Polymeric Fluids for In Situ Remediation of Hexavalent Chromium Using Trap and Treat Technology

by

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Hexavalent chromium (Cr(VI)) contamination is hazardous to the surrounding environment as well as posing chronic and acute health risks, emphasizing the importance of remediation methods that are cost-effective, environmentally friendly, and effective. Due to the rapid mobility of Cr(VI) in the subsurface, simultaneously immobilizing and treating the contaminant is of great importance. In this work, the natural polymers scleroglucan, xanthan, guar, and carboxymethyl cellulose (CMC), as well as the reducing agent sodium thiosulfate, were used to produce water-based polymeric fluids to simultaneously trap and treat Cr(VI) in the subsurface. The reduction, immobilization, and transport mechanisms were analyzed through batch tests, shear rheology, mechanical compression tests, microfluidic tests, and QCM-D
experiments, proving the proposed remediation technology effective at simultaneously immobilizing and reducing Cr(VI), both with and without the presence of humic acids (HA), naturally occurring in situ.
I would like to express sincere gratitude to my advisor Dr. Erica Pensini for her support, mentorship, enthusiasm and genuine passion for the work, as well as my co-advisor Dr. Christopher Collier for his advice and guidance throughout my degree.

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<table>
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<th>Description</th>
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<tr>
<td>CMC</td>
<td>Carboxymethylcellulose</td>
</tr>
<tr>
<td>DI</td>
<td>Deionized</td>
</tr>
<tr>
<td>Cr(VI)</td>
<td>Hexavalent Chromium</td>
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<tr>
<td>HA</td>
<td>Humic Acids</td>
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<tr>
<td>NZVI</td>
<td>Nano Zero-Valent Iron</td>
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<tr>
<td>QCM-D</td>
<td>Quartz Crystal Microbalance with Dissipation Monitoring</td>
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<tr>
<td>G’</td>
<td>Shear Elastic Modulus</td>
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<tr>
<td>G”</td>
<td>Shear Viscous Modulus</td>
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<tr>
<td>Borax</td>
<td>Sodium Tetraborate</td>
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<tr>
<td>Cr(III)</td>
<td>Trivalent Chromium</td>
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1 Introduction

1.1 Cr(VI) Contamination

Chromium is a naturally-occurring heavy metal that typically exists in either the hexavalent (Cr(VI)) or the more stable, trivalent (Cr(III)) oxidation state [1–5]. The increased mobility of hexavalent chromium can be attributed to its high solubility in water, meaning it readily dissolves in solution, increasing the migration distance of this toxin over a set amount of time [6]. Trivalent chromium is sparingly soluble, meaning it does not readily dissolve in water and often precipitates in aqueous solutions, directly reducing its ability to migrate in the subsurface [3, 6]. In addition, studies have not found definite results regarding the chronic toxicity of Cr(III) and it has not been proven carcinogenic or capable of incurring negative developmental effects [6]. While both forms of chromium are used in many industries, such as tannery operations, stainless steel production, chromium plating, and wood preservation, the hexavalent state is more hazardous and mobile than its trivalent counterpart, making it a priority pollutant [1–11]. Many of these active and abandoned industrial sites have chromium contamination in the soil and groundwater, often from improper waste disposal methods or unintentional leaching, requiring subsequent environmental remediation [2, 3, 5, 7–10, 12].

Specifically, Cr(VI) poses health hazards due to its corrosive and carcinogenic nature, as well as causing hereditary genetic damage involving human development and reproduction [3–5, 7–9, 13, 14]. In addition, the mobility of this heavy metal through the subsurface by natural processes can further extend the affected zone of contamination, causing harm to other living organisms such as plants and animals, consequently disrupting the balance of the surrounding ecosystem [4, 9, 12]. The rapid percolation of Cr(VI) through groundwater flow systems could lead to contamination of aquifers or surface bodies of water that humans and wildlife depend on for their daily water needs, stressing the importance of expeditious problem identification and remediative solutions [9].

1.2 Existing Cr(VI) Remediation Methods

Existing Cr(VI) remediation methods can be broken down into physical, chemical and biological approaches, relying on flexibility to adapt to site-specific conditions [9, 15]. Furthermore, remediation methods can be classified into types of treatment, such as toxicity reduction, destruction and removal, or containment strategies [15].
Physical remediation methods involving excavation of the contaminated soil are costly and time-consuming, not to mention the difficulty, if not impossibility, of entirely removing the contaminant, depending on the scale and extent of said contamination [9]. Subsequent disposal of hazardous soil does little to solve the problem at hand, since remediation is still required. Physical barriers, both vertical and horizontal, have also been developed to prevent contaminant migration through the subsurface, aiding parallel remediative effects, however this does not remove the contamination and embodies a preventative technique for restricting further plume migration in which barrier installation is technologically challenging [13,16]. Polymeric gels have also been utilized to effectively immobilize Cr(VI) in situ as well as create gel barriers for restricting subsurface migration, proving cheaper and less time consuming than other methods, however these gels did not contain reactive species able to degrade the contaminants [2,3,13,17–20]. Therefore, gel technology would need to be used in conjunction with other methods to ensure contaminant treatment [11,20]. Silica-based gel barrier formation in porous media has been investigated through computer modelling, simulating injection scenarios and hindered contaminant mobility through increased viscosity [17]. Permeable reactive barriers (PRBs) act as a filter for the contaminant species, as shown in Figure 1.1, that can employ any combination of chemical, biological or physical methods for either reacting with the Cr(VI) and preventing further movement [9,13,21,22]. Cr(VI) is typically immobilized by PRBs through invoked precipitation into Cr(III) using zero-valent reactive iron, however this method can only be applied to treating intercepted migrant contaminant plumes since it relies on effective understanding of subsurface groundwater flow for successful treatment, not actually remediating the source contamination [21,23]. In addition, the physical placement of a subsurface wall brings concern to surface environmental impacts, as well as the technological challenges associated with installation [21]. A study utilizing a zero-valent iron PRB was found to remain effective at Cr(VI) reduction over a period of eight years, suggesting that naturally present iron minerals in the subsurface were able to increase the capacity of the installed PRB [24]. A contaminated industrial landfill was used to analyze Cr(VI) reduction in another study, noting a significant decrease in Cr(VI) concentration downstream from large amounts of naturally present Fe(II) in the subsurface [3]. The Fe(II) was found to reduce the Cr(VI), acting like a natural PRB, simultaneously preventing further movement due to Cr(III) limited mobility [3]. While natural PRBs cannot be relied on for Cr(VI) remediation purposes, analyzing their effects on contaminant plumes can grant insight into further engineering PRBs for this purpose.

