ENHANCED TRICHLOROETHYLENE REMEDIATION WITH A POLYMER-AIDED ALCOHOL FLUSHING

by

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ABSTRACT

In situ flushing for remediation of dense non-aqueous phase liquids (DNAPLs) contaminated soil and groundwater is done by the injection of a solvent solution into the contaminated zone. The system is followed by downstream extraction of a mixture of groundwater, flushing solution and the contaminants for an aboveground treatment. Permeability is the principal cause which the flushing solution moves through a porous medium and, therefore, determines how effective the remediation is. DNAPLs entrapped in low permeable zones are not easily flushed out diminishing overall treatment efficiency. Moreover, residual DNAPLs are released over a long period of time, which makes our health and safety risky.

The objective of the research is to evaluate effectiveness of polymers to modify permeability for in situ flushing of DNAPLs in the heterogeneous subsurface setting. Trichloroethylene (TCE) was tested as the target DNAPL compound and 5% methanol was used as the flushing solution. Both biopolymers and synthetic polymers were utilized. The parameters measured were the pressure developed due to polymer injection and the time for flushing, transport extent and concentration of TCE. Different methanol concentrations and flushing modes were also evaluated. Natural soils having dissimilar properties were tested. Results indicated that the biopolymer injection could reverse permeability contrast and thereby increase overall TCE removal.

RESUMEN

El enjuague in situ para la remediación de agua subterránea y suelos contaminados con líquidos en fase no acuosa densos (DNAPLs) es realizada por la inyección de una solución solvente dentro de la zona contaminada. El sistema es seguido mediante la extracción aguas abajo de una mezcla formada de agua subterránea, solución de enjuague y contaminantes para un tratamiento en la superficie. La permeabilidad es la principal razón de cómo la solución de enjuague se mueve a través de un medio poroso, y por lo tanto, determina cuán efectivo la remediación es. DNAPLs atrapados en zonas de baja permeabilidad no son fácilmente lavados en detrimento de la eficiencia total del tratamiento. Por otra parte, los DNAPLs residuales son liberados durante un largo periodo de tiempo, lo cual pone en riesgo nuestra salud y seguridad.

El objetivo de esta investigación es evaluar la eficacia de los polímeros para modificar la permeabilidad mediante un enjuague in situ en configuraciones de superficies heterogéneas. Tricloroetíleno (TCE) fue utilizado como el compuesto de estudio del DNAPL y metanol al 5% fue usado como solución de enjuague. Ambos, bio-polímeros y polímeros sintéticos fueron usados. Los parámetros medidos fueron la presión desarrollada debida a la inyección del polímero y el tiempo de enjuague; el alcance del transporte y la concentración de TCE. Diferentes concentraciones de metanol y modos de inyección fueron también

evaluados. Los resultados indicaron que la inyección de bio-polímeros puede revertir el contraste de permeabilidad y por lo tanto incrementar la remoción total de TCE.

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To God, my family and friends.

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Table of Contents

Table List

Tables **Page**

Figure List

Figures **Page**

List of Symbols and Abbreviations

°C	-	degree Celsius
CEC	-	cationic exchange capacity
Cl^-	-	chloride ion
Cp	-	Centipoises
DD	-	degree of deacetylation
DNAPL	-	dense non-aqueous phase liquid
FOC	-	fraction organic carbon
GC	-	gas chromatography
High p	-	High permeability
HPLC	-	high pressure liquid chromatography
Kd	-	Desorption coefficient
Koc	-	Partitioning coefficient
LD_{50}		lethal dose that kills half of the animals tested
Low p.	-	Low permeability
MC10IF	-	a methanol concentration 10% (v/v) with intermittent flushing
MC5CF	-	A methanol concentration 5% (v/v) with continuous flushing
$mg.L^{-1}$	-	miligram(s) per liter
mL	-	mililiter(s)
$mL.min^{-1}$	-	mililiter(s) per minute
mM	-	Milimolar
MW	-	molecular weight
N/A		not applicable
NAPL	-	non-aqueous phase liquid

OM	-	organic matter
PAAF	-	polymer aided alcohol flushing
ppm	-	part per million
PR	-	Puerto Rico
PV	-	Pore Volume
SARA	-	superfund amendments and reauthorization act
SPME	-	solid phase micro extraction
SVE	-	soil vapor extraction
TCE	-	Trichloroethylene
TFe	-	total Iron
TN	-	total Nitrogen
USCS	-	unified soil classification system
v/v	-	volume/volume percentage
VOC	-	volatile organic compound
w/w	-	weight/weight percentage
WHMIS	-	workplace hazardous materials information system

1 INTRODUCTION

1.1 Justification

Soil and groundwater contamination with dense non-aqueous phase liquids (DNAPLs) such as chlorinated solvents is a widespread and serious environmental problem (Padget and Hayden, 1999). In the subsurface, DNAPLs can be present as residual saturation, discontinuous immobile blobs, and/or a continuous mobile phase. In either case, they represent a long-term source for widespread groundwater contamination.

Trichloroethylene (TCE) is a volatile organic compound (VOC) commonly found as a DNAPL. TCE is very dangerous because of their heterogeneous distribution and long-term perseverance in the subsurface environments (NRC, 2000). DNAPLs are also very difficult to locate, characterize, and remediate.

Among the current strategies for remediating DNAPLs in contaminated sites is alcohol flushing (Chawla, 2001). It is a promising in situ remediation technology for the saturated zone contamination. Alcohol solutions have been shown to substantially increase the solubility of chlorinated organic solvents and to enhance dissolution and reduce the interfacial tension between the aqueous and solvent phases (Padget and Hayden, 1999). The change in interfacial tension reduces the capillary forces acting on the DNAPL blobs and can potentially cause them to mobilize. These alcohol solutions flushed through contaminated aquifers could result in significant decrease in clean-up time (Chawla, 2001).

Sweep efficiency can be defined as how uniformly the injected fluid contacts the area contaminated by the DNAPL (GWRTAC, 1997), and this is usually higher in soils with high permeability (Darwish et al., 2003). Hence, its low efficiency in porous media is the major obstacle for using in situ flushing, especially for heterogeneous systems (Jeong et al., 2003).

From the petroleum industry, it is well known that polymer solutions can be injected following a surfactant solution slug to act as a mobility buffer and increase the overall sweep efficiency (Martel et al., 1998). The polymer injection results in relative permeability reversal. This is done by blocking the high permeable zone. This could enhance TCE remediation from a low permeable zone (Giese and Powers, 2002).

It is important to mention that there are other ways to achieve this permeability contrast such as: microbiologically and thermally. For examples, a research demonstrated a permeability modification by the microbially-formed calcium carbonate (Nemati et al., 2005). On the other hand, reducing the soil temperature was effective to modify permeability and, therefore, aquifer flow paths (D'Cunha et al., 2009).

Natural biopolymers can be effectively utilized to achieve reversal of permeability contrast and, therefore, improve the sweep efficiency in heterogeneous subsurface systems (Huang et al., 2000). Despite their inherent advantages, natural biopolymers have not been used in a polymer-aided alcohol flushing (PAAF). In this regard, the research tested the potential of natural biopolymers in comparison to synthetic polymers in PAAF for enhancement of TCE remediation.

1.2 Objectives

The overall goal of this research centered on enhanced remediation of contaminated zones with chlorinated solvents, particularly TCE, using an in situ remediation technology, PAAF.

The specific objectives to attain this goal were to:

- Determine the effect of alcohol injection on TCE remediation from different soil permeability configurations;
- Assess feasibility of enhanced TCE remediation with permeability modification by PAAF in saturated soils;
- Evaluate natural biopolymers for their use as the main polymers for PAAF; and
- Study the PAAF performance in TCE contaminated soils having different characteristics with natural polymers.

2 THEORETICAL BACKGROUND

This chapter presents necessary background and state-of the-art knowledge on DNAPLs such as physical and chemical properties, fate and transport processes, and remediation technologies, especially PAAF. This background and knowledge have been applied for the design of experimental setup and methods, data analysis, and result interpretation.

2.1 DENSE NON-AQUEOUS PHASE LIQUIDS

DNAPLs are defined as a separate-phase, slightly water-soluble liquids having a specific density greater than one. DNAPLs such as chlorinated solvents, coal tars, and heavy mineral oils are among the products most frequently encountered at ground water contamination sites (Darwish et al., 2003). Among these contaminants, TCE is one of the chlorinated solvents most frequently detected at the contaminated sites in US (Moran et al., 2007). It has been detected in 852 Superfund sites across the US, according to the Agency for Toxic Substances and Disease Registry.

Chlorinated solvents form a class of DNAPLs that have been produced in large quantities throughout the world since the middle of the 20th century (Kueper et al., 2003). They have been used for chemical extraction (e.g., chloroform), refrigeration (e.g., methylene chloride), dry cleaning (e.g., TCE), metal degreasing (e.g., TCE), pharmaceutical production,

and pesticide formulation (Serrano, 2008). The scope of this work is on TCE. Therefore, the discussion will focus on relevant physico-chemical properties of chlorinated solvents.

2.1.1 Physico-chemical properties of chlorinated solvents

Chlorinated solvents are volatile organic compounds, only slightly soluble in water, and with a low interfacial tension (Moran et al., 2007). They are commonly found in the subsurface as a separate fluid phase immiscible, and dissolved and volatile in water and air respectively (Kueper et al., 2003). In addition, many chlorinated solvents may move rapidly in the subsurface and disperse easily disperse in the environment with a high toxicity and low degradability (NRC, 2000). In general, the density (ρ) of most chlorinated solvents DNAPLs range from 1.1 to 1.6 $g.cm^{-3}$ and their viscosity (υ) from 0.57 to 1.0 cp. (Kueper et al., 2003). The rapid rates of subsurface migration as immiscible fluids are the result of their higher density and lower viscosity than water (ρ_{water} = 998.2 $kg.m^{-3}$ and υ_{water} = $1.00*10^{-6}$ $m^2.s^{-1}$ at 20°C) (Tood and Mays, 2005).

Like many chlorinated solvents, TCE is a DNAPL having a density of 1.46 $mg.L^{-1}$. The general physico-chemical characteristics of TCE are listed in table 1 (Chawla, 2001)

Table 1: TCE properties
Source: (Chawla, 2001,)

Property	TCE
Formula	C_2HCl_3
Molecular Weight	131.4 g/mol

Property	TCE
Density	1.46 $mg.L^{-1}$
Viscosity	0.5 cP
Boiling Point	86.7°C
Melting Point	-73°C
Water Solubility	1100 $mg.L^{-1}$@25°C
Vapor pressure	77 torr @25°C
K_h	0.00892 $atm\text{-}m^3.mol^{-1}$ @20°C
Log K_{oc}	2.34
Log K_{ow}	2.42

2.2 SUBSURFACE TRANSPORT OF CHLORINATED SOLVENTS

When released in sufficient quantities in the unsaturated or saturated zones, chlorinated DNAPLs spread vertically or laterally in the subsurface. Their distribution can be continuous, discontinuous, or both (Serrano, 2008). The invasion of DNAPL into the subsurface favors its migration within the higher-permeability zones. The hysteretic capillary forces cause retention of a portion of the liquid within the pores as discontinuous globules or ganglia (Christ et al., 2005). The distribution of residual saturation is not uniform and depends on porous media characteristics.

Substantial DNAPL volumes can also be retained because of the presence of non-uniform soil texture, which may result in DNAPL pooling (i.e., zones of DNAPL at much higher saturation) above layers or lenses of lower-permeability media (Christ et al., 2005). The resulting distribution of DNAPL is, thus, typically complex and non-uniform (Figure 1). When vertically moving DNAPLs encounter the water table, they will accumulate until there are enough gravity forces to overcome capillary and hydrostatic forces and displace water.

Efforts to displace a more viscous fluid by a less viscous fluid in the presence of heterogeneous pore-size distribution may result in instabilities in the fluid flow and the

formation or preferential paths, termed viscous fingers, that displacing fluid follows (Powers et al., 1998).

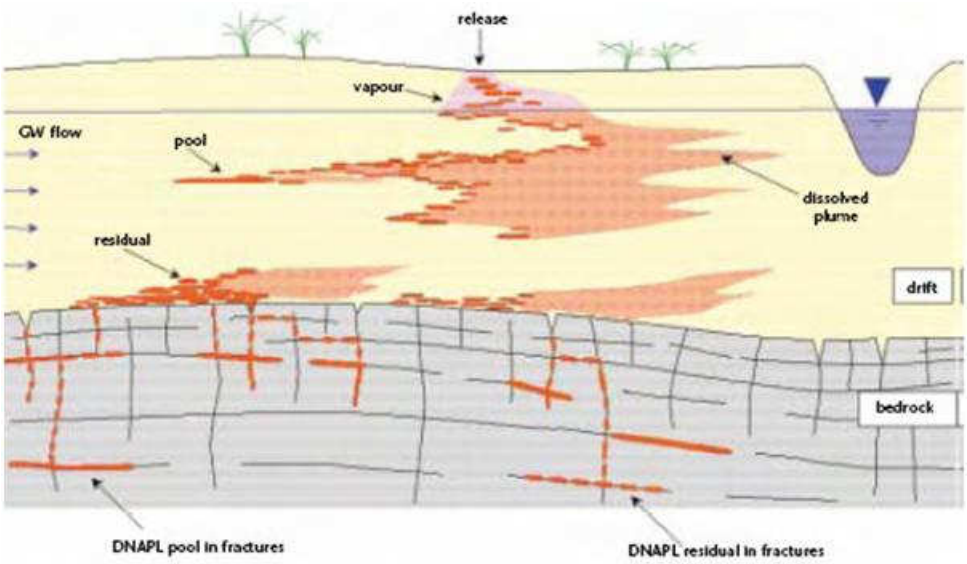


Figure 1: DNAPL distribution in unconsolidated deposits
Source: (Kueper et al., 2003)

As in unsaturated media, residual DNAPL in saturated media, residual DNAPL in saturated porous media forms relatively immobile discrete globules and ganglia disconnected from each other (Serrano, 2008). Entrapped DNAPL mass tends to dissolve slowly into flowing water, serving as a long-term source of groundwater contamination (Christ et al., 2005). DNAPLs pools also form where DNAPLs encounter finer grain media under the water table.

Natural groundwater may flow through source zones containing DNAPL globules, ganglia and pools and, therefore, small amounts of DNAPL can contaminate large volumes of an aquifer and pose greater risks to receptors and the environment (Serrano, 2008).

