fig. 5a. The shear thinning of xanthan solutions is attributed to the orientation of the rod-like polymer molecules on the shear flow direction [21] and the reducing on molecule aggregation in shear flow [40]. It is speculated that at higher xanthan concentrations, the molecule re-orientation and the breaking of molecular aggregation should be easier when shear is applied to the solution, and, therefore, a higher degree of shear thinning is observed. This mechanism is also apparent in Fig. 5a for the trend in n values. The mechanism of lowering the xanthan solution viscosity by addition of salts has already been discussed in Section 3.2, and applies also to the relationship between the fitted K and ionic strength as shown in Fig. 5b. When salt is added to a xanthan solution, the polymer molecules change conformation and reduce hydrodynamic volume [28,39,41]. These changes may result in a reduced potential of shear thinning, as indicated by the n vs. ionic strength relationship in Fig. 5b. Furthermore, the ionic strength of tap water reduced the solution viscosity as shown by the lower K values in Fig. 5a.

3.4. Amendment type and concentration

Amendments to xanthan solutions might contain ionic and non-ionic compounds and might alter the ionic strength [6]. Of interest in this contribution is to test specific amendments to see if their impacts are different than just the type of compounds present in GW or TW. As is shown in Fig. 6, the addition of almost 5 g/L PO₄ to xanthan solutions significantly modified their rheological properties at the tested concentrations. PO₄ lowered the viscosity

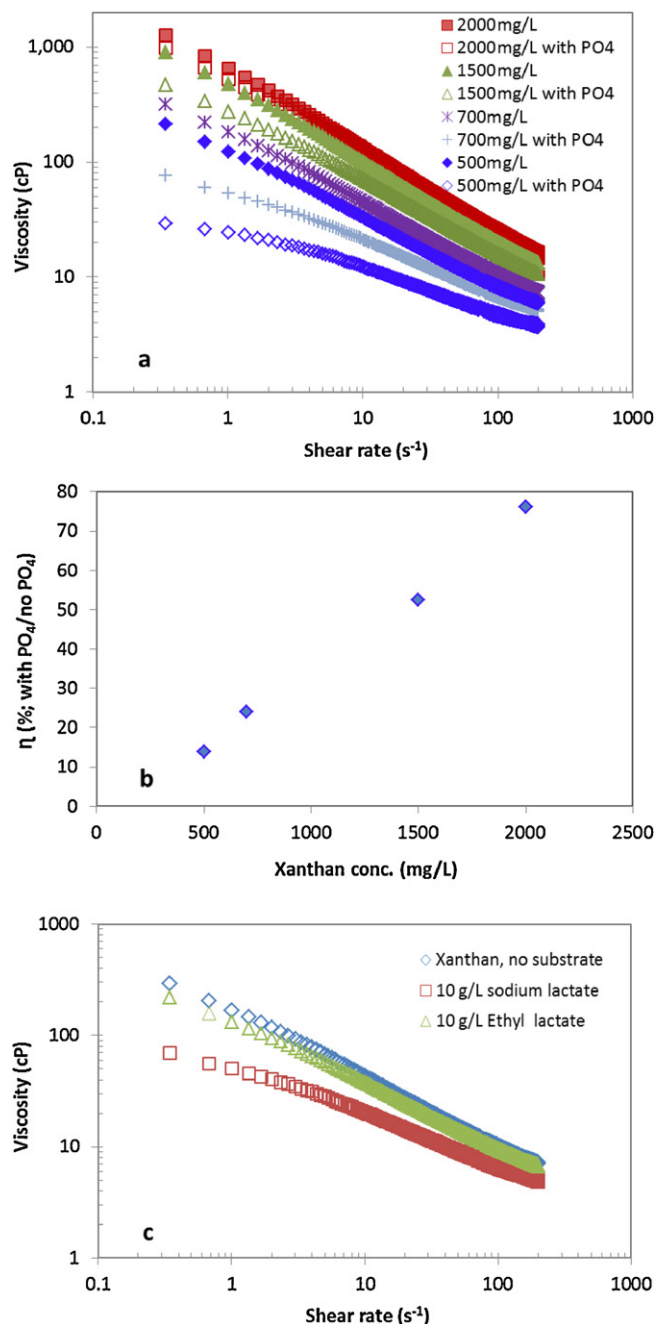


Fig. 6. Remedial amendment influence on xanthan solution rheology: (a) influence of PO₄; (b) viscosity reduction at $\gamma = 0.3 \text{ s}^{-1}$ due to PO₄; (c) influence of lactate.