Remediative strategies focused on destroying or removing Cr(VI) are classified as either ex or in situ technologies [15]. Ex situ remediation methods, specifically
Figure 1.1: Permeable reactive barriers (PRBs) act as a filter for subsurface contaminant plumes and can employ any combination of physical, biological or chemical methods to remediate the contaminant. Multilevel well clusters can be installed to monitor contaminant plume migration through the subsurface, as well as the effectiveness of the PRB treatment.
pump-and-treat techniques, tend to employ technologies such as membrane filtration, ion exchange, granular activated carbon, other adsorbents as well as soil flushing in order to remove the contaminant ex situ before returning treated groundwater back into the subsurface and properly disposing of the waste [9, 15, 21, 25]. The pump-and-treat process is described in Figure 1.2. Polyacrylonitrile fiber as well as chitosan/polymethylmethacrylate filters have been used to affectively adsorb Cr(VI) from groundwater, developed through electrospun micro- and nano-scale fiber membranes [26, 27]. While the grafted functional groups display attractive selectivity for Cr(VI), the membrane filter is ideal for applications of flowing surface water or within a filtration system ex situ [26,27]. Reverse osmosis membranes have also been developed to remove Cr(VI) from effluent streams, proving effective at separating out Cr(VI) before wastewater from industrial sites is expelled [28,29]. However, this provides a means for preventing or reducing environmental Cr(VI) contamination in the future, rather than treating current subsurface contamination. Granular activated carbon has been proposed to adsorb Cr(VI) in several studies, similarly composing a membrane filter through which continuous flow is maintained as well as applications with aligned nanotubes [5,30,31]. Pretreating the granular activated carbon with reducing agents such as ferrous iron or dithionite was not found to improve adsorption, but did successfully reduce Cr(VI) to Cr(III) [30]. In order to maintain removal efficiency, the carbon was required to be flushed with dibasic potassium phosphate, to remove adsorbed Cr(VI), and sulfuric acid, to remove precipitated Cr(III), proving this method relatively complex in terms of operation and maintenance [30]. Laboratory experiments for soil flushing with sodium metabisulfite and ethylenediaminetetraacetic acid for the reduction of Cr(VI) have been conducted, exhibiting insignificant Cr(VI) removal [32]. Overall, the process involved with pump-and-treat techniques is time consuming and residual contamination still remains after treatment since effluent concentration decreases significantly over pumping time once the concentrated zone of contamination is removed, making it impossible to effectively remove all contamination from the diluted zone in an economically viable way [21]. In addition, a contaminant rebound effect tends to occur after pumping is halted, governed by the flow limitations of the subsurface fracture matrix as well as contaminant diffusion from the surrounding substrate [21]. Due to the ineffectiveness of the pump-and-treat technique when considering reasonable expenditure of time and finances, more recent strategies have focused on in situ Cr(VI) remediation for its relatively more efficient and effective treatment of chromium contaminated soils and groundwater [21,25]
Figure 1.2: The pump-and-treat process involves drilling an extraction well into the zone of contamination, as well as two injection wells on opposing sides, shown in the top figure. Contaminated water is pumped out of the extraction well, treated ex situ, then returned into the subsurface via the two injection wells. The bottom figure shows the cone of depression in the water table centered around the extraction well, as a response to water being pumped out of the aquifer. The groundwater flow is represented by the arrows drawn in the aquifer. The water being pumped into the injection wells creates a pressure ridge, further propagating contaminated water towards the extraction well.
In situ remediation technologies are generally considered more safe, simple, and cost-effective than their ex situ counterparts, in addition to having a minimal environmental impact in terms of site disturbance [25]. Biological processes are one example of in situ treatment options, aimed to reduce toxicity, utilizing phytoremediation, bioreduction or bioprecipitation to enhance natural attenuation to effectively treat the Cr(VI) contamination [9, 13, 15, 21, 33–35]. Phytoremediation employs the use of specific plants, capable of accumulating heavy metals, to uptake Cr(VI) through their roots, upon which diffusion into the cell membrane both intoxifies plants and invokes metabolic reduction to Cr(III) [13,36]. This method requires such a significant amount of time that it is considered an indirect remediative effort, however can be paired with bacterial reduction methods to decrease the toxin load on plants or other remediation methods to more effectively address contamination [13, 36]. Plants also have limitations when it comes to grown root depth beneath the soil, meaning they could only be considered for remediating shallow contamination. The sorghum plant has been studied for its use in phytoremediation of contaminated sites, discovering a decrease in plant biomass with increased Cr(VI) concentrations in soil, mitigated by the addition of vermicompost [37]. Various weed plant species found in Thailand have also been studied for their ability to phytoaccumulate Cr(VI) in plant tissues, with *pluchea indica* being found the most efficient at phytoremediation of this contaminant [38]. Furthermore, several bamboo species have been identified for their phytoremediative capabilities, discovered to reduce Cr(VI) content in situ for the purposes of reducing toxicity [39]. Bioreduction or bioprecipitation utilizes chromium resistant bacteria that naturally produce chromate reductase enzymes, able to reduce Cr(VI) to Cr(III) in both aerobic and anaerobic conditions [21, 35]. In one study, bacterial flora was proposed to further reduce low-concentrations of Cr(VI) in wastewater, in which reduction occurred through enzymes naturally present in the indigenous bacteria used [40]. While biological methods prove economical, effective and environmentally safe, the time to degrade contaminants is extensive and other pollutants or chemicals present in the subsurface may inhibit the desired reaction [21, 35].

Electrokinetic methods involve passing electric current between two probes placed in the contaminated soil, creating an electric gradient and subsequent migration of ions and groundwater, as shown in Figure 1.3 [13,25,41]. This technique is only suitable for a small range of contaminated sites, typically those with minimal groundwater flow as seen in clay substrates with low permeability, still having the potential for obstacles such as subsurface rocks, foundations, or metals to interfere with the process [13,41]. A study conducted with citric acid and polyaspartic acid electrolytes found that while a significant amount of energy was wasted towards heating up the
soil, the technique was successful in removing Cr(VI) from the sample soil [42]. Another study utilized conventional electrokinetic techniques, citing a Cr(VI) removal efficiency of 57%, suggesting that this technique might be suited towards toxicity reduction rather than complete contaminant removal [43].

Taking advantage of the less toxic, less mobile attributes of Cr(III), many remediation technologies have focused on chemical remediation through in situ soil flushing, employing a remediation by reduction approach, reducing Cr(VI) to Cr(III) with chemical additives [3, 11, 13, 21, 44]. The main challenges with this method involve potential unwanted interactions, specifically related to the hydrogeology of the contaminated site, as well as the high mobility of Cr(VI) with the groundwater flow system preventing effective contact between the contaminant and reducing agent [9, 11, 13]. In addition, soil conditions, such as pH or composition, can have a significant impact on the chemical reactions taking place, potentially preventing reduction or promoting re-oxidation of treated Cr(VI) [45, 46]. However, the economic benefits and environmentally friendly options present much potential for the use of these types of chemical reduction methods for Cr(VI) remediation [9]. In terms of specific reducing agents, nanoscale zero-valent iron (nZVI) particles have been increasingly popular for their effectiveness at reducing Cr(VI) in situ, with the reduction mechanisms shown in Figure 1.4. However, studies have shown that they have problems with maintaining particle reactivity over time, function only in a narrow pH range, and their potential toxicity is under debate [33, 44, 47, 48]. Amorphous iron sulfide was utilized in a study to reduce 85%-100% Cr(VI), forming stable Cr(III) and iron precipitates in the process [49]. Ferrous sulfate heptahydrate has been proposed as a Cr(VI) reducing agent, with concerns regarding potential re-oxidation post reduction, however sodium thiosulfate was presented as an alternative, showing similar effective reduction for a more economical price [11, 50, 51]. Sodium thiosulfate is a reducing agent that is readily biodegradable and does not bioaccumulate in organisms, favouring its compatibility for environment remediation applications [52]. It is capable of reducing hexavalent chromium, in which the dissolved sodium thiosulfate ions lose electrons while the Cr(VI) ions gain these electrons, specifically affecting its oxidation state, forming the less toxic, less mobile trivalent chromium in the process [2, 11]. Therefore, reducing a known carcinogen to a significantly less toxic and less mobile state both functionally eliminates the threat of contaminant plume migration and the negative health or environmental effects associated with hexavalent chromium contamination.
Figure 1.3: Electrokinetic remediation involves the application of two electrodes within wells on opposite sides of the contaminated zone. Running an electric current through the subsurface provokes migration of cations to the anode and anions to the cathode, with the wells pumping out exhausted electrolytic solution carrying contaminant ions.
1.3 Research Objectives

While many remediation methods have employed reduction or immobilization techniques, few have attempted a combination of the two methods in which the polymeric gels have contained the reactive species. In addition, the effect of elasticity on polymeric transport in small channels or porous media has not been extensively studied in the context of soil remediation. In response to these gaps, this research developed a novel remediation technology to simultaneously immobilize (trap) and treat (reduce) Cr(VI), and investigated the effect of viscoelasticity on the transport of polymeric fluids in microfluidic channels used to model porous geological media. Polymer sorption on silica (sand) was also studied in different water chemistries, since sorption affects transport. Specifically natural and inexpensive polymers, namely guar, xanthan, scleroglucan, and carboxymethyl-cellulose (CMC), were chosen to minimize any further environmental impact on the affected area through an economic solution. In addition, the gelation of scleroglucan and CMC-based polymers in contact with Cr(VI) has been studied previously, as well as guar-based fluid potential for applications of immobilization [20, 53, 54]. Sodium thiosulfate was chosen as the reducing agent due to its low cost and biodegradability to again minimize environmental impact [51, 52].