DNAPL contamination of soils and groundwater has detrimental effects on the environment, limits availability of water resources, and can pose a serious threat to human health (Moran et al., 2007). Chlorinated solvents have been associated with both acute and chronic human-health problems including liver damage and possible kidney effects, spontaneous abortions, reduce fertility, cancer, and childhood leukemia (US EPA, 2005).

2.3 DNAPL REMEDIATION

This section intends to provide a general overview of the various remediation technologies available for source zone remediation. Most of these technologies are also applicable to remediation of dissolved, vapor and sorted contamination downstream of the source.

These are several of in-situ NAPL remediation technologies (Falta et al., 2005). These technologies include: containment of the pollution (capping, hydraulic isolation, soil vitrification, and solidification); removal of pollutants (excavation, pump and treat, soil vapor extraction, hydraulic removal); phase-transfer induction (air sparging); pollutants interception (reactive permeable barrier, funnel and gate); phase-changes induction (thermal

enhancement); chemical degradation of NAPL (oxidation) or chemical or biochemical degradation of NAPL components dissolved in groundwater (oxidation, biodegradation); and changing the physico-chemical properties of the NAPL and or solvent (chemical flushing). Below is brief technical information of these technologies extracted from the reference (Falta et al., 2005).

Containment is done by inhibition of the hydraulic contact between the polluted zone and the rest of the soil system. There are four main kinds of containment: capping, hydrodynamic isolation, solidification and vitrification. Capping involves placing a cover over contaminated material to prevent escape of harmful vapors and stop rainwater from seeping through the polluted zone. The hydrodynamic isolation is in which the polluted zone is isolated by modifying the local flow regime through a strategic place of pumping and injection wells. On the other hand, the solidification involves mixing polluted soil with solidifying materials such as cement. Vitrification is a process that turns the soil into a solid block of glasslike material.

The excavation and pump and treat are examples of technologies of removal, by which the soil and/or groundwater is removed and treated on site. Excavation is a simply the digging up of polluted soil. Pump and treat is the technology by which the contaminated groundwater is brought up to the surface through pumping for a treatment. It relies on advection and dissolution processes of the contaminants.

Examples of inducing phase transfer are soil vapor extraction (SVE) and air sparging. The first removes volatile NAPL components from the unsaturated zone through extraction wells. By creating vacuum in the wells, polluted air is withdrawn from unsaturated zone and volatilization is promoted. In contrast, air sparging involves injecting air below the groundwater table. The air strips soil and groundwater volatile NAPL components from and carries them to the unsaturated zone or the surface where they are collected by a collection system.

In the pollutant interception, the pollutants are removed by means of mechanical and biological methods of the polluted groundwater intercepted downstream of the pollution site. For example, a permeable reactive barrier (PRB) is created by building a long narrow trench in the path of the polluted groundwater and filling it with a material that can clean up dissolved NAPL component. On the other hand, a funnel and gate system is basically similar to PRB, except that the groundwater is forced to pass through the permeable reactive zone (gate) by guiding walls (funnel) along the groundwater flow direction.

Chemical oxidation introduced a chemical agent (Potassium permanganate, Hydrogen peroxide + Fenton's reagent, and Ozone) that degrades NAPL components dissolved in groundwater. Degradation of dissolved NAPL components near NAPL-water interface results in enhanced rates of mass transfer, increasing the efficiency of extraction of groundwater containing dissolved NAPL components.

Thermally enhanced extraction is the steam injection at the periphery of the NAPL contaminated area, heats the subsurface, and drives NAPLS towards liquid extraction wells. Steam injection also vaporizes volatile compounds in NAPL and drives vaporized NAPL components towards vapor extraction wells. Electrical resistance heating vaporizes volatile NAPL components and vaporized components are collected via vapor extraction wells.

In chemical oxidation/thermal enhancement, steam and air are injected into the NAPL contaminated area, creating a heated, oxygenated zone. The injection is stopped and steam condenses and groundwater containing dissolved NAPL components returns to heated zone. The groundwater mixes with the condensed steam and oxygen, which degrades the NAPL components dissolved in water.

Bioremediation involves biochemical reactions degrading NAPL components dissolved in groundwater. Degradation of dissolved NAPL components nears NAPL-water interface results in enhanced rates of mass transfer, increasing the effective rate of dissolution and the efficiency of extraction of groundwater containing dissolved NAPLS components.

Chemical flushing such as surfactant enhanced aquifer remediation and solvent flushing (e.g., alcohols) has shown their effect through either mobilization or solubilization. Mobilization is produced by injection of chemical agent to groundwater and reduces interface tension between NAPL and water. On the other hand, solubilization is produced by the injection of chemical agent to groundwater to increase solubility of NAPL components dissolved in the groundwater.

Each technology and combination of technologies has shown mixed advantages and disadvantages. The type of remediation to use is very site specific. A combination of safety, logistic, throughput, and cost issues often determines the practicality of treatment technologies (US EPA, 2005).

Among the previous strategies for remediating DNAPL contaminated sites is alcohol flushing. It is a promising in situ remediation technology for the saturated zone contamination; therefore the following section will further describe in situ alcohol flushing.

2.4 IN SITU ALCOHOL FLUSHING

Alcohol flushing is an in situ remediation technology commonly utilized for removing DNAPLs from the saturated zone. This is done by injection of an aqueous solution into the zone contaminated with them, followed by down gradient extraction of groundwater and elutriate (flushing solution mixed with the contaminants) and aboveground treatment (Padget and Hayden, 1999). Permeability is the principal factor controlling the flushing solution through a porous medium and, therefore, determines how effective the remediation is (Tood and Mays, 2005).

Containment of the flushed contaminants and flushing solutions allows more successful application of in situ flushing. Application is thus simplified when vertical and horizontal hydraulic gradients are low and/or the treatment zone is bounded geologically by materials with relatively low hydraulic conductivity (GWRTAC, 1997).

Alcohol solutions have been shown to substantially increase the solubility of chlorinated organic solvents, and also enhance dissolution and reduce the interfacial tension between the aqueous phase and solvent phase (Padget and Hayden, 1999). The change in interfacial tension reduces the capillary forces acting on the DNAPL blobs and can potentially cause them to mobilize. A control on DNAPL mobilization is necessary for do not contaminate clean zones. These alcohol solutions flushed through contaminated aquifers could result in significant decrease in clean-up time (Padget and Hayden, 1999). Figure 2 illustrates how contaminated soil and groundwater are remediated with an in situ alcohol flushing technique.

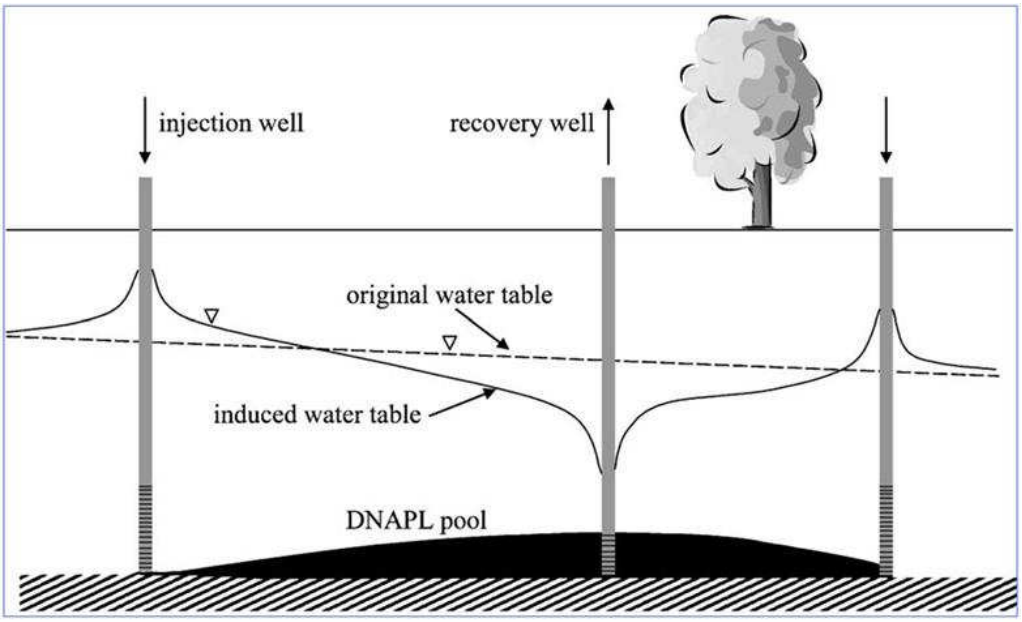


Figure 2: Conceptual diagram of a flooding operation to recover mobile DNAPL pooled on a low-permeability layer
Source: (Giese and Powers, 2002)

The alcohol solution or cosolvents were selected based on their readily biodegradability in soil and water, low toxicity, high solubility and low cost. The relevant physical/chemical properties of these alcohols are listed in Table 2. These alcohols have similar characteristics. The only major difference is the vapor pressure and boiling point of methanol, which means that it will go into the vapor phase before the other alcohols (Chawla, 2001). Methanol is a little cheaper but also slightly toxic and may offset its price advantage if the toxicity issue has to be addressed.

Table 2: Cosolvent properties
Source: (Chawla, 2001)

Property	Methanol	Ethanol	Isopropyl Alcohol
Boiling point(°C)	65	79	80
Vapor pressure @ 20°C(mm Hg)	127	40	33
Melting point(°C)	-98	N/A	-86
Specific gravity @ 20°C	0.791	0.79	0.786
Solubility in water	100%	100%	100%
Carcinogenicity	No	No	No
Biodegradability in soil	Readily	Readily	Moderately
Biodegradability in water	Readily	Readily	Moderately
Half life in soil (days)	1-10	N/A	1-10
Environmental toxicity	Slightly toxic	Not toxic	Not toxic
LD_{50} ($mg.Kg^{-1}$)	5628	7060	5045
Price ($/200L)	672.50	917.80	868.15

All alcohol solutions were found to dissolve similar amounts of TCE, at 5% (v/v), increasing the net organic character of the resulting solvent (water + cosolvent) that decreases the hydrophobic interactions between the solute and water (Chawla, 2001). They were also non-toxic at this concentration.

The additional features of in situ alcohol flushing are such as lower costs associated with in-situ treatment (no soil excavation/ building demolition required) and minimal interruption of commercial/industrial activities at the site. However, treatment rates are generally slower than ex-situ treatments (Boyd and Farley, 1990).

Sweep efficiency can be defined as how uniformly the injected fluid contacts the area contaminated by the NAPL (Boyd and Farley, 1990). Its low efficiency in porous media is the major obstacle for using in situ flushing, especially for heterogeneous systems (Jeong et al., 2003). Efficiency is usually higher in higher permeability layers than in lower permeability ones (Darwish et al., 2003)

From the petroleum industry, it is well known that polymer solutions can be injected following a surfactant solution slug to act as a mobility buffer and increase the overall sweep efficiency (Martel et al., 1998). This could enhance TCE remediation from a low permeable zone (Giese and Powers, 2002).

2.5 POLYMER SOLUTIONS

The polymers are long chains obtained by successive covalent bonding of small units called monomers (Renault et al., 2009). Polymers, such as Xanthan gums, hydrolyzed polyacrylamides, hydroxyethylcellulose, carboxymethylhydroxyethycellulose, and Glucan have been used for enhancement of oil recovery as water-blocking agents (Lake, 1989; Sorbie, 1991). They have also been used in reducing erosion, sealing of cultivated soil, improving soil stability and clay flocculation (Ben Hur et al., 1992; Pefferkorn et al., 1999). In addition, they are applied to eliminate residual concentration of inorganic salts in drinking water (Elfarissi et al., 1998). Polymer solutions were also used in NAPL recovery (Martel et al., 1998; Giese and Powers, 2002). They can therefore be considered environmentally acceptable and can be used in geo-environmental applications (Osada and Kajiwara, 2001; Darwish et al., 2003).

Polymer solutions are used to reach lower residual NAPL saturation in aquifers or to increase the sweep efficiency of surfactant solutions injected for in situ remediation of aquifers (Martel et al., 1998). The experiments and simulations show that polymer injection leads to modification of the permeability contrast that favors a more efficient pump and treat process by blocking the high permeable zone (Darwish et al., 2003)

Also, polymers solutions may improve mobile DNAPL recovery by increasing the ratio of DNAPL to water viscosity and by decreasing the aqueous phase velocity. The change in aqueous phase flow behavior increases the front stability, thereby reducing viscous finger formation and improves pore-level displacement efficiency (Giese and Powers, 2002).

Therefore, the polymer solutions can be injected to increase the overall sweep efficiency (Martel et al., 1998).

There are two kinds of polymers: natural and synthetic. The advantages of natural polymers over synthetic counterparts are: higher safety to human health, greater biodegradability and treatability (Kawamura, 1991; Bailey et al., 1999). Among the biopolymers or natural polymers, alginic acid and chitosan are safer because they are not toxic, ecologically acceptable, and environmentally friendly (Renault et al., 2009).

The selection of the best polymer to be used depends on criteria such as: the physical properties of the polymer solution, the interactions of the polymer with the alcohol and the contaminant; and the interactions of the polymer with the porous media. The polymers that were tested include two natural polymers (chitosan and alginic acid) and two synthetic polymers (POL EZ 8736 and POL EZ 675).

2.5.1 Chitosan

Chitosan is a linear copolymer (polysaccharide) of D-glucosamine and N-acetyl- D-glucosamine produced by the deacetylation of chitin (Figure 3), a natural polymer of major importance. Chitin is the second most abundant biopolymer in the world, after cellulose. The main sources exploited are two marine crustaceans, shrimps and crabs. Chitosan has unique properties among biopolymers especially due to the presence of primary amino groups and it

is a commercially interesting compound because of its high nitrogen content in comparison to cellulose (Renault et al., 2009).