of the solutions and also decreased the degree of shear thinning (Fig. 6a). However, significant shear thinning behavior was still observed for the solutions with the presence of PO₄. When the same concentration of PO₄ was added to solutions at different xanthan concentrations, the viscosity decrease was more pronounced in the solutions with lower concentrations compared to the solutions with higher concentrations (Fig. 6b). At 500 mg/L xanthan concentration, the viscosity reduction at 0.3 s^{-1} shear rate was more than 85%; while at 2000 mg/L concentration, the viscosity was lowered less than 25%.

Sodium lactate and ethyl lactate (both at 10 g/L) lowered the viscosity of 700 mg/L xanthan gum solutions while the solutions still showed shear thinning behavior (Fig. 6c). Sodium lactate lowered the viscosity at 0.3 s^{-1} shear rate by 76% and the ethyl lactate decreased the viscosity only by 25% (Fig. 6c). The significant

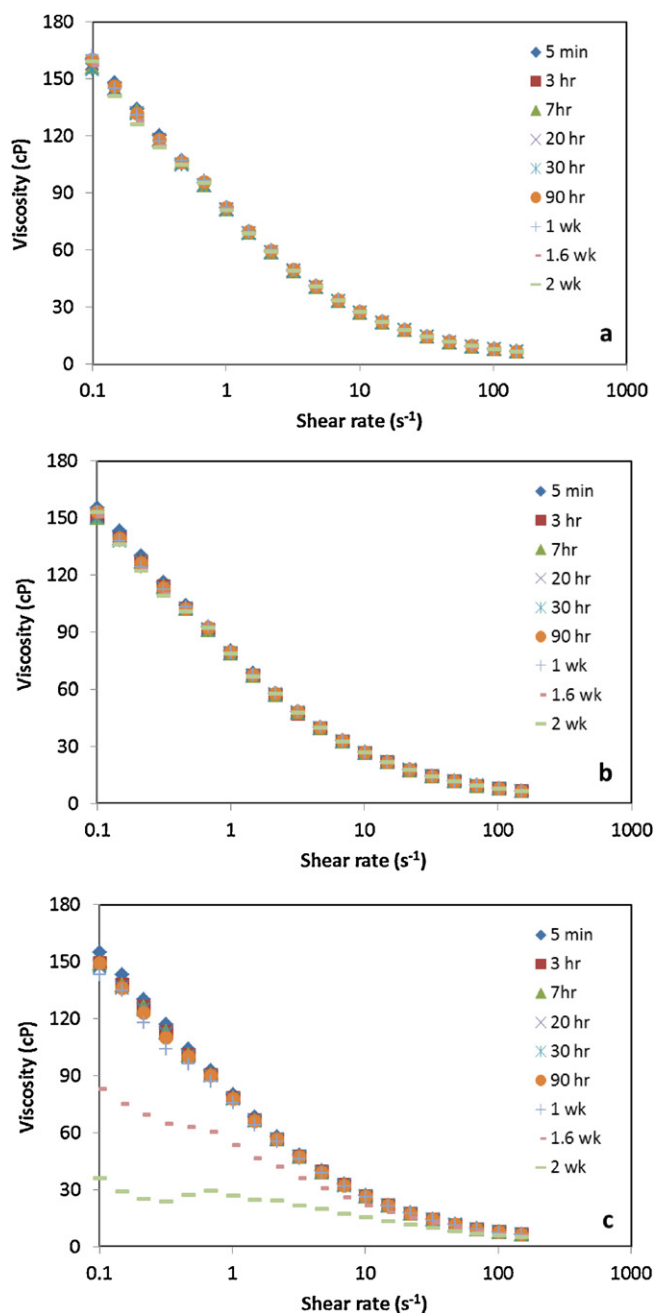


Fig. 7. Sediment influence on 800 mg/L xanthan solution viscosity: (a) no sediment; (b) Accusand; (c) Hanford site sediment.

difference between the viscosity impacts of the two substrates was presumably due to the presence of Na^+ in the sodium lactate ($\text{C}_3\text{H}_5\text{NaO}_3$) while there was no salinity in ethyl lactate ($\text{C}_5\text{H}_{10}\text{O}_3$). When higher viscosity is desired for substrate delivery in corresponding to the aquifer heterogeneity settings, ethyl lactate is preferred over sodium lactate.