Figure 1.4: NZVI sorbs onto Cr(VI) and invokes its reduction into Cr(III) by accepting an electron donated from Cr(VI), and forming Fe(III) in the process.
This thesis discusses the work published in Natural guar, xanthan and carboxymethylcellulose-based fluids: Potential use to trap and treat hexavalent chromium in the subsurface [11], and the work submitted in Effect of rheology and humic acids on the transport of environmental fluids in sandy media: Potential implications for soil remediation [55], discussing the potential for polymeric based fluids to immobilize hexavalent chromium in order to more effectively and simultaneously remediate the contaminant. An explanation of the experimental methodology and the materials used throughout testing is presented in Chapter 2, detailing the three main elements of this thesis: (1) the entrapment mechanism, (2) the treatment mechanism, and (3) the effect of viscoelasticity and polymer sorption on the transport of polymeric fluids through geological media. Chapter 3 focuses on the trap and treat mechanism of the proposed remediation method, analyzing the effectiveness of immobilizing the contaminant upon contact while simultaneously treating it, as well as discussing the polymeric gel stability over time. Chapter 4 focuses on the transport aspect of actually flowing the polymeric gel to the contaminated zone and the effects of humic acids on the gelation, reduction and transport mechanisms.
2 Experimental Methodology

In order to address the research objectives, studies were conducted with three main goals: (1) the treatment or specifically the reduction of Cr(VI) to Cr(III) completed by reagents carried in a polymer gel that would (2) immobilize or trap the Cr(VI), with regard to (3) the delivery or transport of this polymeric gel through the subsurface considering the effects of humic acids, naturally found in the subsurface. The experiments conducted for each section, as well as the materials used throughout testing, are summarized in the following.

2.1 Materials

Food grade guar and xanthan gum were purchased locally as oppose to high grade products with the purpose of environmental applications in mind, where minimizing cost is desired. Carboxymethylcellulose (CMC) and humic acid sodium salts (abbreviated as humic acids, HA) were purchased from Sigma Aldrich. Potassium dichromate ($K_2Cr_2O_7$) (99% pure) was purchased from Fisher Scientific. Calcium chloride ($CaCl_2$), potassium chloride ($KCl$) salts (99% pure), and Sodium thiosulfate ($Na_2S_2O_3$) (99% pure) were purchased from Fisher Scientific. Sodium thiosulfate was used for the purpose of reducing Cr(VI) to Cr(III). Ottawa sand was purchased from BEI/PECAL (Stake Technology Ltd.) and limestone was purchased locally. Sodium tetraborate ($Na_2B_4O_7$)(Borax, 20 Mule Team) was purchased locally to use as a proof of concept for crosslinking instead of potassium dichromate in specified experiments. Scleroglucan was donated by Cargill (Actigum CS6). Deionized water (DI) was utilized in all proceeding experiments, in which the pH was neutral unless otherwise stated. Translucent PVA filament was purchased from Filaments.ca and extruded through a Prusa MK3 i3 3-D printer to produce microfluidic channels.

2.2 Reduction

The reduction of Cr(VI) to Cr(III) is essential in effectively treating the contamination, as well as ensuring that the Cr(III) will not oxidize and revert back to Cr(VI) over time. Theoretically, the trivalent oxidation state of chromium is considered more stable than its hexavalent counterpart, suggesting that it should not oxidize over time under static conditions [5, 6]. This section of experimentation focused on proving the reduction mechanism effective and ascertaining its stability over time.
2.2.1 Batch Tests

Batch tests with 0.1 M potassium dichromate, 10 g/L sodium thiosulfate and respectively 1 wt% guar, xanthan and CMC natural polymers were conducted at a neutral pH to qualitatively assess the reduction of Cr(VI) to Cr(III) by sodium thiosulfate, as indicated by the associated colour change from bright yellow to dark brown. Samples were further monitored over a three month period to ensure that the Cr(III) did not revert back to Cr(VI), indicated by the described colour change.

Guar-based polymeric fluids were also mixed with 300 g of Ottawa sand and limestone respectively, to ascertain its ability to reduce Cr(VI) in a sample substrate. Samples were left to gel for 4.5 h after mixing.

2.3 Immobilization

The effectiveness of remediation technologies using only reduction mechanisms for hexavalent chromium contamination can suffer from the extensive and rapid mobility of Cr(VI) in the subsurface [55]. Even if optimal amounts of reactive species were to reach the contaminant, sufficient contact time may not occur in regards to achieving the desired reduction due to the aforementioned mobility of Cr(VI) [55]. The mechanism of contaminant immobilization prior to reduction in this study aims to increase the effectiveness of the prescribed treatment by ensuring contact between reductive and contaminant species regardless of compound mobility. Gels entrapping Cr(VI) would have to be stable for the whole duration of the remediation, to ensure that Cr(VI) is immobilized while it is being treated. Once remediation of the Cr(VI) polluted area is completed, the gels would degrade since they are composed of natural polymers. Gel degradation ensures that the hydrology of the aquifer is restored after remediation is complete.

The use of guar, xanthan, scleroglucan, and CMC-based polymers were explored for their ability to crosslink with Cr(VI) upon contact, forming a gel to entrap the contaminant. Since these polymers are food safe and biodegradable, their introduction into the environment should not cause any negative ecological impacts or impose any health hazards either during remediation or degradation over time. This section of experimentation focused on analyzing the immobilization of Cr(VI) through the use of these polymer gels, as well as ascertaining their stability over time.
2.3.1 Mechanical Compression Tests

An Instron 5982 was utilized for mechanical compression testing of pre-gelled samples in Ottawa sand, limestone and no geologic media respectively. The samples consisted of 1 wt% guar per 100 mL of DI water, 0.1 M potassium dichromate, 10 g/L sodium thiosulfate and 300 g of respective geologic media, if added. After mixing, the samples were left for 4.5 hours to gel before beginning the mechanical compression testing, having a 3.5 cm height and a 5 cm diameter. Bluehill 3 software was used to determine the maximum load during compression testing, completed at a strain rate of 50 mm/min until the yield point was reached or up to a maximum load of 80 000 N, whichever occurred first.

The geologic media was chosen to represent coarse grained substrate and finer grained substrate respectively, attempting to understand the effects of these two varying types of soil on the gelation kinetics of the polymeric fluids.

2.3.2 Optical Microscopy Imaging

Images of all samples were taken before and after compressional testing described in Section 2.3.1, using a Keyence VHX-5000 digital microscope. This allowed visual analysis of the geologic media and gelled polymer structure with respect to the effects of compression on samples.

2.3.3 Shear Rheology

A rotational torque-controlled MCR302 Anton Paar rheometer was used to conduct strain sweep and time sweep testing of samples at 23°C room temperature. Samples consisted of 1 wt% guar, xanthan, and CMC respectively, 10 g/L sodium thiosulfate, and 0.1 M potassium dichromate. The strain sweep testing also included samples without the addition of potassium dichromate in order to analyze the differences between non-crosslinked and crosslinked samples. The viscoelastic response of samples to strain increasing from 0.01 % to 1000 % was measured at a frequency of 2 rad/s. Time sweep testing was conducted to observe the changes in rheology of samples during and after gelation, measuring the viscoelastic moduli versus time at a constant strain of 0.01 % and a frequency of 2 rad/s, all within the linear viscoelastic region. The selected strain of 0.01 % was intended to minimize oscillatory shear motion in order to mitigate structural damage to the samples, increasing confidence in the rheological measurements obtained. The experiments were conducted using single-gap concentric-cylinder (cone and bob) geometry, having an inner radius of 13.33 m and a height of 40 mm, and parallel plate geometry, having a diameter of
50 mm, respectively. In order to minimize slippage during testing, 600 grit sandpaper was affixed to the parallel plates. During testing utilizing concentric cylinder geometry, the minimum oscillation torque was set at 0.0005 µN·m, as specified by the rheometer manufacturer.