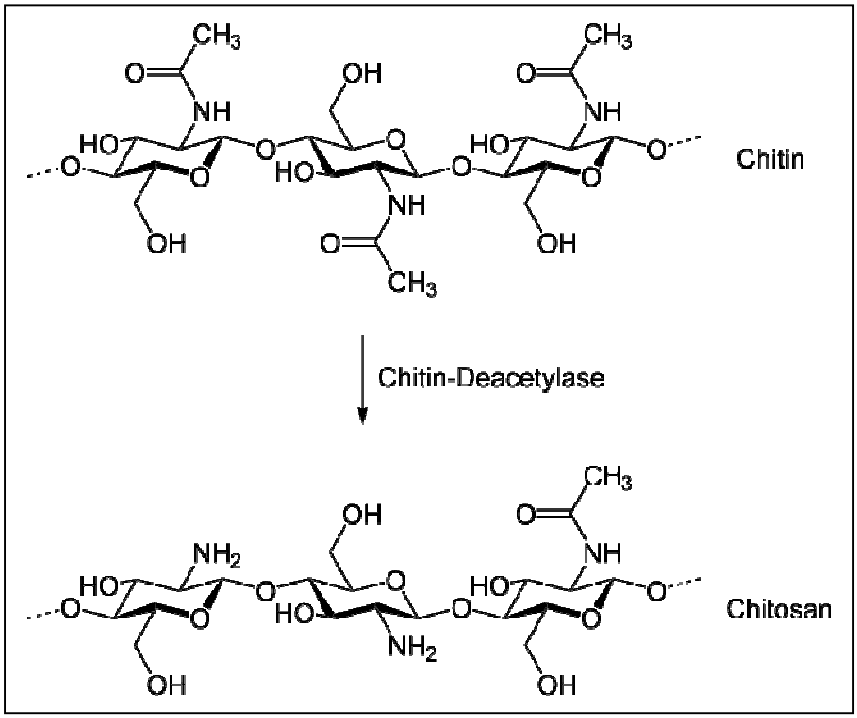


Figure 3: Chitosan structural formula
Source: (Renault et al., 2009)

2.5.1.1 Properties

Chitosan does not cause chemical burns and they are non-toxic. Also it is a powerful cationic coagulant/flocculant that has the unique ability to bind contaminant particles together so that they can be filtered or gravity settled. It is completely biodegradable and do not persist in the environment (Renault et al., 2009). The main parameters influencing the characteristics and properties of chitosan are: its molecular weight (MW), degree of

deacetylation (DD) representing the molar fraction of deacetylated units, and crystallinity. These parameters are determined by the conditions set during the preparation.

2.5.2 Alginic acid

Alginic acid, also called as algin or alginate, is a naturally occurring hydrophilic colloidal polysaccharide obtained from the various species of brown seaweed (Phaeophyceae) (Ding et al., 2009). It is a linear copolymer consisting mainly of residues of β-1,4-linked D-mannuronic acid and α -1,4-linked L-glucuronic acid. Its structural formula is shown in Figure 4. These monomers are often arranged in homopolymeric blocks separated by regions approximating an alternating sequence of the two acid monomers.

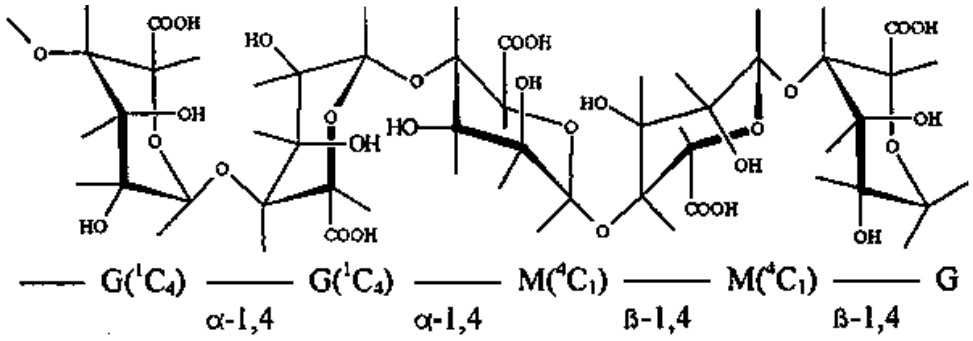


Figure 4: Algin structural formula
Source: (Ding et al., 2009)

2.5.2.1 Properties

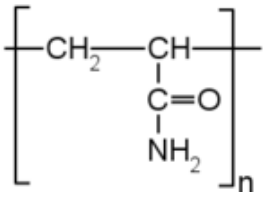
Algin is a gelatinous material structural that can be found as white to yellowish brown filamentous, grainy, granular or powdered forms. This polymer is used main as stabilizer, thickener, gelling agent and emulsifier. In general, it is insoluble in water and organic solvents and dissolves slowly in solutions of sodium carbonate, sodium hydroxide and trisodium phosphate (Ding et al., 2009).

2.5.3 Synthetic Polymers

Synthetic polymers are chemically manufactured from separate materials. Synthetic polymers require human intervention. For the current study, two synthetic polymers were tested for PAAF: polymer blends (POL EZ 675) and a polyacrylamide (POL EZ 8736). The following is the toxicity analysis for these polymers (Table 3).

Table 3: Comparison of Toxicity between POL EZ 675 and POL EZ 8736
Source: (Nalco, 2008)

Parameters	POL EZ 675	POL EZ 8736
Category	Coagulation and Flocculation	Coagulation and Flocculation
Official Name	Polymer Blends or Polyacrylamide	Polycrylamide
Maximum Product Application Dosage	3.5 $mg.l^{-1}$	0.8 $mg.l^{-1}$
Hazardous Substance	*Straight Run Middle Distillate *Ammonium Chloride	*Straight Run Middle Distillate
Environmental Precaution	It is toxic to fish	-
Toxological Information	No toxicity studies have been conducted on this product	No toxicity studies have been conducted on this product
Acute Fish	Essentially no toxic	Essentially non toxic
Acute Invertebrate	-	Essentially non toxic
Federal Water Pollution Control Act	Listed in the regulation by Ammonium	-

Parameters	POL EZ 675	POL EZ 8736
	Chloride	
State Right to Known Laws	*Straight Run Middle Distillate *Ammonium Chloride	*Straight Run Middle Distillate
WHMIS classification	Toxic Material	Toxic material
SARA/SUPERFUND amendments and reauthorization ACT of 1986 (TITLE III). Section 313 - List of toxic chemicals (40 CFR 372)	Does not contain substances on the list of Toxic Chemical	Does not contain substances on the list of Toxic Chemical
Structural formula	No available	

3 METHODOLOGY AND MATERIALS

The methodology that was developed and used throughout the experiments is discussed in this section. This chapter also includes a general description of materials used, experimental procedure, and chemical analysis.

3.1 Methodology

The methodology implemented to accomplish the objectives of this research was divided into three phases. The first phase was for the selection of an optimum configuration of heterogeneous soil systems for use of PAAF. The second phase was the design developed for assessment of the efficiency of alcohol flushing for TCE removal in a one-dimensional, vertically-oriented column setup. The final phase was the evaluation of natural biopolymers in PAAF. Also, in this final phase, the remediation efficiency between a typical alcohol flushing and a PAAF system was compared.

3.1.1 Variables evaluation for best permeability matrix

A series of the experiments were initially made with sand columns to reproduce a simple heterogeneous matrix consisting of sand layers with different permeabilities. Each layer was essentially homogenous. A glass column with a dimension of 20 cm long and 2.5 cm internal diameter (Kimble Chase Kontes) was used for the reactors. Experimental matrix

variables were organized and tested with in five categories: packing method, saturation direction, configuration, columns in the test, and polymers. These are described below:

3.1.1.1 Packing method

Several methods were used for determination of reactor packing to ensure the saturation of the system. These are described below:

- Soil saturation followed by reactor packing: The soils were saturated with water outside the reactor prior to packing. A beaker was used to mix 180 grams of soil and 60 mL of water. Then, the wet soils were carried to the reactor with a spoon and packed in the reactor by small amounts from the bottom to the top of the reactor.
- Soil packing followed by saturation: Each reactor was packed in incremental steps with dry soils layers of ten (10) grams each one to establish uniform bulk density, and then the systems were saturated with water. Saturation was done by pumping water from the bottom at a rate of 1 mL min^{-1} or less to ensure the trapped bubbles to come out of the system.
- Concurrent soil packing and saturation: This method consisted of adding a small fraction of the dry soil (~ 3g) to the reactor and then saturating it by pumping the water from the bottom at a small rate (e.g., 1mL min^{-1} or less). The procedure was repeated until the top of the reactor was reached by the saturated soil.

3.1.1.2 Reactor Layouts

There were two layout methods for saturating the reactors: horizontal and vertical. In the horizontal position, the reactor and the flow were horizontal. In the vertical position, the reactor and the saturation flow was vertical. Pressures were developed higher in the vertical position in comparison to the horizontal position.

3.1.1.3 Reactor Composition

Several configurations (Figure 5) of the porous media type were tested in the experiments. A brief description is listed below:

- Configuration 1 (Sand/clay-soil/sand (in series)): The high permeability reactor was packed with a coarse sand layer of eight (8) centimeters on the top and bottom of the reactor, with the clay soil layer of four (4) centimeters being in the middle. The low permeability reactor was packed with the same manner as for the high permeability reactor, but with the fine sand. TCE was placed in the clay layer as a contaminant source.
- Configuration 2 (Coarse sand and fine sand in parallel): It was an intermediate permeability configuration: low permeability on one half (fine sand) and high permeability on the other half (coarse sand). DNAPL was placed in the transversal half.

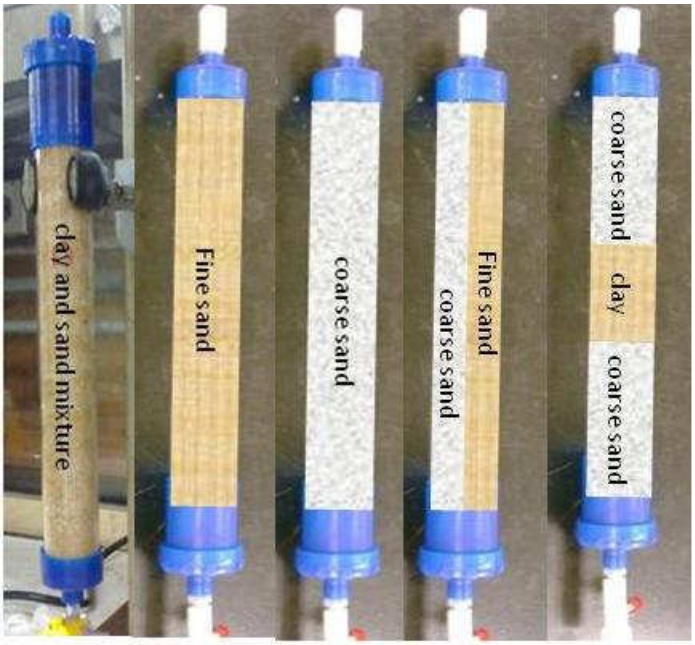


Figure 5: Soil layers configuration

- Configuration 3 (Fine sand in one reactor and coarse sand in the other reactor): This corresponded to a separate configuration of a low permeability in one reactor and a high permeability in the other reactor. TCE was placed in the middle of each reactor.
- Configuration 4 (Coarse sand-clay mixture and fine sand-clay mixture): These were very similar to the last arrangement, but the systems were closer to the real soil systems. For the high permeability reactor, the coarse sand was mixed homogenously with the clay soil at a ratio of 60% (sand, wt.) to 40% (clay). The fine sand was mixed homogenously with the clay soil at the same ratio (60:40) for the low permeability reactor.

- Configuration 5 (Coarse sand-natural sandy soil mixture and fine sand-natural sandy soil mixture): For the high permeability reactor, the coarse sand was mixed homogenously with the natural sandy soil at a ratio of 60% (sand, wt.) to 40% (natural sandy soil). The fine sand was mixed homogenously with the natural sandy soil at the same ratio (60:40) for the low permeability reactor.
- Configuration 6 (Coarse sand-natural sandy soil mixture and fine sand-clay soil mixture): A high permeability reactor was composed with coarse sand (60%, by wt.) and natural sandy soil (40%), whereas a low permeability reactor was with fine sand (40%) and clay soil (60%).

3.1.2 Design for efficiency of alcohol flushing for TCE removal

After the higher and lower permeability configuration had been determined, the next step was to assess efficiency of alcohol flushing for TCE removal in a one-dimensional setup. The scope was to evaluate the relationship between TCE removal percentage, flushing mode in the reactor, and alcohol concentration.

Methanol was used for this study as the testing alcohol. It was selected because it is less toxic and smaller with regard to the molecular weight than other alcohols. The alcohol concentrations used were: 5% and 10%, and two injection methods were tested: continuous and intermittent injection. Continuous injection consisted of application of five pore volume (PV) of methanol solution uninterrupted. On the contrary, for intermittent injection, one PV

was applied to the column per day for five days. The alcohol injection was done after saturating the reactor. The efficiency was tested from each configuration analyzing the ratio between the volume of alcohol injected and TCE removal rate

3.1.3 Evaluation of polymers in PAAF

In the experiments, natural and synthetic polymers were analyzed using the configuration 3. . In the reactors, the solvents and polymers were injected individually using the PAAF technology. The syringe pump was used to inject 15 mL of polymer solution in each reactor with a rate of 1 $mL.min^{-1}$ after injecting 60 mL of alcohol (5% v/v) with a rate of 15 $mL.min^{-1}$. Finally alcohol was injected again.

The pressure was monitored before to the inlet from each reactor. First, the trend of pressure development after polymer injection was studied for each polymer tested. This behavior was used to pre-select the polymers that generated a better permeability contrast. Then, the pre-selected polymers were studied using the configuration 4. The reactor effluents were analyzed for TCE concentrations via the Gas Chromatography (GC). This analysis was done to verify and decide polymers that generated a better permeability contrast.

Afterward, the polymer selected was used in the parallel configuration. The purpose was to validate the application of the polymer in PAAF technology for different

heterogeneously configurations. The reactors had the same characteristics that the previous experiment. The pressure was also monitored.

Natural soils having dissimilar properties were tested with the same procedure aforementioned in the parallel system with the configuration 5 and 6. The polymer chosen was used for this experiment. This experiment simulated a more realistic case scenario of polymer injection that would occur in field. This was accomplished by flushing the polymer solution without intervening its flow path. Briefly, these experiments were conducted with parallel columns of different permeabilities, in which the polymer was allowed to flow into both columns simultaneously. More details are given in section 3.3.1. It is important to note that in the previous experiments, the polymer solution was injected only to the high permeability reactor by blocking the flow with a valve. The pressure was monitored while the process was running.

Additional experiments were performed to investigate the effects of TCE aging in the soil. The process simulated long-term and slow accumulation of contaminant in soils. Artificial aging was conducted with a continuous alcohol injection. Once the reactor was saturated, these columns were left 10 days. After that, 4 PV with 5% (v/v) methanol solution were injected in the reactors.

3.2 Materials

The materials used to attain the experimental goals include natural and synthetic polymers, methanol, TCE, and porous media. These are described below:

3.2.1 Chitosan polymer (a natural biopolymer)

Chitosan polymer (ChitoVan) was acquired from the CascadeEcosolutions.

3.2.2 Alginic acid (a natural biopolymer)

Alginic acid was acquired from the Cole-Parmer in a powder form.