The results of Eq. (1) fits to the curves in Fig. 6a and c are listed in Table 5. The data in the Table show that when an amendment addition showed more impact on the solution viscosity, the reduction in shear thinning potential was also more significant.

3.5. Contact with sediment in batch and column test systems

In the batch tests, when no sediment was added to the xanthan-in-TW solution (800 mg/L), the viscosity kept its initial value for

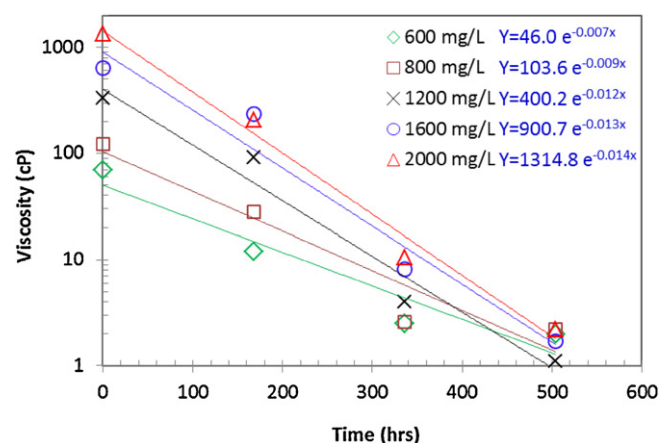


Fig. 8. Xanthan concentration influence on viscosity degradation rate. Plotted are the viscosities at $\gamma = 0.3 \text{ s}^{-1}$ vs. degradation time. The viscosity values were fitted with exponential regression to evaluate the degradation rate. The fitting equations are shown in this figure. The xanthan solutions were prepared with 52.7 mM PO_4 in TW.

336 h (2 weeks) (Fig. 7a). Similarly, a xanthan-in-DI water solution maintained its initial viscosity for 1680 h (10 weeks). When Accusand was added to the xanthan-in-TW solution (800 mg/L), the viscosity was maintained for over 336 h (2 weeks) (Fig. 7b.). However, when Hanford sediment was present, the solution started to lose its viscosity after 168 h (1 week). At 336 h (2 weeks), the viscosity at 0.1 s^{-1} shear rate was only 24% of the initial value (Fig. 7c.).

In the batch degradation tests with multiple xanthan concentrations, the viscosity for the solutions mixed with sediments dropped