2.4 Polymeric Fluid Transport

The adequate delivery of the reactive gels comprised by natural polymers and sodium thiosulfate is necessary to ensure that Cr(VI) is trapped and treated. Important factors influencing polymer flow in the subsurface (studied using microfluidic channels) include the rheological properties of the polymeric fluids (studied using a shear rheometer) and polymer sorption onto the geological media (studied using a QCM-D). Following contact with Cr(VI), the reactive fluids gelled. Microfluidics experiments were used to demonstrate the correlation between high elasticity and poor flow, supporting the hypothesis that Cr(VI) is trapped upon gelation of the polymeric fluids. The materials and methods utilized to study the transport, rheology and sorption of polymeric fluids are outlined in the following sub-sections.

2.4.1 Shear Rheology

A rotational torque-controlled MCR302 Anton Paar rheometer was used to conduct strain sweep and time sweep testing of samples at 23°C room temperature. The experiments were conducted using single-gap concentric-cylinder (cone and bob) geometry, having an inner radius of 13.33 mm and a height of 40 mm, and parallel plate geometry, having a diameter of 50 mm, respectively. In order to minimize slippage during testing, 600 grit sandpaper was affixed to the parallel plates. The sample fluids consisted of 2.5 g/L guar, CMC, or scleroglucan with 2.5 g/L sodium thiosulfate mixed into DI water, either with or without the addition of 1 g/L HA. One set of guar-based polymeric fluids were tested with the addition of 1 g/L borax without potassium dichromate, in addition to tests of all polymeric fluids respectively with the addition of 0.1 M potassium dichromate.

Polymeric fluids without the addition of borax or potassium dichromate have low shear viscoelastic moduli due to the lack of crosslinking and gelation, therefore single-gap concentric-cylinder geometry was required for the rheometric analysis. Strain sweeps were conducted at a fixed frequency of 6 rad/s to determine the rheological properties associated with their migration through the subsurface, towards the contaminant.
Polymeric fluids containing borax or potassium dichromate have significant shear viscoelastic moduli due to the crosslinking and gelation, therefore parallel plate geometry was used for rheometric analysis. Strain sweeps were conducted for guar-based polymeric fluids mixed with borax at a fixed frequency of 6 rad/s, while both strain and time sweeps were conducted for CMC, guar and scleroglucan-based polymeric mixed with potassium dichromate. Strain sweep measurements were conducted 24 hours after mixing the potassium dichromate into the polymeric fluid samples, at a fixed frequency of 2 rad/s, whereas time sweep measurements began immediately after mixing the potassium dichromate into the polymeric fluid samples, at a fixed shear strain of 0.01 % and frequency of 2 rad/s. Since high frequencies caused samples to be ejected from the parallel plate geometry over extended measurements, the lower frequency of 2 rad/s was used for time sweeps, and maintained in the correlating strain sweeps for consistency.

### 2.4.2 Microfluidics Tests

Microfluidic experiments were conducted to study the flow of polymeric fluids in micron-sized channels, mimicking pore spaces and fractures in geological media. The goals of these tests were to (1) correlate the shear rheology data with microfluidic flow results for guar-based polymeric fluids and (2) analyze the effects of HA on guar, CMC and scleroglucan-based polymeric fluids on microfluidic flow. The channels themselves were modelled in SolidWorks® software from Dassault Systèmes and 3-D printed in translucent PVA filament on a Prusa I3 MK 3 printer. The tested channel diameters were 600 µm, 500 µm, and 350 µm, with 0.05 µm tolerance for printed layers, as shown in Figure 2.1. An Elegoo Mega2560 R3 Arduino controlled NEMA 17 stepper motor (1.8° step angle, 200 steps/revolution, four-phase unipolar permanent-magnet), utilizing an Easydriver stepper motor driver plate V44 A3967, was used to create a syringe pump, as shown in Figure 2.2. With the aid of 3-D printed parts, the motor converted rotational to linear movement in order to provide consistent pressure on a syringe filled with sample polymeric fluid. The motor was programmed to initially rotate 100 degrees to calibrate each experiment to have a consistent starting location, collecting the exiting fluid in a waste beaker. After a 10 second delay, the motor rotated 500 degrees, displacing the fluid in the syringe, pushing it through the microfluidic channel, and collecting it in a dry, zeroed beaker, to be weighed after the completed run. The comparison between the fluid masses exiting the channels was used as a measure of the resistance opposed by the fluids to the flow through the microfluidic channels. The delay between steps of the motor was calibrated to produce a testing run time for 500 µm and 350 µm channels of
Figure 2.1: The 3-D printed microfluidic channels with 600 µm, 500 µm, and 350 µm inner channel diameters, and their respective syringe tips for attachment onto the syringe for trials.

30 seconds whereas the run time for the 600 µm channel was 10 seconds, due to restricted motor power and high fluid resistance in smaller diameter channels.

The first set of microfluidic experiments measured the flow of 2.5 g/L guar in DI water, both with and without the addition of 1 g/L borax as a crosslinker. The fluid flow through channels was measured as explained above. Borax was used instead of potassium dichromate as a proof of concept during testing, since both borax and potassium dichromate act as crosslinkers, with the exception of borax being relatively harmless compared to potassium dichromate, and similarly promote gelation in these polymeric fluids as detailed in the immobilization aspects of this paper. With the goal of this experiment to note changes in flow of guar-based polymeric fluids before and after crosslinking, and correlate the results to shear rheology data, the use of borax as a safer working substitute to Cr(VI) can be justified.
Figure 2.2: Microfluidics syringe pump setup including the 3-D printed parts used to convert rotation of the stepper motor to linear movement of the syringe plunger, and the Arduino and driver board were used to control the stepper motor rotation. The microfluidic channel was attached to the end of the syringe during trials.

The second set of microfluidic experiments compared the flow of 2.5 g/L guar, scleroglucan, or CMC-based fluids in DI water, mixed with 2.5 g/L sodium thiosulfate, both with and without the addition of 1 g/L HA. The fluid flow through channels was measured as explained above.

A one factor ANOVA analysis was conducted using the Excel Analysis ToolPak and a significance of 0.05 in order to determine the statistical significance of differences measured in flow through the microfluidic channels.

2.4.3 QCM-D Tests

Silica sputtered coated sensors QSX 303 were purchased from Q-Sense to model sandy geological medium in sorption tests conducted with a laminar quartz crystal microbalance with dissipation monitoring (QCM-D). The sensor is oscillated within a flow cell at overtones, meaning the odd multiples, of a set resonant frequency. Deposition on the sensor causes changes to be recorded in the oscillations, as well as the
dissipation of oscillations corresponding to the softness of deposited films. Experiments required the QCM-D cell to be flushed with DI water until both dissipation and overtone signals were stable, then injecting sample solutions through the flow cell for 10 min each, eventually backtracking to DI water and analyzing changes from the calibration datum. One trial of the experiment proceeded as follows, with each step representing the injection sequence consisting of 10 min of flow times per step through the cell: (1) DI water, (2) 1.25 g/L sodium thiosulfate, (3) 1.25 g/L sodium thiosulfate with 1.25 g/L guar, (4) 1.25 g/L sodium thiosulfate, and (5) DI water. The same injection sequence was also completed with the addition of 0.5 g/L HA in steps two through four.
3 Treatment and Entrapment of Cr(VI)

The novel remediation technology developed in the research presented in this thesis allows simultaneously trapping and treating (reducing) Cr(VI) in situ. Immobilizing the Cr(VI) contaminant in the subsurface prevents migration of the contaminant plume, preventing negative environmental impacts on the surrounding areas downstream. However, simply entrapping the Cr(VI) does not prevent it from causing harm in its immediate vicinity or eventually mobilizing again when the method of entrapment mechanism degrades. Combining immobilization with a method of reduction is essential in ensuring that Cr(VI) does not migrate during its treatment, ensuring its safe and effective remediation.

This chapter discusses the results of experiments conducted to entrap and reduce the contaminant within a polymeric gel, as well as analyzing the effects and corresponding insights gained.