3.2.3 Synthetic polymers

Two synthetic polymers, POL EZ 675 (Polymer blends) and POL EZ 8736 (Polyacrylamides), were tested in the study. They are widely used in water and wastewater treatments as coagulants and flocculants (Nalco, 2008). Polymer solutions were acquired from the Nalco..

3.2.4 Alcohol solution

Methanol was used for this study as the testing alcohol. Methanol was acquired from Cole-Parmer Company

3.2.5 TCE

TCE was tested as the target DNAPL compound. Analytical grade TCE (>99% purity) was purchased from Aldrich Chemical. Stock solution of TCE at solubility was prepared in four liters (4 L) of deionized water added 8 mL of pure TCE.

3.2.6 Porous media

For the simulation of the porous medium of high and low permeability, sands in different sizes of 6/20 and 30/65, respectively, were used. The sand 6/20 means the sand particles passed the sieve #6 but retained on the sieve #20. Likely, the number 30/65 corresponds to the sieve #30 and #65. They were bought from the Standard Sand and Silica Co from Florida, USA and used as received. These sands are mainly comprised of quartz. The bulk density is 1.41 g cm^{-3} and the specific gravity is 2.65 (Standard Sand, 2009). Permeability of these sands was tested in accordance to ASTM. ASTM test method covers the determination of the coefficient of permeability by a constant-head method for the laminar flow of water through granular soils. Under the reactor setup used for this study, the coarse sand had permeability ($cm.sec^{-1}$) of $7.38x10^{-2}$ whereas the fine sand produced $2.53x10^{-2}$.

Clay was also used for the simulation of the porous medium. Experiments were conducted using Cotto clay soil collected from Isabela, PR. This soil is mainly composed of

kaolinite and quartz mineralogy (Molina, 2006). The physical and chemical characteristics are shown in Table 4 and Table 5.

Table 4: Physical characteristics of clayey soil collected from Isabela, PR
Source (Molina et al., 2006)

Isabela Clay	
USCS Classification	CL*
Liquid Limit %	46.6
Plastic limit %	25.4
Plastic Index %	21.2
Specific Gravity ($g.cm^{-3}$)	2.62
Specific Surface Area ($m^2.g^{-1}$)	44.4
Mineralogy	Quartz/kaolinite

*Clay, as definded by the Unified Soil Classification System (USCS)

Table 5: Chemical characteristics of clayey soil collected from Isabela, PR
Source (Molina et al., 2006)

Property	Value	Property	Value
Ca (ppm)	307.9	FOC %	0.67
Mg (ppm)	42.3	OM %	1.52
Na (ppm)	42.3	TFe ($mg.kg^{-1}$)	7938.8
HCO_3^- ($mg.kg^{-1}$)	1	TN ($mg.kg^{-1}$)	914
CO_3 ($mg.kg^{-1}$)	<1.00	pH	5.1
Cl^- (ppm)	77	CEC [$mg.(0.01g^{-1})$]	25.7

Table 6 shows the physical and hydraulic properties of the clay in the field (Rodriguez et al., 2007). The bulk densities are in the field range from 1.36 $g.cm^{-3}$ to 1.52 $g.cm^{-3}$, and the hydraulic conductivities are relatively large (for a clay soil) near the surface,

but decreases at depth. For the experiments proposed in this research, the clay was sieved through a 0.71 mm (# 25) sieve.

Table 6: Physical and hydraulic properties of Coto Clay in the field
Source (Harmsen et al., 2003)

Depth (cm)	Sand (%)	Silt (%)	Clay (%)	Bulk Density ($g.cm^{-3}$)	Porosity	Hydraulic conductivity ($cm.hr^{-1}$)
0-20	35.1	19.35	45.6	1.36	0.48	50.42
20-40	28.72	1.85	69	1.36	0.48	13.21
40-60	22.5	5	72.5	1.31	0.5	2.92
60-80	20	5.8	74.2	1.29	0.51	0.5

It should be noted that the sands were the surrogate materials packed for simulation of high and low permeable zones. Later, natural sandy soil from Guayama, PR and clayey soils representing high and low permeable zones, respectively, were mixed with the surrogate porous media.

The last experiments were conducted with a sandy soil collected from the Bay of Guayama, Puerto Rico. Chemical soil properties are listed in Table 7.

Table 7: Chemical characteristics of sandy soil collected from Guayama, PR
Source (Hernandez, 2009)

Property	Value
pH	7.94±0.057
Total Nitrogen (as N) (mg/g)	0

Property	Value
Total Phosphorous (as P) (mg/g)	0.002±0.001
Lead (mg/g)	0
OM %	1.92±0.086

The particle sizes for sand and clay soils, determined using sieve analyses (Molina et al., 2006; Hernandez, 2009), are shown in Figure 6. The Guayama sand is composed of 74.5 % sand sizes, 9.3% silts, and 16.2% of clays. The Isabela clay, on the other hand, is composed of 24% sands, 22% silts, and 54% clays.

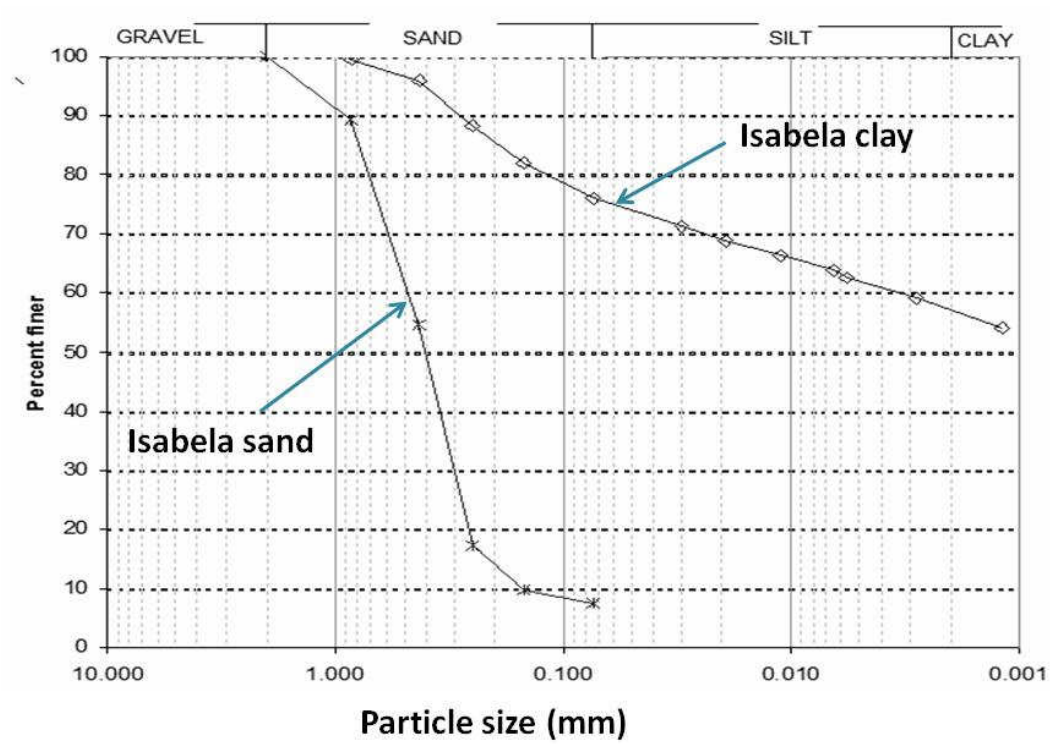


Figure 6: Particle size distribution for Isabela sand and clay
Source (Molina et al., 2006)

3.3 Experimental Procedure

The enhancement of alcohol flushing efficiency for TCE removal via polymer injection was evaluated under various experimental conditions (e.g., different flow rates of polymer injection and alcohol flushing, use of natural and synthetic polymers, and the configurations described in the Chapter 3.1.1). This section consists of system components, general description of the procedure used, the flushing method, chemical analysis, and tracer study.

3.3.1 System Components

The following is a description about the different components of the system: syringe pump, connections, pressure gage and the reactor (Figure 7).

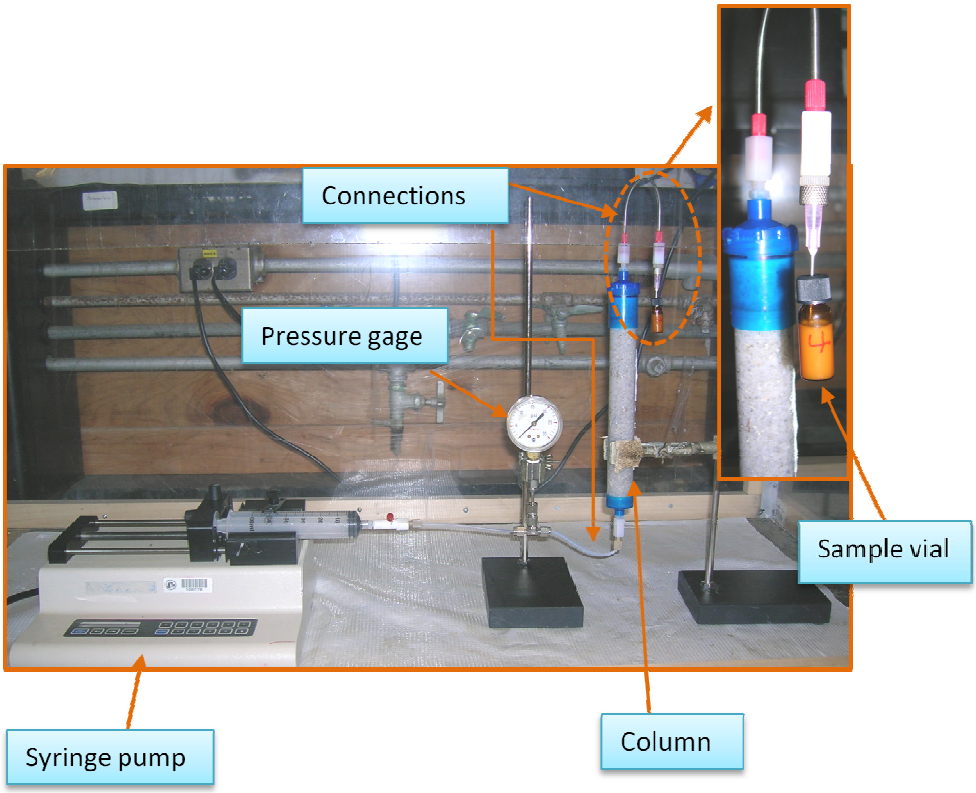


Figure 7: Developed System

KD scientific syringe pump - KDS 200: This pump provided a constant flow rate and has a linear force of 40 lb (18 kg). Depending on the experimental situation, it was run for: a) water to saturate the column: at 0.5 mL min^{-1}, b) methanol flushing of the column: 60 mL at 15 mL min^{-1} and c) polymer injection to the column: 15 mL at 1 mL min^{-1}.

Connections: Master Flex teflon tubes of 1/8" were used to prevent TCE from adsorption to the tube wall. They were acquired from Cole Parmer Company.

Pressure gauge: Pressure development during the course of PAAF experiment was monitored with a winters quality process pressure gage (EW-02) with a capacity of 15 Psi,

installed at the entrance of the soil reactors. It showed the physical behavior of the column with respect to the pressure developed due to the solution injected to the different permeability matrix. It was acquired from Cole Parmer Company.

Sampling port: The end part of the reactor was equipped with an effluent sampling port. Among three configurations tested, a semi-circular (a U-shape) stainless steel tubing showed the best results avoiding extra pressure creation due to an excess friction and providing structural integrity for the sample collection (Table 8). Sampling was done using a needle connected to the end of the port with a vial of 2 mL which collected the effluent.

Table 8: Design of the sampling port at the end of the reactor

Stainless steel semi-circular		Stainless steel rectangular output		Teflon free output	
					
Advantages	Disadvantages	Advantages	Disadvantages	Advantages	Disadvantages
Repeatability in shape		Repeatability in shape			No repeatability in shape
Low pressure			High pressure	Low pressure	
Minimal losses		Minimal losses			

3.3.2 Method

The following procedure was used with different configurations for development of PAAF technology. This includes the sequence of reagent application; volume, flow rate and concentration of TCE in water; methanol and polymer; and the time between each injection.

a) The soil reactor was saturated with a TCE solution at solubility and was left being circulated for 24 hours to make the system saturated with TCE. This time was necessary to assume saturation in the reactors.

b) 60 ml of methanol (5% v/v in a NaCl salt solution with a concentration of 500 ppm) was applied to each reactor at a rate of 15 ml min^{-1} with a KD scientific syringe pump: KDS 200. The pressure developed before from the inlet in the reactor was monitored at each 5 ml of the applied flushing solution. This was the first alcohol flushing prior to the polymer addition to the high permeability reactor.

c) During the first alcohol flushing, the volume of the effluent and TCE and salt concentrations in the effluent were taken in the outlet from each reactor. The effluent samples were collected in vials of 2 mL.

d) Fifteen mL of the respective polymer solution was applied to the high permeable reactor at a rate of 1 mL min^{-1} with a KD scientific syringe pump: KDS 200. The pressure developed was monitored with a Winters quality process pressure gage, EW-02, at each 3 mL of polymer addition.

e) To ensure the effect of polymer addition to the high permeable column, the systems were kept undisturbed for 24 hours. After polymer injection, 60 ml of 5% methanol (in a salt solution) was added to each reactor and the pressure developed was measured at each 5 ml of input solution. This step was the post-alcohol flushing after the polymer addition. Again, the volume of the effluent and TCE and salt concentrations in the effluent from each reactor were measured. TCE concentrations were measured in the GC and salt concentrations in the IC.

3.3.3 TCE injection in the reactor

Three methods were tested for TCE injection in the reactors. First, both coarse sand reactor and fine sand reactor had a TCE source zone, which was prepared by spiking 5 mL of TCE to 35 g of a clayey soil in a 40 mL vial with a cap. They were mixed homogeneously and kept undisturbed overnight. The clay TCE source zone was laid in the middle of the reactor (Figure 8).