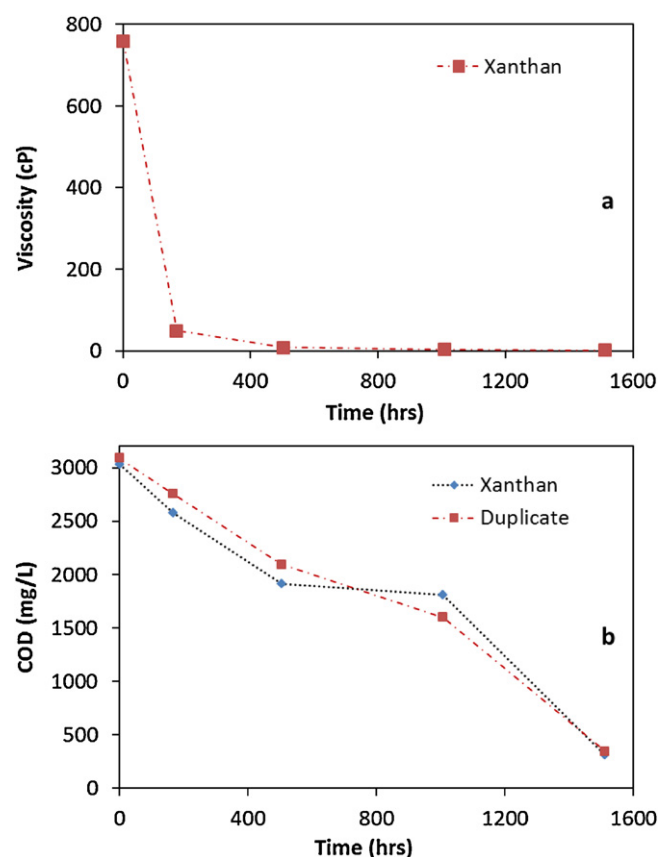


Fig. 9. Xanthan gum degradation: (a) solution viscosity vs. time for $\gamma = 0.3 \text{ s}^{-1}$; (b) chemical oxygen demand (COD) vs. time. All solutions originated from packed site sediment columns.

Table 5
Influence remedial amendment on shear thinning fluid rheology: Fitted *K* and *n* values according to Eq. (1) including *R*² values.

Influence of PO ₄ amendment								
Xanthan conc. (mg/L)	500		700		1500		2000	
	DIW	With PO ₄	DIW	With PO ₄	DIW	With PO ₄	DIW	With PO ₄
<i>K</i>	119.09	27.94	183.81	62.13	481.57	303.54	652.63	563.50
<i>n</i>	0.58	0.38	0.62	0.48	0.69	0.64	0.71	0.69
<i>R</i> ²	0.996	0.993	0.997	0.996	0.998	0.999	0.998	0.999
Influence of ethyl lactate and sodium lactate with xanthan conc. of 700 mg/L								
	DIW		E. lact.		S. lact.			
<i>K</i>	183.81		141.11		57.48			
<i>n</i>	0.62		0.58		0.47			
<i>R</i> ²	0.997		0.997		0.997			

DIW: de-ionized water.