3.1 Cr(VI) Treatment

3.1.1 Batch Tests

Batch tests were conducted to qualitatively assess the reduction of the Cr(VI) to Cr(III) by sodium thiosulfate during gelation with guar, xanthan, and CMC respectively, both with and without the presence of two sample geologic media: Ottawa sand and limestone. Scleroglucan-based polymeric fluids were analyzed in a previous study, discovering an increase in viscosity after mixing with Cr(VI) [20]. This increasing viscosity was attributed to crosslinking, hypothesized to occur between both carboxylated and non-carboxylated scleroglucan, and Cr(III) [20].

Figure 3.1 shows the resulting gelled guar-based polymeric fluids in the specified geologic media with sodium thiosulfate used to reduce potassium dichromate. The CMC-based experiments had similar results, therefore the images are not shown. The polymeric fluids respectively were significantly visually less viscous prior to mixing with potassium dichromate and sodium thiosulfate, and fully gelled within 5 min to appear as shown in Figure 3.1. The colour change from bright orange to dark brown was clearly noted in all samples with sodium thiosulfate and potassium dichromate, suggesting successful reduction of Cr(VI) to Cr(III) by sodium thiosulfate during gelation with each tested polymer in sample geologic media. Samples without the addition of sodium thiosulfate did not exhibit this colour change as there was no reduction of potassium dichromate. Over a period of three months, samples did not
exhibit a colour change and remained dark brown throughout, suggesting the Cr(III) was not re-oxidized to Cr(VI) over the observed time.

These results suggest the potential to simultaneously immobilize and treat Cr(VI) in situ by the proposed technique, however, since the results were collected in a model lab environment, different types of soils or compounds present in situ can have unexpected effects on the reduction mechanism. Future work should focus on analyzing the effects of prevalent compounds in situ, such as sulfate, chloride or carbonate and bicarbonate anions, as well as the addition of other heavy metal or organic contaminants, which are often encountered at remediation sites and can invoke competing nonproductive reactions [25, 56].

The reduction of Cr(VI) by thiosulfate ions is presented in Equations 3.1 and 3.2, representing the reactions at low and high Cr(VI) concentrations, respectively [57]. The batch tests conducted utilized 0.1 M of potassium dichromate and 0.6 M sodium thiosulfate, following the reaction as described in Equation 3.1, therefore the potassium dichromate is the limiting reagent in the test reaction and sodium thiosulfate should be in excess. This suggests that all Cr(VI) has the possibility to be reduced to Cr(III) since there should not be a lack of reducing agent, however future work could still focus on experimentally quantifying the Cr(VI) reduction to further validate these results, possibly through mass spectrometry measurements.

\[
\begin{align*}
2 \text{CrO}_4^{2-} + 6 \text{S}_2\text{O}_3^{2-} + 16 \text{H}^+ & \rightarrow 2 \text{Cr}^{3+} + 3 \text{S}_4\text{O}_6^{2-} + 8 \text{H}_2\text{O} \\
8 \text{CrO}_4^{2-} + 3 \text{S}_2\text{O}_3^{2-} + 34 \text{H}^+ & \rightarrow 8 \text{Cr}^{3+} + 6 \text{S}_4\text{O}_6^{2-} + 17 \text{H}_2\text{O}
\end{align*}
\]

### 3.2 Cr(VI) Immobilization

#### 3.2.1 Gelation

As discussed in Section 3.1.1, the batch tests produced gelled samples within 5 min of mixing potassium dichromate and sodium thiosulfate into guar, xanthan, and CMC-based polymeric fluids respectively. This gelation can be attributed to the crosslinking occurring between polymer chains upon contact with chromium. Carbohydrates composed of repeated anhydroglucose units, such as those contained within guar and CMC, have been found to be effective in adsorbing heavy metals such as Cr(VI) [58, 59]. Studies have reported that CMC is crosslinked by chromium in its trivalent form, and since the gelation of guar-based fluids was not observed in the
presence of potassium dichromate, without the addition sodium thiosulfate, it is hypothesized that guar is also crosslinked by Cr(III) as oppose to Cr(VI) [60]. It is speculated that Cr(VI) first adsorbs onto the polymers, then is reduced to Cr(III) by the sodium thiosulfate present in the polymeric fluids, and finally crosslinks the polymers, causing gelation. Hypothetically, the gelled fluids would still immobilize the contamination, possibly forming barriers around the contaminated zone and trapping the Cr(VI) during treatment. Since the polymers used in testing are natural, they degrade over time and do not alter the hydrology of the aquifer of the local ecosystem after remediation is complete. However, the gels remain stable long enough for reduction to occur, as shown in batch tests conducted.

3.2.2 Shear Rheology

Shear rheology experiments were conducted to determine the gelation kinetics of guar, xanthan, and CMC-based polymeric fluids containing sodium thiosulfate and potassium dichromate to analyze the effectiveness of trapping the contaminant during treatment. A summary of the results can be found in Table 3.1, with the ideal polymeric fluid having a minimized initial viscosity and elasticity in order to facilitate fluid flow in the subsurface, and minimizing gelation time to allow for fast immobilization of the contaminant plume. The elasticity and viscosity of fluids affect their ability to flow, meaning the effectiveness of gelation or the resistance to applied force can be quantified through rheological measurements. The viscous (G") and elastic (G’) moduli of guar, xanthan, and CMC-based fluids containing sodium thiosulfate before and after mixing with potassium dichromate are shown in Figures 3.2, 3.3, and 3.4, respectfully.
The 1 wt% guar-based polymeric solutions containing sodium thiosulfate behaved as viscoelastic fluids prior to mixing with Cr(VI) in which $G''$ and $G'$ nearly overlapped, as shown in Figure 3.2. Visual observations showed the guar-based fluids flowed relatively easily and studies have observed guar solutions flowing through sandy aquifers with average hydraulic conductivities of $8.2 \times 10^{-5} m/s$ [61]. The results suggest that guar-based fluids are able to flow through substrate with average permeability, prior to gelation. CMC solutions containing sodium thiosulfate exhibited very low viscous and elastic moduli prior to contact with potassium dichromate, as shown in Figure 3.4. These low viscoelastic moduli suggest CMC-based solutions would flow well through aquifers with low permeability as they flow relatively easily prior to gelation. The ability to easily flow through substrate is an essential component of actually reaching the contaminant and enabling immobilization.

The gelation kinetics upon contact with Cr(VI) are important factors with regard to successful immobilization. Relatively rapid gelation is desired immediately after contact with Cr(VI), in order to promote rapid entrapment and prevent migration during reduction. As shown in Figure 3.4, CMC-based fluids gelled after approximately 20 minutes, exhibiting significant viscoelastic moduli, whereas guar-based fluids gelled within 5 minutes, the resulting samples shown in Figure 3.1. While the CMC-based fluids were able to flow when poured from beaker to beaker for up to 20 minutes after mixing with potassium dichromate, no flow was possible after gelation. Similarly, the addition of potassium dichromate to the guar-based fluids, initially able to flow when poured from beaker to beaker, eventually completely prevented flow from occurring after 5 minutes. This highlights the importance of increased viscosity and elasticity on flow and fluid transport as something to further investigate in future studies. The fast gelation upon Cr(VI) contact and fairly low viscoelastic moduli of guar-based polymeric fluids make them an attractive potential candidate for the proposed trap and treat Cr(VI) remediation strategy compared to the other tested polymeric fluids as summarized in Table 3.1.