Second, a separate, parallel system with two reactors was tested without clay TCE source zone. Instead, one reactor was packed only with the coarse sand and the other was only with the fine sand (Figure 9). In this case, 3 mL of pure TCE as the source contamination was injected at the two thirds depth of the reactor

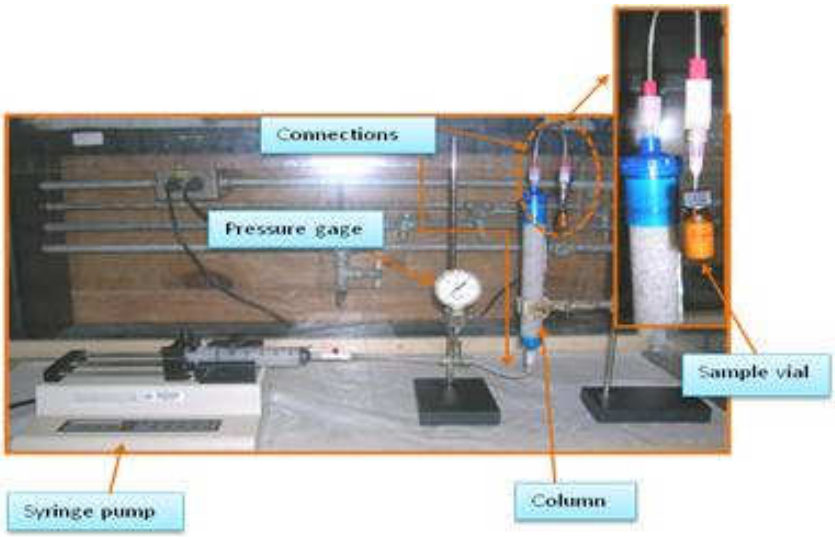


Figure 8: Reactor compositions. TCE source was prepared in a clayey soil which was laid in the middle of the reactor

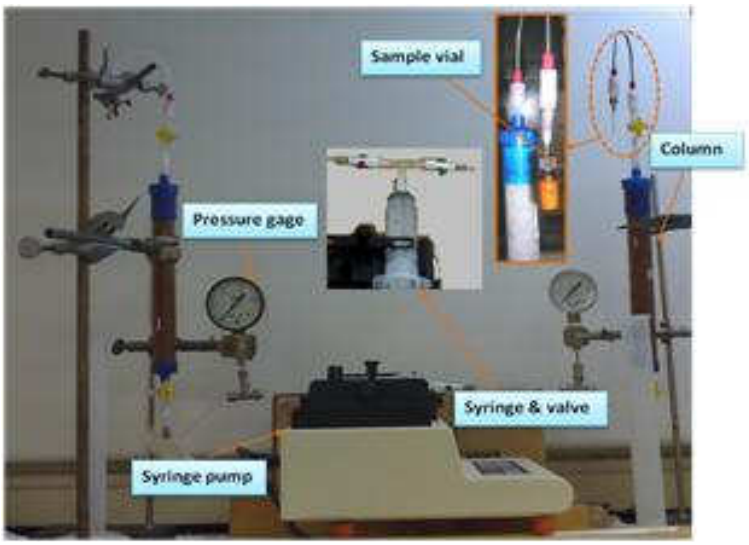


Figure 9: TCE was created by an injection of pure TCE at two thirds depth in the reactor

In the third option, the columns were saturated with a TCE solution at solubility by circulating for 24 hours. This saturation method was used for one or two columns in parallel (Figure 10 and Figure 11).

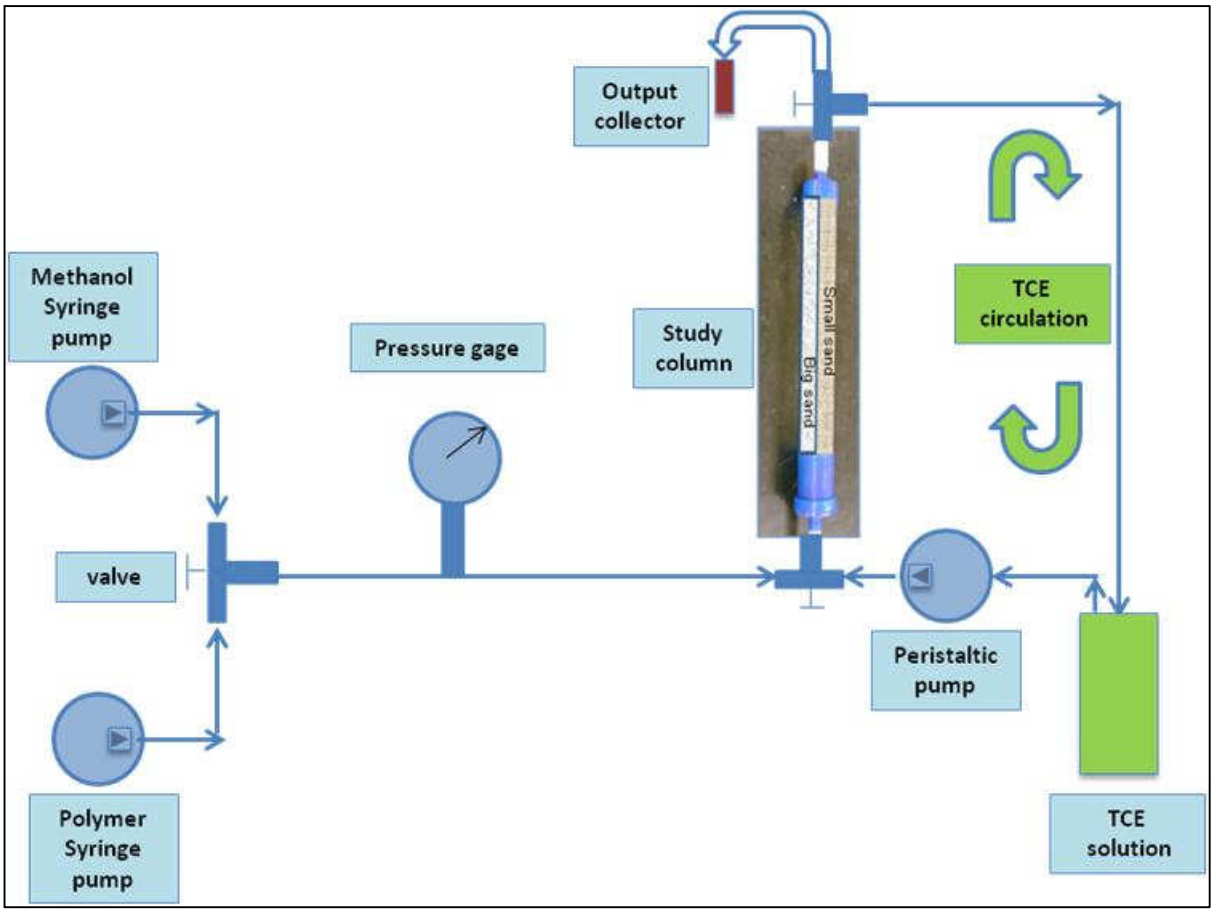


Figure 10: Singular system

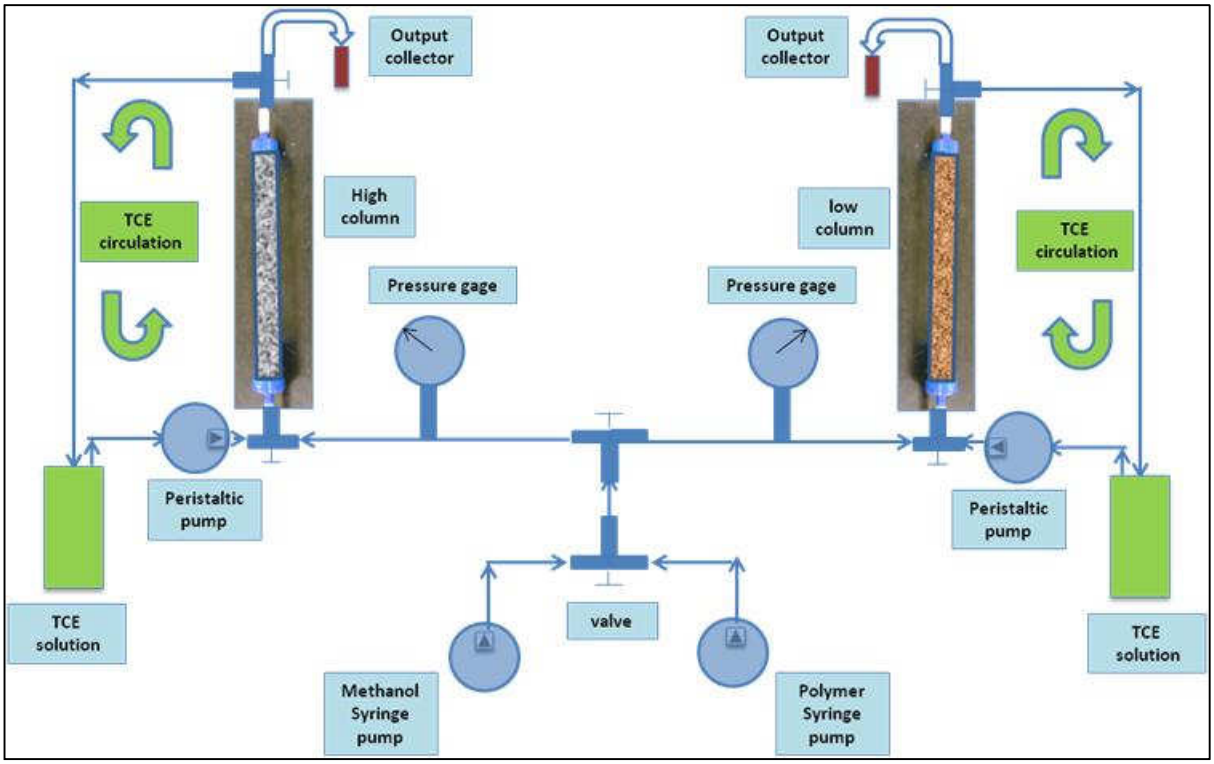


Figure 11: Parallel system

In this arrangement, configuration four (4) was selected. Less manipulation losses and preferential ways in the injection were the main reasons to choose this alternative. Accordingly, the error percent in mass balances were lower.

3.4 Reactor characteristics

In order to characterize the reactor, granulometric curves and tracer experiments were made. The methodology used is described below.

3.4.1 Granulometric curves

The granulometric curve of the soil study was determined using a sieve analysis. The sieves numbers chosen for the analysis were: 10, 20, 40, 60, 100, and 200. The sieves column with the soil was placed in the sieve shaker for 15 minutes. After that, each sieve with the soil was weighed. Then, the percent of soil retained in each sieve, the accumulative percent retained and the percent of fine soil were calculated and used to make the granulometric curve.

3.4.2 NaCl experiments

Tracer studies are a useful tool to unmask the heterogeneous structure of groundwater flow. A transport experiment was conducted using NaCl as a conservative tracer during the injection of the flushing solution in the reactors of high and low permeability. A NaCl concentration of 500 ppm (approximately 8.5 mM) was injected as standard solution. The effluents were collected in vials of 2 mL for subsequent analysis in the IC.

3.4.3 Flushing Method

The flushing method consisted of a sequential application of methanol and polymer solutions to high and low permeable zones as follows:

Pre-alcohol flushing: Alcohol is expected to transport more rapidly through larger pore spaces (i.e., high permeable zones) and solubilize/mobilize TCE contained in such

zones during four (4) minutes of the flushing period. Solubilization/mobilization was done by the water polarity change.

Polymer injection: After the first alcohol flushing, polymer solution was injected only to the high permeable reactor. The reactor composition depends on the configuration studied. The polymer will occupy pores in the high permeability zones via an adsorption(s) or similar processes due to its high viscosity. The polymer is expected to block flow in these large pores, thus reversing the relative permeability of the "higher" and "lower" permeability zones. Specifically, the polymer will penetrate deeply into the higher permeability zones, and only slightly into the lower-permeability layers. Consequently, the polymer will substantially reduce the flow of flushing solution through the higher permeability zones, while it can increase the flow of flushing solution through the lower permeability zones.

Post-alcohol flushing: The column is flushed again with alcohol solution for DNAPL removal. More alcohol flushing is expected in the lower permeability reactor, leading to the improvement of overall TCE removal.

3.4.4 Chemical Analysis

For a better chemical analysis of TCE, two extraction methods were developed for a gas chromatography (GC) a liquid/liquid extraction with hexane and a solid-phase micro

extraction (SPME). Temporal concentration breakthroughs curves generated were then analyzed using the method of moments.

3.4.4.1 Liquid/liquid extraction with hexane

Hexane was initially used to extract TCE from the aqueous samples (Xu et al., 1996; Penell et al., 1997; O'Niell et al., 1999; Delinsky et al., 2005; Urynowicz and Siegrist, 2005). The aqueous TCE samples (1.8 mL) were added in 2 mL GC/IC vials (amber) that had already contained 0.2 mL of hexane. These samples were agitated on a shaker table for 48 hours. Finally, 0.1 mL of hexane extracted was injected into the Perkin Elmer Autosystem GC.

The GC was equipped with a 30 m x 0.53 mm x 5 um Dimethylpolysiloxane column with a flame ionization detector (FID). In the FID, the hydrogen and air are combined and ignited electrically. Organic compounds are ionized in the flame, producing electrons that are measured as the signal, or response (Delinsky et al., 2005). As shown in Table 9, several operating parameters were evaluated to obtain the best analytical performance and results.

Table 9: Testing of several GC operating parameters

Variables	TCEiii
Initial temperature(°C)	40 deg for 2 min
Ramp 1	20.0 deg.min^{-1} to 160 deg, hold for 0.0 min
Oven (°C)	40
Injector (°C)	225

Variables	TCEiii
Detector (°C)	250
Experiment time (min)	8
Delay time (min)	0
Run time (min)	8
Injection	Manual
Detector	FID
Injection volume (µl)	3
Carrier gas Type	Helium
Flow rate ($ml.min^{-1}$)	4.5

The TCE detection and calibration were achieved with the TCEiii . The calibration curve showed an excellent regression coefficient of 99% (). Calibration ranged between 550 - 8800 mg TCE in a liter of hexane. The retention time for TCE was between 6.0 and 6.2 minutes.

Extractions were done at 8:1 sample/solvent ratio by mixing for 48 hours, followed by a separation period of 5 minutes. Between mixing and separation, there were additional steps of pre-heating for 1.5 minutes, manual mixing for 10 minutes, and additional vortex mixing for 5 minutes. Once extracted, the sample was injected manually and then analyzed in gas chromatography (GC) equipped with a FID.

As a means of quality control, after an injection of the sample, the syringe underwent a cleaning process. This process consisted of exposing the needle in a syringe cleaner at a

high temperature (250 ^{o}C) under the vacuum pressure. Also, this process was accompanied with nitrogen purging and acetone cleaning.

The solvent selection process also included isoamyl acetate and methyl chloride. But, these solvents did not provide clear TCE peaks.