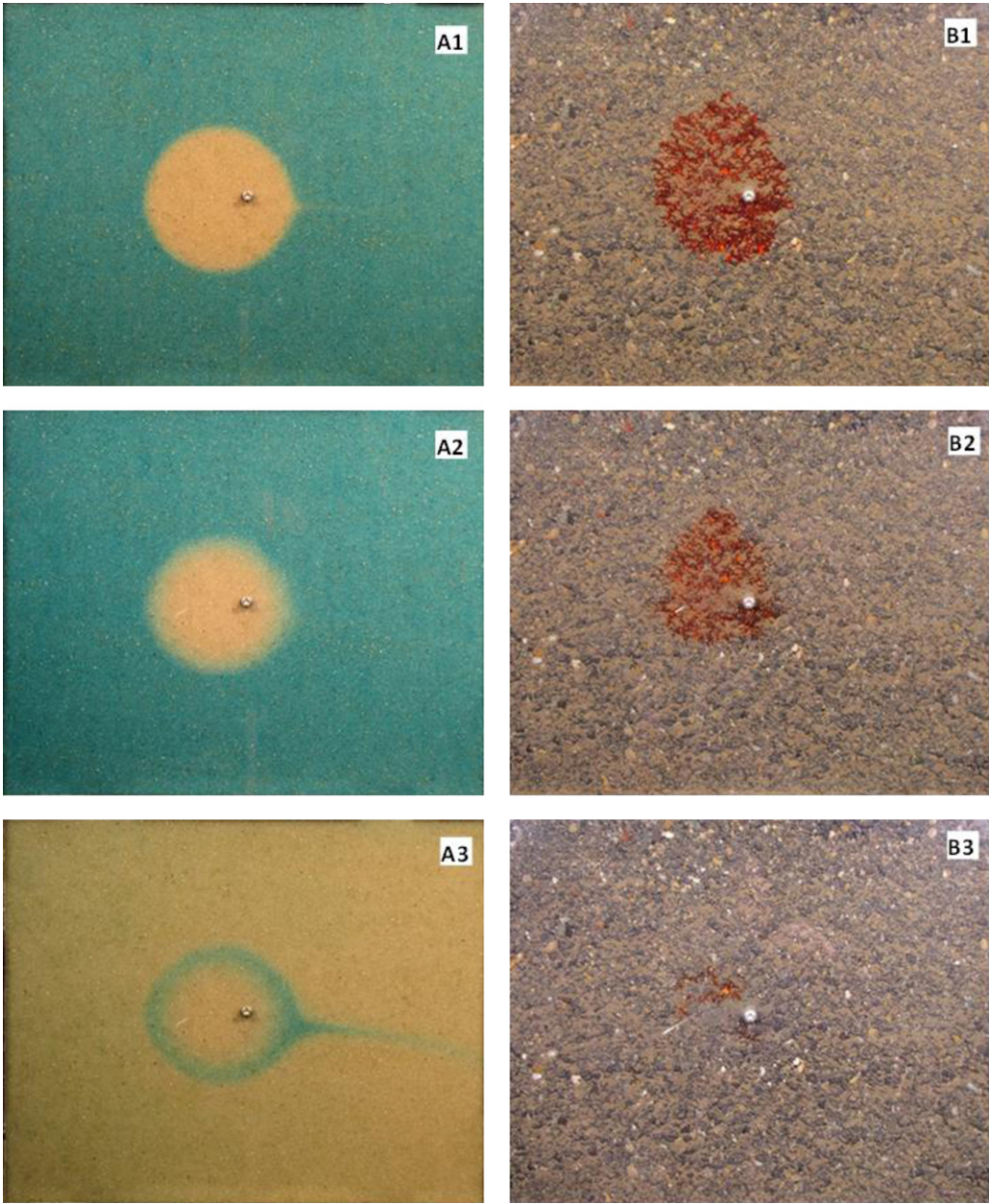


Fig. 10. Distribution of xanthan solution in sediments in flow cell experiments FC-1 (A1, A2, A3) and FC-2 (B1, B2, B3). A1, A2: solution in Accusand after 0d, 10d water flushing, respectively; A3: after flushing with clear water in the 14th day. B1, B2, B3: solution in Hanford site sediment after 0d, 10d, and 14d water flushing, respectively. The polymer solution injection rates and water flushing flow rates were the same for FC-1 and FC-2 tests.

more than 65% after 168 h (1 week), and more than 95% after 336 h (2 weeks) (Fig. 8). After 168 h of degradation, the solutions still exhibited shear thinning prosperity; but after 336 h of degradation, shear thinning behavior was not observed. Exponential regression was applied to the viscosity values to evaluate the xanthan degradation rate. The fitting equations are shown in Fig. 8. Solutions with higher xanthan concentrations showed higher degradation rate. In the control test where no sediment was added, the solution viscosity kept its initial value throughout the testing period (data not shown).

In the degradation test where the xanthan solution was in contact with the Offutt sediment in packed columns, the solution lost 93.5% of its initial viscosity in the first 168 h (1 week) and more than 98.5% in the first 504 h (3 weeks; Fig. 9a). The COD of the solution had a much slower degradation rate: After 168 h (1 week), the COD decreased by only 10.9% of the initial concentration, while after 504 h (3 weeks), the COD decreased by 32.2% of the initial concentration (Fig. 9b). Because the solution viscosity is linearly related to the xanthan concentration (Fig. 1b), the rapid viscosity decrease shown in Fig. 9a may lead to a conclusion that the xanthan concentration in the solution also decreased at a similar rate, i.e., the xanthan molecules were fully degraded. However, the COD data shown in Fig. 9b implied that the xanthan degradation was not as fast as the decrease in viscosity. It is possible that the xanthan molecules were broken down into shorter chains, reducing the viscosity, which is consistent with the findings of Renaud et al. [42] and Milas et al. [43] who demonstrated that viscosity of xanthan solutions is a nonlinear function of the average molecular weight. Our results suggest that in the xanthan degradation process, a considerable amount of the xanthan molecules quickly break down into shorter segments with a reduced molecular weight, resulting in a nonlinear loss of solution viscosity. The molecules can continue to degrade and may eventually be mineralized, causing the solution to lose its shear-thinning property.