### 3.2.3 Mechanical Compression Tests

Compressional tests were conducted to investigate the behaviour of 1 wt % guar-based polymeric fluids containing sodium thiosulfate and potassium dichromate after gelation, the same fluid compositions as rheologically studied in Section 3.2.2. Tests were conducted 4.5 hours after mixing the fluids together either with or without geological media, of which two types were tested respectfully: Ottawa sand and limestone. In addition, the presence of 100 mM KCl and CaCl$_2$ were tested respectfully for each type of sample to analyze the effects that various water chemistries
Figure 3.2: Viscous (G") and elastic (G’) moduli of 1 wt % guar solutions containing sodium thiosulfate before (top) and after (bottom) contact with potassium dichromate. Strain sweeps measured at a frequency of 2 rad/s.
Figure 3.3: Viscous ($G''$) and elastic ($G'$) moduli of 1 wt % xanthan solutions containing sodium thiosulfate before (top) and 18 hours after (bottom) contact with potassium dichromate, as well as over a time sweep (center) at 0.01 % strain. Strain sweeps measured at a frequency of 2 rad/s.
Figure 3.4: Viscous ($G''$) and elastic ($G'$) moduli of 1 wt % CMC solutions containing sodium thiosulfate before (top) and 18 hours after (bottom) contact with potassium dichromate, as well as over a time sweep (center) at 0.01 % strain. Strain sweeps measured at a frequency of 2 rad/s.
Table 3.1: Performance summary of guar, CMC, and xanthan polymeric based fluids with regards to gelation time upon contact with Cr(VI) and their initial viscosity. The ideal qualities being low initial viscosity to allow for fluid flow and fast gelation time to quickly immobilize the contaminant plume.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Gelation Time (min)</th>
<th>Initial Viscous Moduli (Pa)</th>
<th>Initial Elastic Moduli (Pa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Guar</td>
<td>~5</td>
<td>~10</td>
<td>~10</td>
</tr>
<tr>
<td>CMC</td>
<td>~20</td>
<td>~0.1</td>
<td>&lt;0.00001</td>
</tr>
<tr>
<td>Xanthan</td>
<td>~180</td>
<td>~10</td>
<td>~45</td>
</tr>
</tbody>
</table>

might have on gelation, as well as the effects of pH change by using NaOH to adjust solution pH to 7 and 9 respectively. Optical microscopy was used to visually observe changes regarding structure of polymer gels and composites before and after compression testing.

Table 3.2 displays the observed maximum loads in which the samples became plastic in the absence of geologic media. The data shows that the water chemistry, meaning the addition of KCl or CaCl$_2$, strongly affected the maximum load (N) above which the samples exhibited plastic behaviour. While all samples remained realltively intact post compression, the ejection of fluid from the samples was visually noted, particularly with samples containing CaCl$_2$ and followed by those containing KCl. The decreased compressional strength of the gel samples upon syneresis, meaning the ejection of liquids during gel contraction, can be justified by gel weakening shown to occur with phase separation [62].

Since guar has been shown to bind and be crosslinked by calcium ions (Ca$^{2+}$), in addition to the potassium dichromate influencing guar crosslinking in samples, overcrosslinking of guar polymer chains may have occurred, leading to syneresis and weaker samples [58, 63–66]. Similarly, potassium ions (K$^+$) have been shown to bind the -OH groups involved in the crosslinking mechanism of guar, specifically increasing the syneresis of gels with other crosslinkers such as borax [67, 68]. Since K$^+$ is monovalent, it can only occupy one guar binding site, as oppose to the two possible occupied binding sites with Ca$^{2+}$, explaining how the addition of CaCl$_2$
<table>
<thead>
<tr>
<th>System</th>
<th>Maximum load (N)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DI, pH = 7</td>
<td>139 ± 7</td>
</tr>
<tr>
<td>DI, pH = 9</td>
<td>180 ± 8</td>
</tr>
<tr>
<td>100 mM KCl</td>
<td>89 ± 10</td>
</tr>
<tr>
<td>100 mM CaCl₂</td>
<td>17 ± 1</td>
</tr>
</tbody>
</table>

Table 3.2: Maximum load beyond which samples become plastic in the absence of geological media, measuring 4.5 hours after gel preparation.

to gels resulted in mechanically weaker systems as oppose to those with added KCl. Similar interactions between CMC and calcium ions have been observed, suggesting the presence of these ions would also affect the mobility of CMC-based fluids in the subsurface [69]. These results emphasize the importance of understanding water chemistry for the purposes of chemical remediation, as the optimal polymer to Cr(VI) ratio is entirely dependant on any existing species in situ that might occupy needed binding sites.

The compressional tests with geological substrate yielded the results shown in Figure 3.6, with the corresponding optical microscopy images shown in Figure 3.7. The samples appeared cohesive both before and after compressional testing as shown in Figure 3.5, and were not plasticized up to loads of 80 000 N, displayed in Figure 3.6. These results indicate that the geological material used in testing did not interfere with the gelation of guar-based polymeric fluids, therefore showing potential for utilizing this technology to effectively immobilize and reduce Cr(VI) contamination in situ. While the two types of grain size and uniformity were explored with the coarser grained, high grain size variability limestone substrate and the fine grained, more uniform grain size Ottawa sand, future work could focus on expanding to other types of geologic material such as clays, silts, or gravels for example.
Figure 3.5: Guar-based polymers in limestone (left) and Ottawa sand (right) geologic media after gelation both pre (top) and post (bottom) compression testing.
Figure 3.6: The compressional curves showing strain and load on guar-based polymer samples in limestone (top) and Ottawa sand (bottom) geologic media post gelation.
Figure 3.7: Optical microscopy images of guar-based polymeric fluids in limestone and Ottawa sand geologic media post gelation, before and after compression testing.
4 Polymeric Fluid Transport

It is essential to consider the transport of the polymeric fluid to the Cr(VI) polluted zones in common groundwater chemistries. Since humic acids are naturally present in the subsurface, their effect on transport was analyzed. With regards to future work, as further discussed in Chapter 5, studying the effects of other contaminants or naturally occurring chemicals in the subsurface on these aspects would be helpful in further determining the effectiveness of this strategy or suggested improvements.

This chapter discusses the results of experiments conducted to evaluate transport and the effects of humic acids on polymers gels, as well as analyzing the corresponding insights gained.

4.1 Effects of Shear Rheology on Transport

Microfluidic and shear rheology experiments were conducted to correlate the shear viscoelastic moduli of polymeric fluids with their flow through microfluidic channels, used to mimic the pores and fractures found in geologic media. The viscoelastic moduli of guar-based polymeric fluids, both with and without the addition of crosslinking borax, are shown in Figures 4.1 and 4.2, respectively, and summarized in Table 4.1.

<table>
<thead>
<tr>
<th>System</th>
<th>Shear Moduli (Pa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>G”</td>
<td>0.10 ± 0.06</td>
</tr>
<tr>
<td>G” with Borax</td>
<td>0.28 ± 0.11</td>
</tr>
<tr>
<td>G’</td>
<td>0.005 ± 0.02</td>
</tr>
<tr>
<td>G’ with Borax</td>
<td>0.27 ± 0.12</td>
</tr>
</tbody>
</table>

Table 4.1: Shear viscous (G”) and elastic (G’) moduli of guar-based polymeric fluids with and without borax.

Without the addition of borax, guar-based fluids were dominated by viscosity, as shown in Figure 4.1 with the viscous (G”) moduli higher than the elastic (G’) moduli. However, the addition of borax, as shown in Figure 4.2, represented a more equal viscoelastic behaviour with the elastic (G”) moduli hovering just above the
Figure 4.1: The shear viscous (G’”) and elastic (G’) moduli of guar-based polymeric fluids comprised of 2.5 g/L guar in DI water.

viscous (G’”) moduli on average. Borax causes crosslinking between guar polymer chains, similarly to Cr(III) as discussed in Section 3.2.1, meaning reversible links between the -OH groups of the guar polymer chains and the oxygen atoms in the borate ion are formed [70]. In Figure 4.2, the addition is borax is shown to promote the formation of an elastic network, and consequently, the elastic moduli of these fluids, while the viscous moduli of these fluids remains approximately the same.