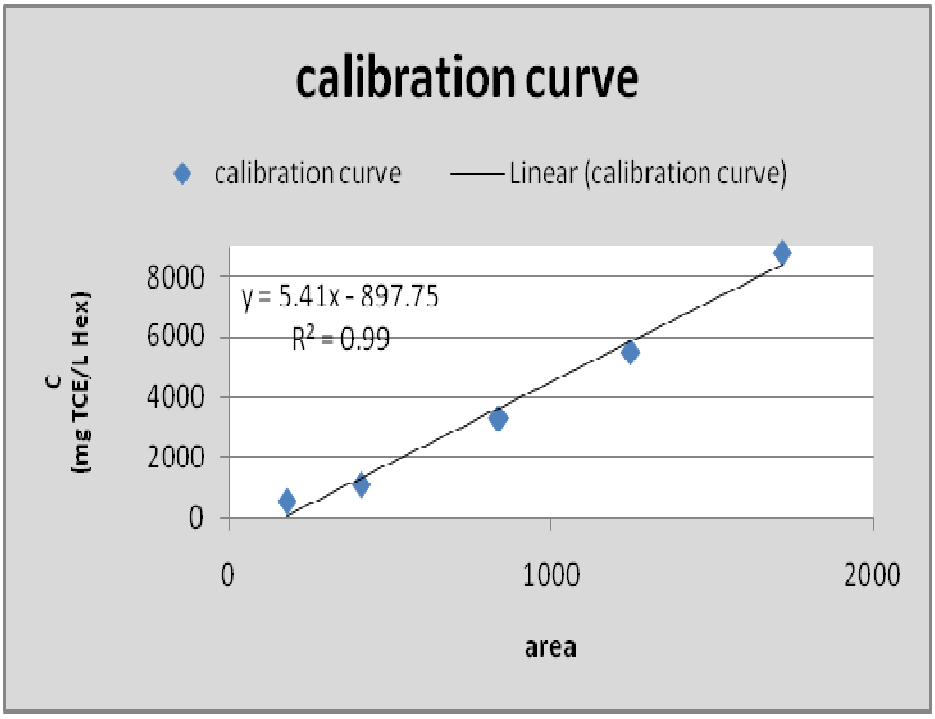


Figure 12: Results of the liquid/liquid extraction GC calibration for TCE Analysis

The detection was variable ranging from 550 to 8800 mg.L^{-1}. For this reason, it was necessary to develop another method to lower TCE concentrations. An SPME was tested for this reason and the results were explained in the next section.

3.4.4.2 Solid phase microextraction

In the SPME process, the aqueous TCE solution was shaken for five minutes before the adsorption. SPME was performed using the SPME sampling method (Figure 13), which inserted the SPME fiber Polydimethylsiloxane (100 μm film coating from Supelco) into the sample for four-minutes. The adsorption time was allowed for TCE to partition from the aqueous phase to the stationary phase. The SPME syringe was then inserted manually in the GC injector port. The fiber was exposed at 225°C injector temperature for four minutes to desorb the analytes into the GC Dimethylpolysiloxane column and the detector temperature was set at 250°C (Delinsky et al., 2005). The Perkin Elmer Autosystem GC was equipped with a flame ionization detector (FID) for TCE desorption and analysis.

Calibration ranged between 0 – 1100 mg TCE in liter of water. The calibration curve also showed an excellent regression coefficient of 99% (Figure 14). TCE in the samples of PAAF was, therefore, analyzed with the SPME during the research.

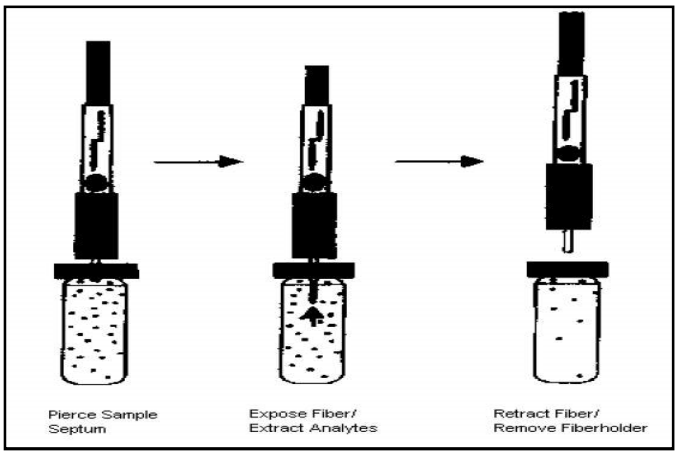


Figure 13: SPME sampling method

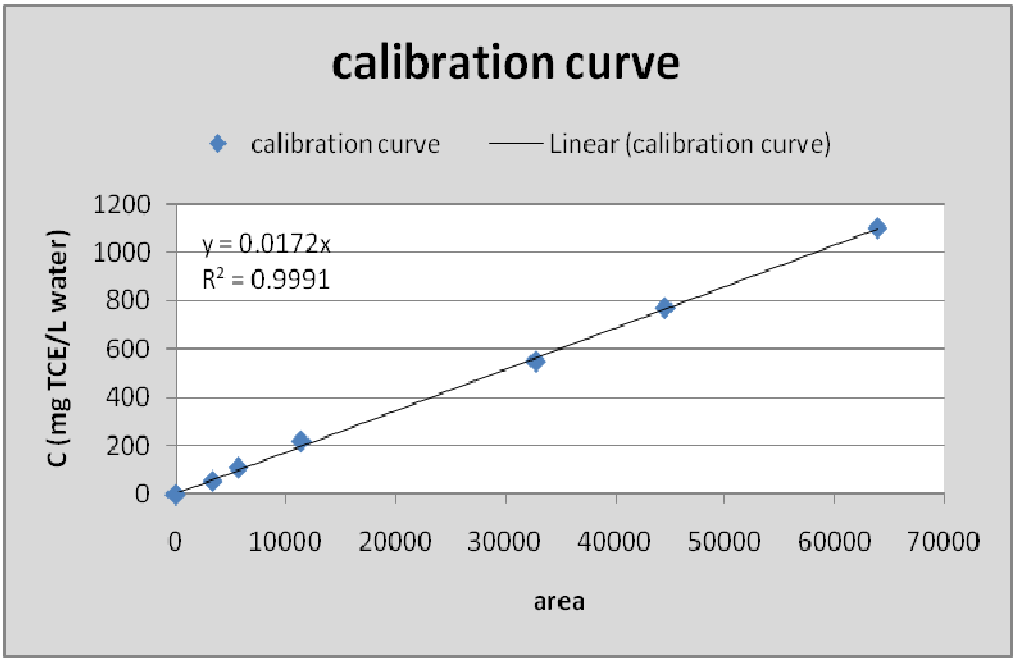


Figure 14: Results of the SPME GC calibration for TCE Analysis

3.4.4.3 Mass Balance

The method of moments was used to analyze the temporal concentration breakthrough curves. This method characterizes the transport behavior of analytes (TCE and NaCl). Experimental absolute moments (M_n) are obtained by numerical integration of the breakthrough data using the trapezoidal rule (Padilla, 1998).

$$M_n = \int_0^\infty t^n \, C(z,t)dt \qquad \textbf{Equation 1}$$

Using the method, the zero (M_0) and first (M_1) moments are calculated as:

$$M_0 = \int_0^\infty C(z,t)dt = \sum \left(\frac{C_1+C_2}{2}\right)(t_{i+1} - t) \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \qquad \textbf{Equation 2}$$

$$M_1 = \int_0^\infty tC(z,t)dt = \sum \left(\frac{C_1 t_1 + C_{i+1} t_{i+1}}{2}\right)(t_{i+1} - t) \ldots\ldots\ldots\ldots\ldots\ldots\ldots \qquad \textbf{Equation 3}$$

The first normalized absolute moment of the input pulse and the effluent concentration signal are used to estimate the mean arrival time of the center of mass (μ) (Padilla, 1998).

$$\mu = \frac{M_1^{II}}{M_0^{II}} - \frac{M_1^{I}}{M_0^{I}} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \qquad \textbf{Equation 4}$$

Where the I and II superscripts refer to the moments of the input and outputs signals, respectively. One approximation of mean arrival time (μ) is presented as $V_{inj\ 50}$, where it is the volume injected at the time the observed concentration reached 50 percent of its

maximum value (Padilla 1998). The mean arrival time is used in conjunction with the column length L to calculate the pore water velocity ($\nu = L/\mu$).

3.4.5 Tracer study

Aqueous NaCl concentrations were analyzed measuring the mean arrival time of the center of solute mass in the reactors. The flushing solution contained NaCl concentration of 500 ppm. NaCl concentrations in the effluents, specifically Cl^- ion, were measured with the ion chromatography (IC). The IC utilizes a conductivity detector (Model 550, Alltech) is connected to a HPLC pump delivering mobile phase (0.9 mM Na_2CO_3 and 0.85 mM $NaHCO_3$) in constant flow (2.0 $mL.min^{-1}$). Sample volume (0.2 mL) was injected in a high pressure switching valve (Model 7000, Rheodyne) which delivers samples to the detector. The conductivity detector IC was calibrated with NaCl solutions (1, 5, 8, and 10 mM).

4 RESULTS AND DISCUSSION

The following chapters present the results and discussion of each study which were conducted to meet the objectives of the research.

4.1 Effects of reactor configurations of PAAF

A series of experiments were conducted to obtain a better configuration of the reactors for assessment of PAAF performance. The following results were obtained from the experiments (Table 10):

Table 10: Selected configurations of the reactor setup for PAAF

Variable	Selected variable	Explanation
Packing & Saturation	Soil packing followed by saturation	This method consists of filling the entire reactor with the soil to the top of the column and then saturating it at an up flow pumping rate of 0.5 $mL.min^{-1}$. The advantages of this method over others include ensuring the most trapped bubbles to come out of the soil system and preventing additional bubbles from being formed in the system. This procedure also allows an easy management and quantification of each component.
Reactor Layout	Vertical	The reactor was laid out vertical. This is also related to the reasons outlined above.
Reactor Composition	Separate reactors: one packed with coarse sand and the other with fine sand	This corresponds to a separate configuration of low permeability sand in one reactor and high permeability sand in the other reactor.

In relation to the packing method, both high and low permeability reactors were packed to achieve a homogenous density through the column height. The soil was packed in the reactor following the procedure shown in section 3.1.1.1 to make bulk densities and soil porosities consistent and reproducible. The reactors were designed with the specifications detailed in Table 11.

Table 11: Specifications in the packing method

Compact energy		
Variable	High permeability reactor	Low permeability reactor
# Layers	16	15
# Knocks	26	30
Hammer weight (grams)	79.83	79.83
Fall height (cms)	6.35	6.35
Mold volume (cm^3)	113	113
Energy (gr-cm.cm^{-3})	**1,864.8**	**2,017.2**
Resultant density ($gr.cm^{-3}$)	**1.42**	**1.33**

Regarding the reactor layout, detailed comparisons between two methods (horizontal vs. vertical) were made (Figure 15). For these experiments, only coarse and fine sand were used to simulate the high and low permeability reactors, respectively. Pure chitosan was the polymer used in these experiments.

As shown in Table 12, the horizontal reactor layout was unable to develop high pressure enough to induce the effect of the polymer injection on the coarse sand reactor. Also the reactors had bubbles entrapped during the course of experiments. Contrarily, the vertical

configuration worked better developing pressures in the coarse sand reactor after the polymer injection and during the post-alcohol injections. In addition, no bubbles were found entrapped during the experiments.

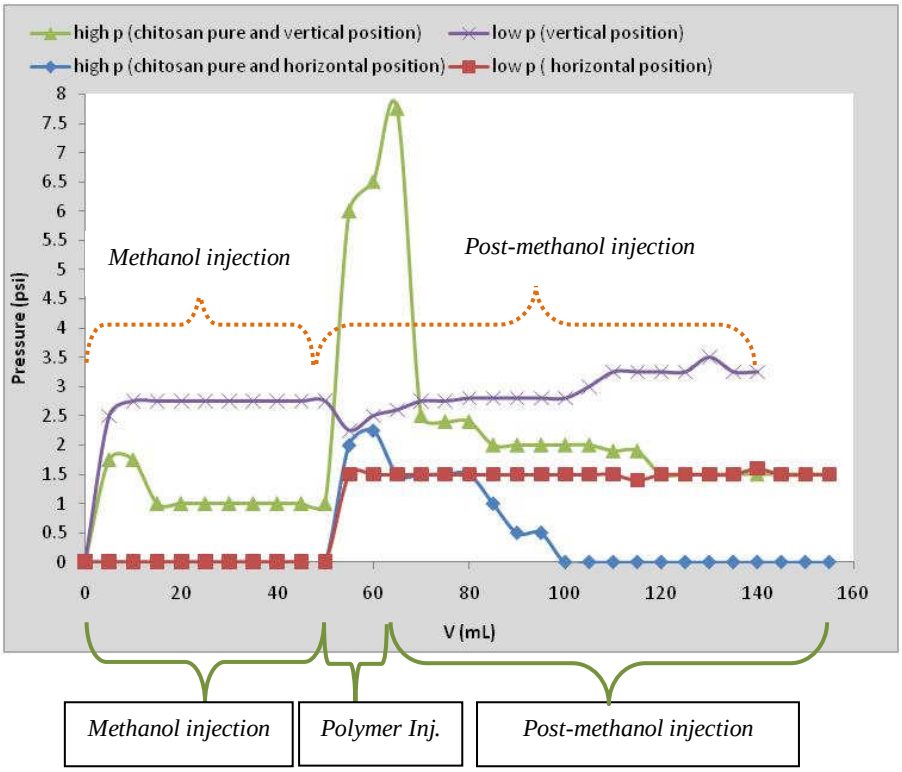


Figure 15: Behavior of the reactor layouts

Table 12: Comparisons of the reactor layouts (horizontal vs. vertical)

Land	Saturation Method @0.5mL min^{-1}	Quality	Presence of Bubbles	Flow rate Methanol (mL min^{-1})	Range Pressure (Psi)	Flow rate Polymer (mL min^{-1})	Measured Range pressure (Psi)
C*	H*	G*	Yes	25	0	5	1.5-2.3
F*	H	G	Yes	25	0	N.A	N.A
C	V*	VG*	Not	25	1-1.8	25	6-7.8
F	V	VG	Not	25	2.5-2.8	N.A*	N.A

C*= Coarse sand, F*= Fine sand, H* = Horizontal position, V* = Vertical position, G= Good quality, VG*= Very good quality, N.A* = Not applied

On the other hand, the results about saturation mode were agreed with the ones obtained by other researchers (Rodriguez et al., 2007; Giese and Powers, 2002), who also saturated their reactors from the bottom at a constant flow rate of 0.5 mL min^{-1}. Moreover, they found that the vertical position minimized the contribution of density in finger formation.