3.6. Contact with sediments in a 2-D flow cell system

The injection of 5000 mg/L xanthan solution into Accusand in the flow cell displaced the blue-dye water and formed a regular spherical xanthan solution blob in the laboratory sediment as shown in Fig. 10, A1. This process was due to the higher viscosity of the xanthan solution and the even distribution of porosity in the Accusand. It was shown that over time, the xanthan blob did not move considerably towards the outflow end of the flow cell (Fig. 10, A2). The stability of the blob was the result of the high viscosity of the xanthan solution. After two weeks, flushing of water without dye revealed considerable diffusion of the blue dye into the xanthan solution blob (Fig. 10, A3). The size and shape of the xanthan blob, outlined by the blue color in Fig. 10 A3, indicated that blob remained mostly unchanged after 14 days within the laboratory sediment.

Due to local variations in porosity, the injected 5000 mg/L xanthan solution formed a somewhat irregular blob in the flow cell packed with the Hanford sediment (Fig. 10, B1). The xanthan blob remained fairly constant for the first week. After that, the xanthan solution was washed away by the flowing water, and a rapid decline in size took place resulting in a ~50% reduction after 10 days (Fig. 10, B2), and almost complete disappearance after 14 days (Fig. 10, B3), indicating substantial viscosity reduction in the polymer solution.

The persistence of xanthan solution in the Accusand for over 2 weeks and the washing away of the same xanthan solution starting after a 10 day duration in the Hanford site sediment was qualitatively in consistent with the observation from the batch experiments described in Section 3.4; that is, clean laboratory sand had a smaller impact on xanthan rheology than the impact of a site sediment.

The xanthan polymer solution has been shown to preserve up to 60% of its initial viscosity 300 days after injection for enhanced oil recovery application [44]. Faster biodegradation of the xanthan gum is anticipated in a GW setting due to more microbial degradation [45]. The relatively quick decrease in viscosity of xanthan in the presence of sediment implies that the solution will be washed away in a short time after injection.

4. Conclusions

Shear thinning xanthan solutions can be used to enhance the remedial amendment delivery into low permeability zones in subsurface heterogeneous formations. The influence of (1) polymer concentration, (2) solution ionic strength and composition, (3) remedial amendment type and concentration, (4) interactions with sediments, and, (5) polymer degradation on the rheology of the shear thinning solution were studied. The solution viscosity increased linearly with polymer concentration when the concentration was lower than 2000 mg/L. The viscosity of the xanthan solution was substantially lowered when salt was added. The degree of shear thinning of the solution was also decreased. However, when the polymer concentration was increased to and beyond a critical concentration of about 2000 mg/L, addition of salt increased the solution viscosity. Polymer solutions prepared with tap water and groundwater had much lower viscosity compared to solutions prepared with deionized water, presumably due to the ionic strength and composition of these waters. Addition of remedial amendments to the xanthan solution also significantly lowered its viscosity. When the polymer concentration was increased, the influence of salt and amendment additions decreased. For field remedial amendment delivery applications, higher polymer concentrations may be required to compensate for the viscosity loss caused by the ions and amendments in solutions. The results show that the xanthan solution shear thinning behavior can be well described by a power law. The power law fitting consistency index (K) is a linear function of the xanthan concentration, while its actual value appears to be a strong function of the ionic strength. The fitted degree of shear thinning (n), however, is best described using a logarithmic function. The presented empirical relations are useful for field applications, although the parameter values may need to be determined independently if local tap water or site groundwater is used to make the xanthan solutions.

When no sediment was added to the solution, its initial viscosity was maintained for months; while when field sediment was present, the viscosity dropped 70% or more in a week. The start of the polymer degradation is the breakdown of long molecule chains into short segments. These results implied that the xanthan solution may not be a candidate for holding amendment in formation for long time. However, the rather fast viscosity degradation makes it a good means for amendment delivery to permeable reactive barrier. Once the amendment is delivered to the barrier zone, the polymer degrades and is washed away, and the groundwater returns to natural flow.

Acknowledgements

Funding of this research is provided by the U.S. Department of Defense (DoD) Environmental Security Technology Certification Program (ESTCP), project ER-0913. A portion of the supplementary laboratory experiments were conducted in the William R. Wiley Environmental Molecular Sciences Laboratory (EMSL), a Department of Energy user facility operated by PNNL. PNNL is operated by Battelle for the U.S. Department of Energy.

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