The increase in the shear elastic moduli caused by the addition of 1 g/L of borax to 1.25 g/L guar completely impeded fluid flow in 350 µm channels, while having a negligible impact on the flow in 500 µm and 600 µm channels, as shown in Table 4.2. Higher concentrations of guar and borax were also tested, conducting experiments using 5 g/L guar and with 5 g/L guar and 2.5 g/L borax [55]. Shear rheology experiments showed that the two systems has identical viscous moduli (G’ is 2 Pa in the linear regime), whereas G’ was much higher for (G’ is 40 Pa in the linear regime) guar with borax than with guar alone (G’ is 2 Pa in the linear regime). The data indicates that there is a correlation between the magnitude of the elastic moduli at which flow is impeded and the size of the channels in which fluids flow. Guar forms aggregates in solution, and the fractal size of the aggregates increases both upon crosslinking, due to the formation of an elastic network [71,72]. The fractal
Figure 4.2: The shear viscous ($G''$) and elastic ($G'$) moduli of guar-based polymeric fluids comprised of 2.5 g/L guar in DI water, crosslinked with 1 g/L borax.

dimension of polymer aggregates may also increase with polymer concentration, and was observed for polyvinyl alcohol, for instance [73]. In the case of small microfluidic channels (350 µm), the increased size of the fractal aggregates in the presence of a crosslinker may explain in part why crosslinked guar could not flow. Additionally, the formation of an elastic network prevents polymer chains from sliding past one another (i.e. flowing). The results obtained here are in agreement with studies investigating the flow of polyethylene oxide (PEO) fluids through porous media, to assess their effectiveness in displacing crude oil during polymer flooding [74]. The PEO-based fluids were obtained with PEO having different molecular weight distributions, and had similar viscous moduli but different elastic moduli, similar to the guar-based fluids in the present study. These studies showed that shear elasticity increased the resistance of the PEO fluids to flow through porous media [74]. Also, computational studies of fluid flow through porous media demonstrated that elasticity can significantly increase the pressure drop in the porous media for a given flow rate [75]. Therefore, low shear elastic moduli are desirable to promote the transport of polymeric fluids through geological media before contact with Cr(VI), ensuring
that they reach target polluted zones. High elasticity is instead desirable to ensure that Cr(VI) is trapped, following mixing between the polymeric fluids and Cr(VI).

<table>
<thead>
<tr>
<th>Polymeric Fluid Composition</th>
<th>600 µm Channel Fluid Mean (g)</th>
<th>500 µm Channel Fluid Mean (g)</th>
<th>350 µm Channel Fluid Mean (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DI water</td>
<td>2.34</td>
<td>2.32</td>
<td>2.29</td>
</tr>
<tr>
<td>2.5 g/L guar</td>
<td>2.31</td>
<td>2.30</td>
<td>1.98</td>
</tr>
<tr>
<td>2.5 g/L guar and 1 g/L borax</td>
<td>2.29</td>
<td>2.29</td>
<td>No Flow</td>
</tr>
<tr>
<td>F_{calculated}</td>
<td>2.23</td>
<td>2.65</td>
<td>N/A</td>
</tr>
<tr>
<td>F_{critical}</td>
<td>7.71</td>
<td>6.61</td>
<td>N/A</td>
</tr>
<tr>
<td>P</td>
<td>0.21</td>
<td>0.16</td>
<td>N/A</td>
</tr>
</tbody>
</table>

Table 4.2: Microfluidics results comparing flow of various guar-based polymeric fluids, with and without the addition of borax, through 600 µm, 500 µm, and 350 µm channel diameters. The flow of DI water through channels is also shown for comparison. An ANOVA analysis compared the 2.5 g/L guar and 2.5 g/L guar with 1 g/L borax systems for the 600 µm and 500 µm diameter channels, with $F_{critical} > F_{calculated}$ meaning values are not statistically different.

### 4.2 Effects of Humic Acids on Polymeric Fluid Transport

As explained in Section 3.2.3, the water chemistry can have a significant impact on the gelation of polymeric fluids, intended to effectively immobilize Cr(VI). Humic acids are amphiphilic, organic compounds found naturally in soil and water, an essential component of soil chemistry for plant growth as they aid in nutrient delivery from the surrounding soil to the roots [76–79]. Keeping in mind the importance of fast gelation for rapid contaminant entrapment, as well as the ability to flow effectively through the subsurface to the contaminated zone, the effects of these
prevalent compounds on both gelation and transport of these fluids were analyzed. Specifically, the effect of HA on the rheology of CMC, guar, and scleroglucan-based polymeric fluids, their flow through through microfluidic channels, and their sorption onto sample geological medium was studied. Xanthan-based polymeric fluids were not included in testing since they prove very viscous and would not be able to flow through the channels considering the applied pressure limitations of utilized testing equipment, namely the stepper motor in microfluidic experiments.

Before mixing with Cr(VI), the shear elastic ($G'$) and viscous ($G''$) of CMC, scleroglucan and guar were low and were not affected by HA, as summarized in Table 4.3 from the Figures 4.3, 4.4, and 4.5. Microfluidic channel experiments showed that the differences between the velocities of CMC, guar and scleroglucan fluids were small (less than 3%) and that the effect of HA was negligible in microfluidic channels of either 500 µm or 600 µm, shown in Table 4.4. Experiments were not conducted using 350 µm microfluidics channels.

<table>
<thead>
<tr>
<th>Polymeric Fluid Composition</th>
<th>$G'$ (Pa)</th>
<th>$G''$ (Pa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Guar</td>
<td>0.39 ± 0.19</td>
<td>0.41 ± 0.50</td>
</tr>
<tr>
<td>Guar with HA</td>
<td>0.29 ± 0.27</td>
<td>0.37 ± 0.18</td>
</tr>
<tr>
<td>CMC</td>
<td>0.27 ± 0.55</td>
<td>0.35 ± 0.55</td>
</tr>
<tr>
<td>CMC with HA</td>
<td>0.26 ± 0.26</td>
<td>0.36 ± 0.48</td>
</tr>
<tr>
<td>Scleroglucan</td>
<td>0.05 ± 0.21</td>
<td>0.18 ± 0.24</td>
</tr>
<tr>
<td>Scleroglucan with HA</td>
<td>0.07 ± 0.08</td>
<td>0.25 ± 0.36</td>
</tr>
</tbody>
</table>

Table 4.3: The shear viscous ($G''$) and elastic ($G'$) moduli of 2.5 g/L guar, CMC, and scleroglucan-based polymeric fluids, each containing 2.5 g/L sodium thiosulfate both with and without the addition of 1 g/L HA. Summary of results from Figures 4.3, 4.4, and 4.5.
Table 4.4: The resulting output fluid masses (g) from microfluidics experiments with 600 µm and 500 µm channel diameters, utilizing 2.5 g/L guar, CMC, and scleroglucan-based fluids with 2.5 g/L scleroglucan, both with and without the addition of 1 g/L HA. An ANOVA analysis compared the polymeric fluid flow with and without HA for the 600 µm and 500 µm diameter channels, with $F_{\text{critical}} > F_{\text{calculated}}$ meaning values are not statistically different.
Figure 4.3: The shear viscous ($G''$) and elastic ($G'$) moduli of guar-based polymeric fluids comprised of 2.5 g/L guar in DI water, with 2.5 g/L sodium thiosulfate and 0.1 g/L potassium dichromate, as well as both with and without 1 g/L HA. Tests were conducted at 0.01 % shear strain and an angular frequency of 2 rad/s, both immediately after mixing (top) and after gelling overnight (bottom).
Figure 4.4: The shear viscous ($G''$) and elastic ($G'$) moduli of scleroglucan-based polymeric fluids comprised of 2.5 g/L scleroglucan in DI water, with 2.5 g/L sodium thiosulfate and 0.1 g/L potassium dichromate, as well as both with and without 1 g/L HA. Tests were conducted at 0.01 % shear strain and an angular frequency of 2 rad/s, both immediately after mixing (top) and after gelling overnight (bottom).
Figure 4.5: The shear viscous ($G''$) and elastic ($G'$) moduli of CMC-based polymeric fluids comprised of 2.5 g/L CMC in DI water, with 2.5 g/L sodium thiosulfate and 0.1 g/L potassium dichromate, as well as both with and without 1 g/L HA. Tests were conducted at 0.01 % shear strain and an angular frequency of 2 rad/s, both immediately after mixing (top and center) and after gelling overnight (bottom).
As highlighted in the previous section, guar is likely the most promising candidate for the treatment of Cr(VI) using the trap and treat technology, due to its rapid gelation kinetics in the presence or in the absence of HA. QMC-D experiments hence focused on the effect of HA on the sorption of guar onto silica, used as model geological substrate. QCM-D experiments were conducted to complement rheology and microfluidic channel experiments, and to further understand guar transport in the subsurface. In the absence of HA, the changes in the overtones ($\Delta F$) and the dissipation factor ($\Delta D$) relative to the baseline were significant even after rinse-off of the flow cell with DI water following guar injection, shown in Table 4.5. These results indicate that guar remained irreversibly adsorbed at the silica surface. The changes in $\Delta F$ and $\Delta D$ relative to the baseline recorded in DI water were significantly smaller with HA than without HA, suggesting that HA hindered adsorption of guar onto silica, as shown in Table 4.6.