4.2 Reactor characteristics

In order to characterize the reactor, granulometric curves and tracer experiments were made. Their results of the final configurations for PAAF, high and low permeability, are described below.

4.2.1 Granulometric curves

The granulometric curve of the soil study was determined using the methodology presented in the section 3.4.1. In the x-axis the graph has the particulate size and in the y-axis the percent of finer by weight. The high and low permeability granulometric curves are shown in Figure 16 and Figure 17, respectively.

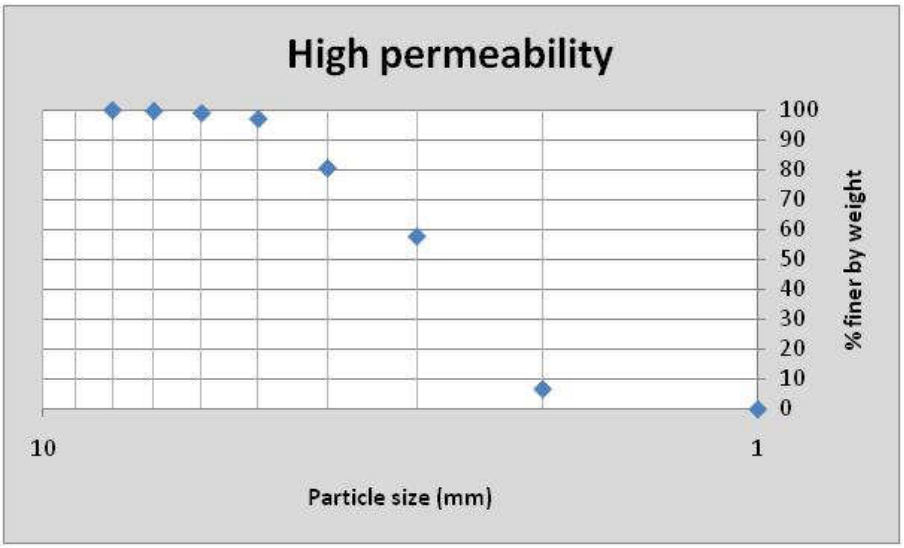


Figure 16: High permeability granulometric curve

High permeability reactor was primarily composed of 99.67% sand sizes, and 0.33% of fines. On the other hand, low permeability reactor had 99.44% sand sizes, and 0.56% of fines (silts and clays). The granulometric curves superposition (Figure 18) was shown a different gradation in each reactor.

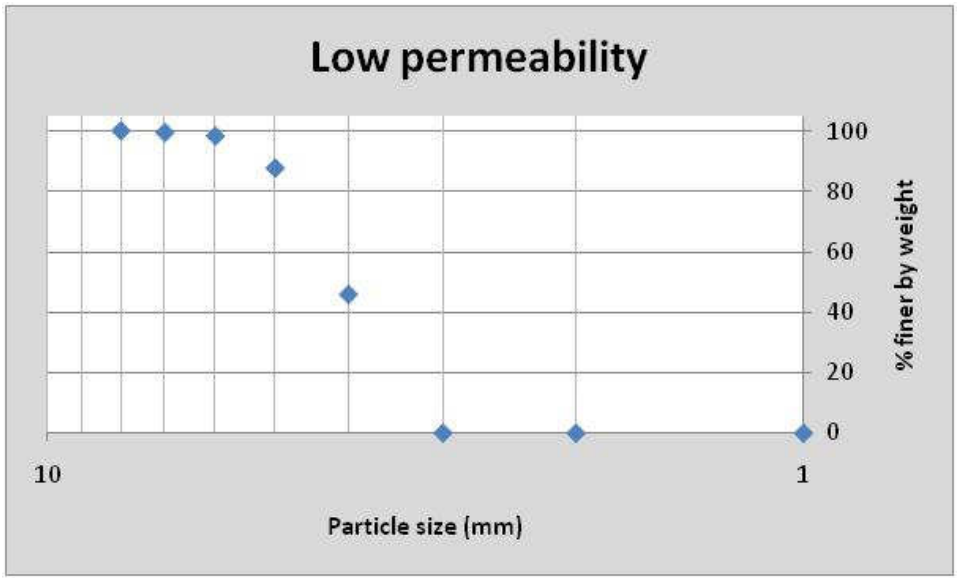


Figure 17: Low permeability granulometric curve

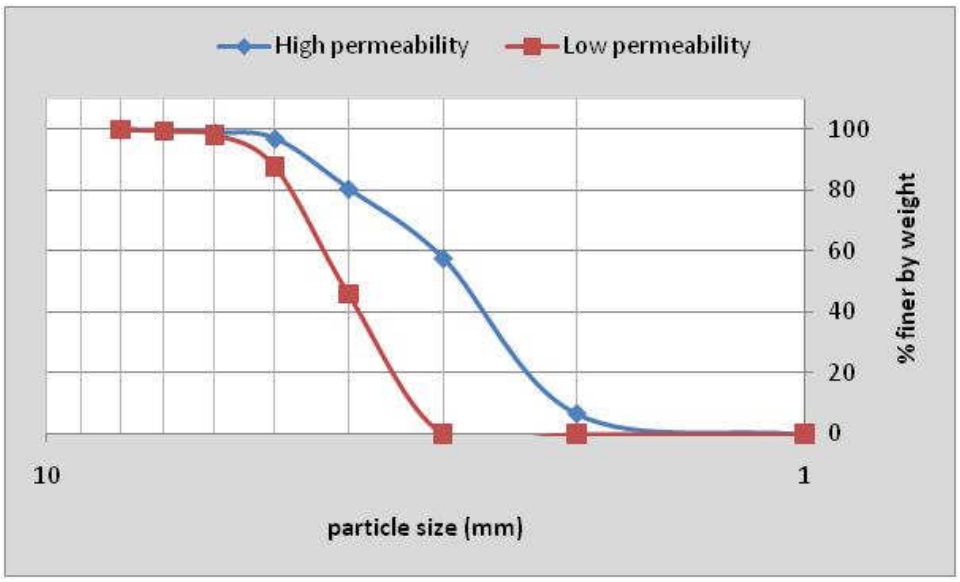


Figure 18: Granulometric curves superposition

4.2.2 NaCl experiments

Tracer studies are a useful tool to unmask the heterogeneous structure of groundwater flow. The effluents were collected in vials of 2 mL for subsequent analysis in the IC. The results are shown in Figure 19, Figure 20 and Figure 21

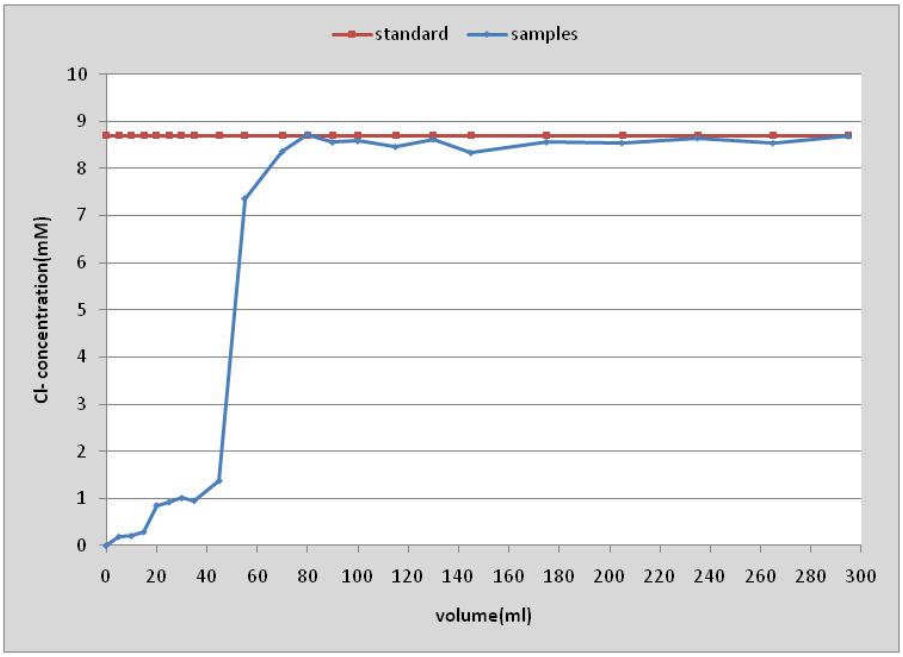


Figure 19: Tracer in low permeability

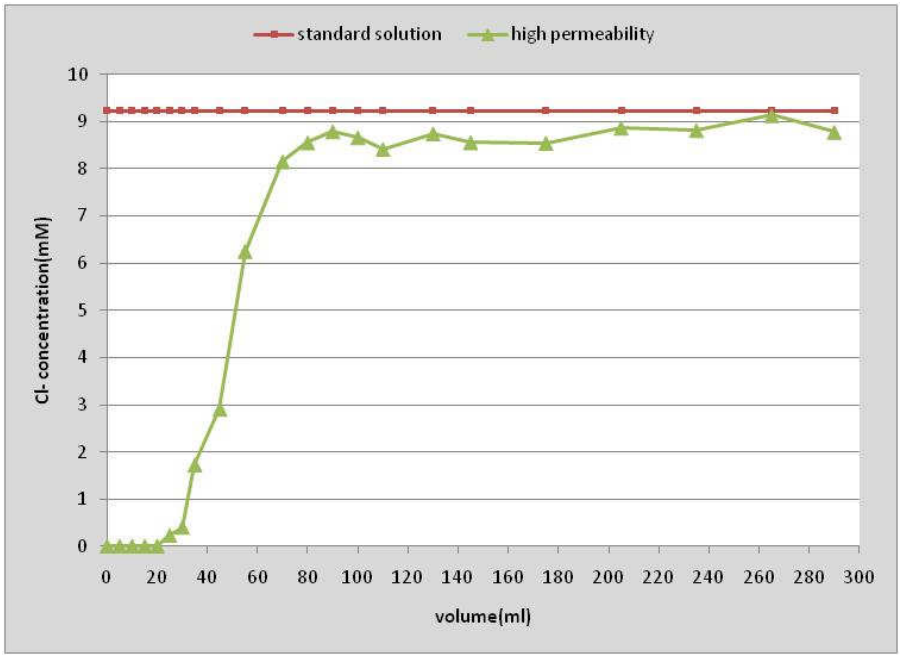


Figure 20: Tracer in high permeability

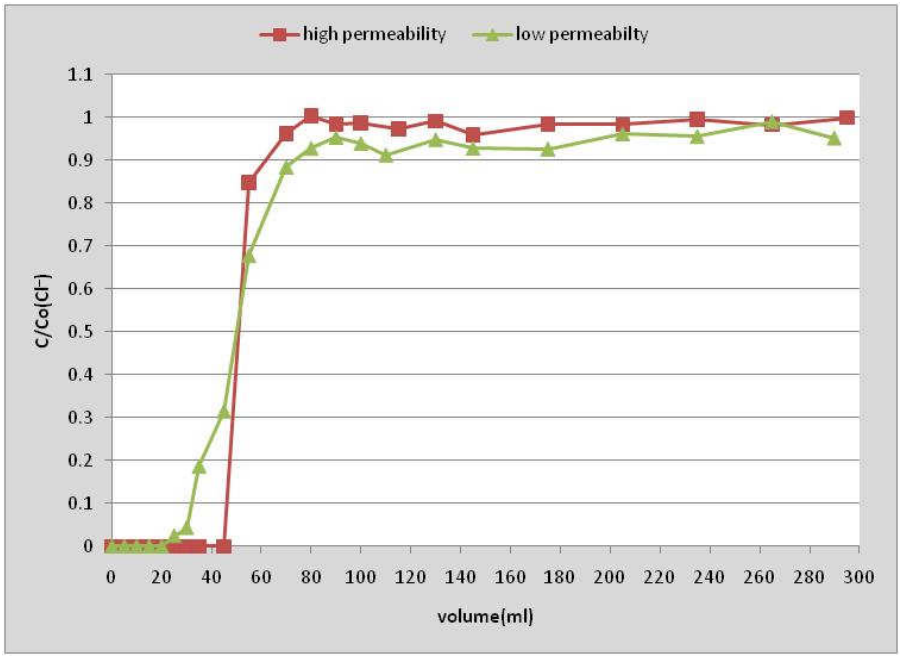


Figure 21: Tracer concentration superposition in the reactors

Figure 21 summarizes the tracer trend in the reactor. The axis "y" was normalized from Cl^- concentration to Cl^- concentration/standard concentration (500 ppm). In the first 50 mL, which is approximately equal to one pore volume, high permeability reactor showed that the solute mass center moved faster than low permeability reactor. On the other hand, after this first 50 mL, both high and low permeability reactors had the same trend. This behavior can be explained by similar clay content in either column, where the clay was the dominant factor over the sand in controlling hydraulic characteristics of the reactor.

According to definition of $V_{inj\ 50}$ (section 3.4.4.3), this volume corresponded to 50 mL in both reactors. Although the value is equal, the way of developing breakthrough curves is totally different in each column. This means that in the high permeability reactor, the breakthrough curve had a continuous development. On the other hand, low permeability reactor had an abrupt development, especially after 40 mL.

4.3 Effects of methanol concentration on PAAF performance

Several experiments were done with different methanol concentrations and injection methods to evaluate the efficiency of alcohol flushing for TCE removal. The methanol concentrations used were 5% and 10% (v/v). Two flushing methods used were continuous and intermittent flushing. The efficiency was determined by the effects of concentrations and flushing modes on TCE removal. For this experiment, the configuration four (4) was used.

4.3.1 Effect of flushing mode

Two methods were used for this purpose: continuous and intermittent flushing. Initially, continuous flushing with 5% (v/v) methanol concentration in high and low permeability reactors was analyzed. The contact time was equal to twenty (20) minutes for this configuration. The results showed that greater TCE removal percentage was achieved in a high permeability reactor in comparison to low permeability reactor (Figure 22). This behavior was observed due to low contact area and sweep efficiency of methanol in low permeable, porous medium (Darwish et al., 2003). The axis "y" was normalized from sample mass to sample mass/total mass (M/Mo). On the other hand, the axis "x" represented the injected methanol volume.