<table>
<thead>
<tr>
<th>Injection Step Solution</th>
<th>$\Delta F$ (Hz)</th>
<th>$\Delta D$ $(1 \cdot 10^{-6})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1) DI water</td>
<td>0.0 ± 0.0</td>
<td>0.0 ± 0.0</td>
</tr>
<tr>
<td>(2) 1.25 g/L sodium</td>
<td>−1.5 ± 0.3</td>
<td>0.4 ± 0.0</td>
</tr>
<tr>
<td>thiosulfate</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(3) 1.25 g/L sodium</td>
<td>−21.7 ± 0.7</td>
<td>2.8 ± 0.0</td>
</tr>
<tr>
<td>thiosulfate and 1.25 g/L</td>
<td></td>
<td></td>
</tr>
<tr>
<td>guar</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(4) 1.25 g/L sodium</td>
<td>−20.3 ± 0.2</td>
<td>2.0 ± 0.0</td>
</tr>
<tr>
<td>thiosulfate</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(5) DI water</td>
<td>−18.4 ± 0.1</td>
<td>1.5 ± 0.0</td>
</tr>
</tbody>
</table>

Table 4.5: The resulting shifts in the third overtone and its dissipation factors for each 10 min step of the injection sequence. Results at other overtones showed similar trends, therefore are not shown. (1) DI water was first pumped to establish a baseline, followed by (2) the background solution, (3) polymeric solution with background solution, and (4) background solution again, respectively. A final (5) DI water rinse was run to compare with the initial baseline.
Table 4.6: The resulting shifts in the third overtone and its dissipation factors for each 10 min step of the injection sequence. Results at other overtones showed similar trends, therefore are not shown. (1) DI water was first pumped to establish a baseline, followed by (2) the background solution with HA, (3) polymeric solution with HA and background solution, and (4) background solution with HA again, respectively. A final (5) DI water rinse was run to compare with the initial baseline.

<table>
<thead>
<tr>
<th>Injection Step Solution</th>
<th>ΔF (Hz)</th>
<th>ΔD (1 · 10⁻⁶)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1) DI water</td>
<td>0.0 ± 0.0</td>
<td>0.0 ± 0.0</td>
</tr>
<tr>
<td>(2) 1.25 g/L sodium thiosulfate and 0.5 g/L HA</td>
<td>−1.5 ± 0.1</td>
<td>0.7 ± 0.0</td>
</tr>
<tr>
<td>(3) 1.25 g/L sodium thiosulfate, 0.5 g/L HA, and 1.25 g/L guar</td>
<td>−2.0 ± 0.1</td>
<td>1.6 ± 0.1</td>
</tr>
<tr>
<td>(4) 1.25 g/L sodium thiosulfate and 0.5 g/L HA</td>
<td>−2.5 ± 0.1</td>
<td>0.9 ± 0.0</td>
</tr>
<tr>
<td>(5) DI water</td>
<td>−0.2 ± 0.0</td>
<td>1.0 ± 0.0</td>
</tr>
</tbody>
</table>

A previous QCM-D study showed that HA also hindered the sorption of scleroglucan onto silica, and it is hypothesized that HA formed complexes with scleroglucan [20]. The data shows that ΔF and ΔD were small upon injection of the background solution containing HA and sodium thiosulfate. These results suggest that sorption of HA onto silica was limited, in agreement with previous studies [80]. Therefore, it is hypothesized that HA inhibited the sorption of guar onto silica by binding guar, rather than by competing with it for sorption sites on the silica surface. This hypothesis is supported by the differences in the softness of the guar films sorbed on the silica surface in the presence and in the absence of HA. The ΔD/ΔF ratio is related to film softness, and high ratios are indicative of soft films [81]. The ratio ΔD/ΔF increased from $8 \cdot 10^{-8} Hz^{-1}$ without HA to $5 \cdot 10^{-6} Hz^{-1}$ with HA, suggesting film softening. The significant values of ΔF and ΔD indicate that guar films at the silica surface are comprised of multiple layers of guar molecules (rather
than of a monolayer). The softening of the films suggested by the increase in the $\Delta D/\Delta F$ ratio with HA may be correlated to changes in the structure of the stacked guar layers, possibly caused by the presence of HA in the guar films. As previously highlighted, HA are naturally present in groundwater. Their presence can promote the transport of guar fluids in sandy aquifers by inhibiting guar sorption onto sand. Also, their ad-hoc addition to guar-based fluids may further enhance fluid transport in sandy aquifers contaminated by Cr(VI). Finally, HA do not decrease the rate of guar gelation upon contact with Cr(VI), warranting effective trapping of Cr(VI), as discussed above.
5 Conclusions and Future Work

The work presented in this thesis outlines the potential for guar, scleroglucan, xanthan, and CMC-based polymeric fluids to be used for the transportation of Cr(VI) reducing sodium thiosulfate and the immobilization of this targeted contaminant. The ability to effectively reduce Cr(VI) to Cr(III) by sodium thiosulfate was explored in batch tests and geological media, suggesting reduction by sample colour change. Future work should further verify these conclusions by analyzing sample Cr(VI) concentration post reduction quantitatively to ensure effective reduction has occurred. In addition to the successful reduction of Cr(VI), tests also suggested effective contaminant immobilization could be achieved through the crosslinking of polymers and gelation of polymeric fluids. The significance of rheological properties on the gelation and flow of polymeric fluids was explored and stressed, through complimentary shear rheological and microfluidic testing, discovering that increased elasticity of guar-based polymeric fluids restricted flow. The potential effects of varying water chemistries on the transport, reduction and gelation kinetics of proposed polymeric fluids were explored through tests involving humic acids, KCl and CaCl$_2$. Humic acids were found to significantly decrease the sorption of guar onto silica, potentially aiding transport in sandy aquifers, as well as have no significant effect on the transport and gelation of polymeric fluids in microfluidic and rheological tests. KCl and CaCl$_2$ salts significantly reduced the maximum compressional load above which the polymers, gelled in sample geologic media, became plastic. Future work should focus on ascertaining the effects of other compounds naturally present in situ on the gelation kinetics, reduction, and transport mechanisms of this technique. Nevertheless, the use of guar-based polymeric fluids was shown as the most attractive option out of the three polymeric fluids studied, due to its fast gelation kinetics, relatively low elastic modulus prior to Cr(VI) contact and the inhibition of sorption onto silica in the presence of naturally occurring humic acids.

Future work could expand the preliminary investigations outlined in this thesis by conducting soil column tests and potentially field work on a Cr(VI) contaminated site to test the in situ effectiveness of the trap and trap mechanism. In addition, studying the potential to encapsulate reactive particles in order to prevent unwanted subsurface reactions from occurring prior to contact with Cr(VI) could be valuable. Combining the trap and treat mechanism with encapsulation of reagents would further improve the efficiency of contaminant removal since reagents would not be consumed during the transportation to the contaminated zone. This could improve the cost of the remediative technique as less reactive species would be required. The
effective encapsulation and transportation of reactive species would have the potential to expand to other heavy metal contamination, specifically those that do not have the ability to crosslink with guar, CMC, or scleroglucan. This encapsulation mechanism could be engineered to sorb onto contaminants, effectively maintaining contact between them and the reactive agents.
References


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