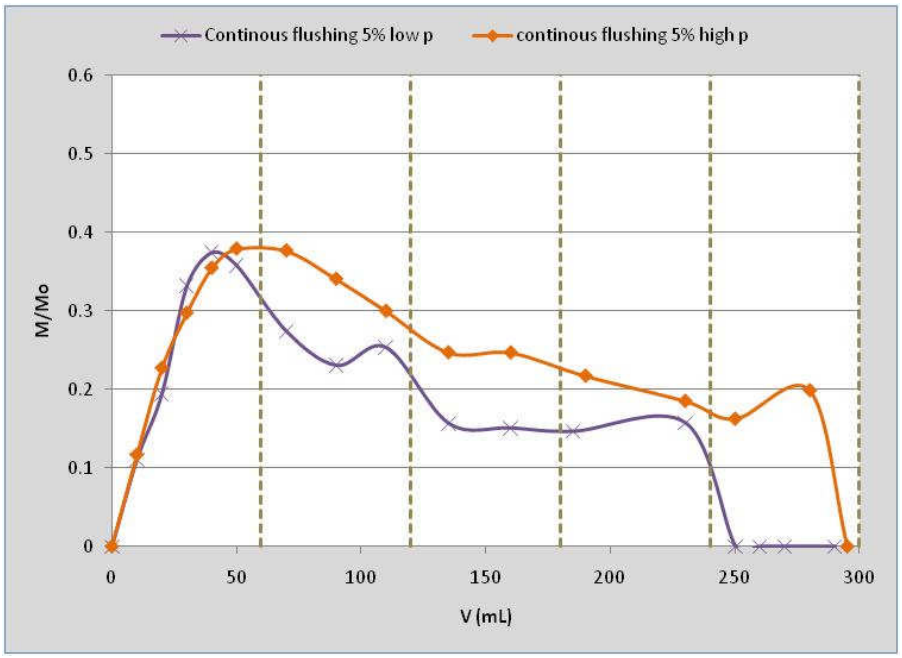


Figure 22: Alcohol Flushing Comparison with a 5% methanol concentration

In the intermittent flushing, approximately one PV per each day was applied in the reactor for five days. The contact time was equal to 1,444 minutes for this configuration between each injection. This method increased the TCE removal percentage at both 5% and 10% methanol concentrations in comparison to continuous flushing method (Figure 23). Intermittent injection with 10% removed more TCE from the reactor. A results summary is shown in Figure 26. For example, a 16% TCE removal was achieved with the continuous alcohol flushing, whereas the overall removal percentage of TCE increased to a 32%with the intermittent alcohol flushing.

This enhanced performance was attributed to the increase of contact time between methanol and TCE in the porous medium. Increasing the solubility of TCE is known to enhance dissolution and reduce the interfacial tension between the aqueous phase and solvent phase (Padget and Hayden, 1999).

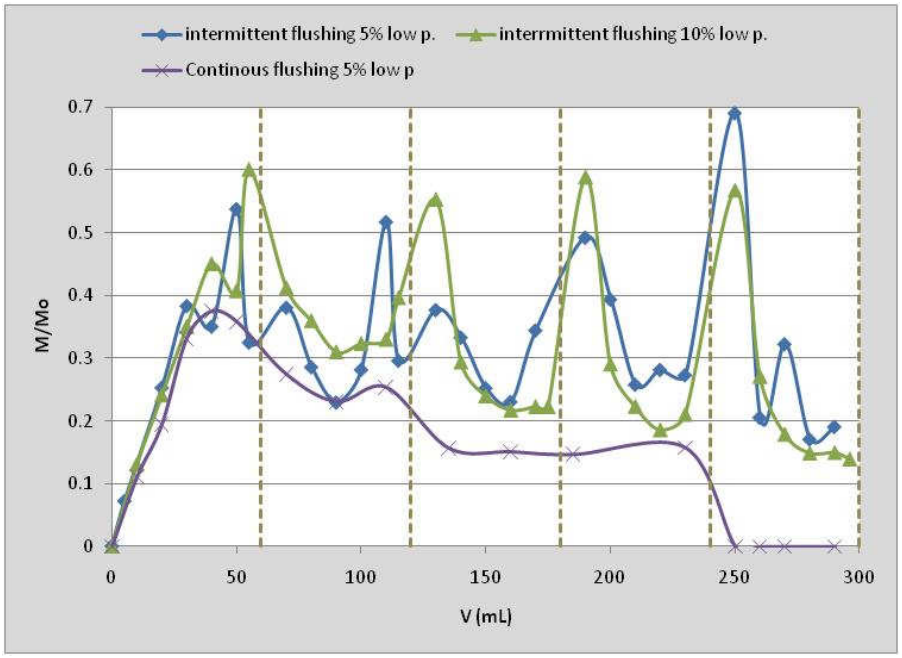


Figure 23: Effect of flushing mode

4.3.2 Concentration effect

Figure 24 shows a direct relationship between methanol concentration and TCE removal percent: better TCE reduction with greater methanol concentration. For example, when the methanol concentration increased from 5% to 10% in continuous flushing, the removal percent improved from 17% to 27%. That behavior was due to increased TCE solubility in higher methanol concentration.

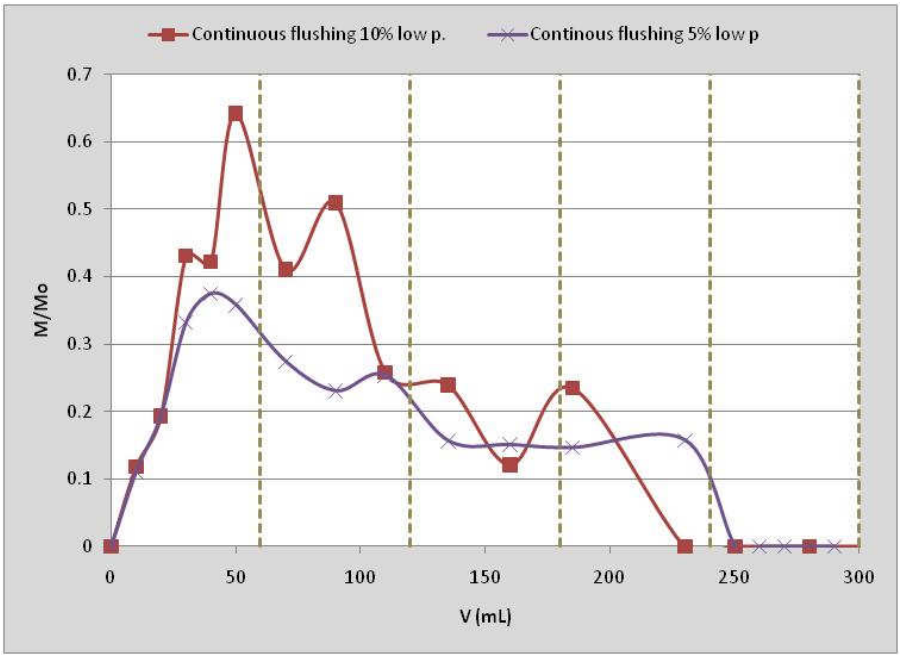


Figure 24: Continuous flushing concentration effect

Overall, a general trend of methanol concentration and flushing mode effects showed that a better TCE removal was achieved when the methanol concentration or contact time increased. However, when methanol was applied intermittently, 10% (v/v) and 5% (v/v) methanol concentrations showed a similar result (Figure 25).

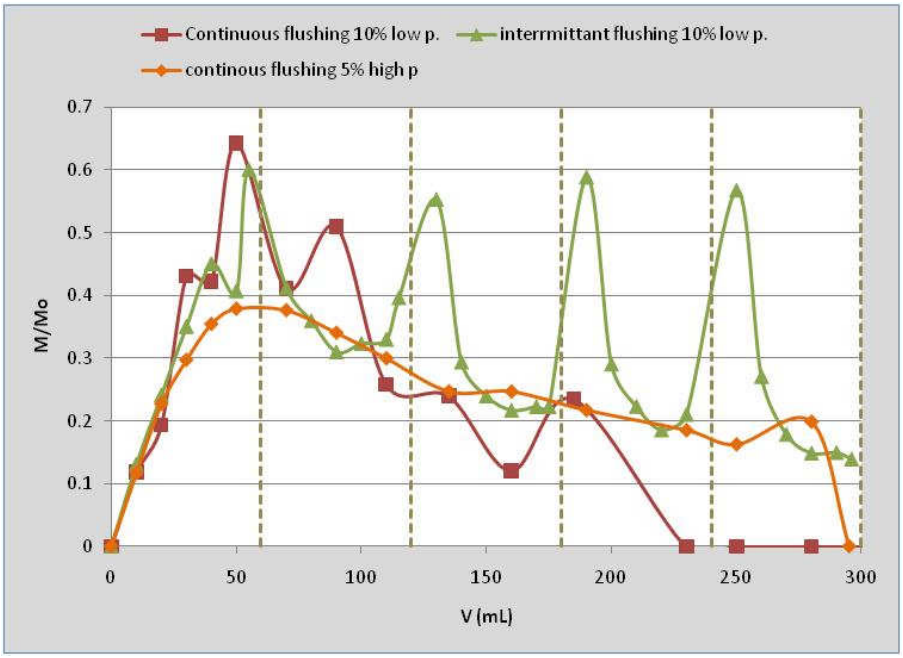


Figure 25: Intermittent flushing concentration effect

Effects of methanol concentration and flushing mode on TCE reduction are summarized in Figure 26. As shown, the higher TCE reduction percent was 32% and the lower was 17%. The lower value was achieved by the continuous flushing with 5% (v/v) methanol concentration, under which there was shorter contact time and less concentration of methanol.

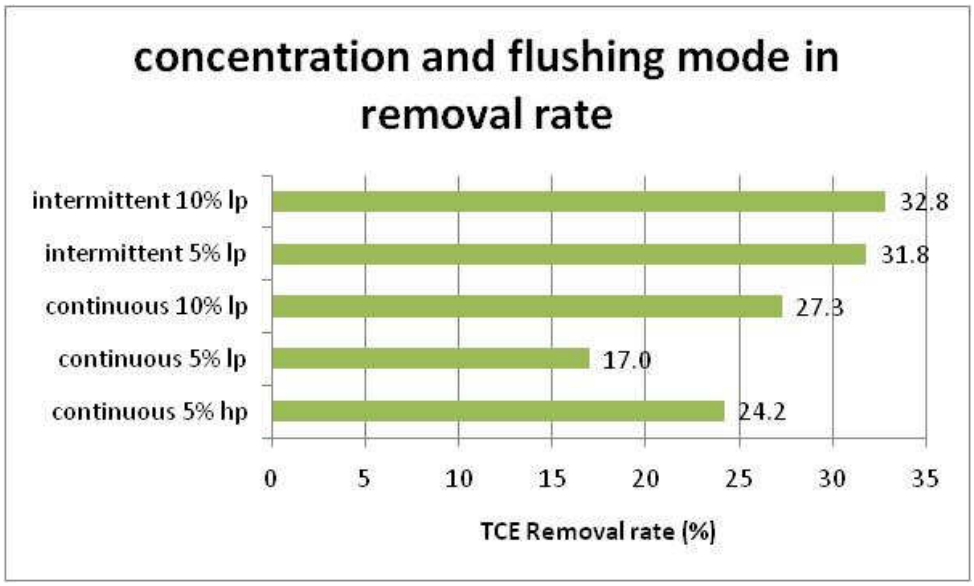


Figure 26: Effect of concentration and flushing mode on TCE removal

4.4 Effects of polymer types on permeability modification

The polymers tested were two natural polymers (chitosan and alginic acid) and two synthetic polymers (POL EZ 8736 and POL EZ 675). Initially, the physical behavior between polymer and porous medium was analyzed. The hypothesis was in that an increase in pressure could reflect a permeability contrast in porous medium. After preliminary studies, the polymers with better results were chosen.

For this experiment, the reactors were composed only of coarse and fine sand for high and low permeability (configuration 3), respectively, and no TCE was added. Also, it is noted

that only high permeability reactor received polymer injections. The purpose was to evaluate the pressure development in each reactor as mentioned above.

4.4.1 Natural polymers

As chitosan is soluble in acetic acid, 20/80 chitosan was tested, which was comprised of 20% of pure ChitoVan and 80% of acetic acid. However, 20/80 chitosan did not exert any effect of the polymer injection to the high permeability reactor (configuration 3) in terms of pressure development (Figure 27). This behavior could be caused by its low adhesion capacity to the porous medium, by which generation of permeability contrast was ineffective.

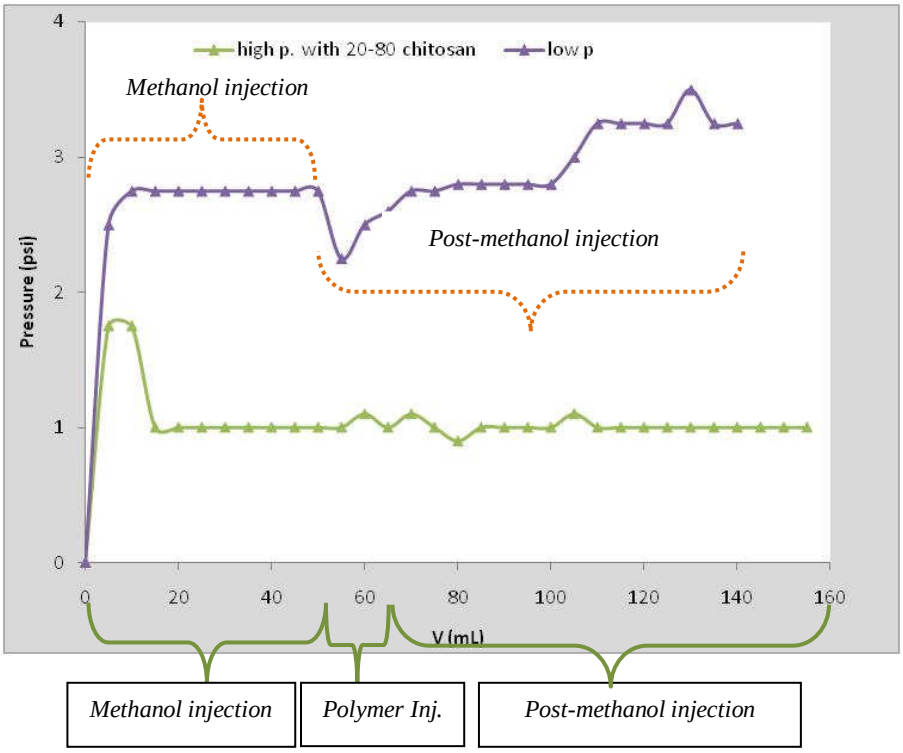


Figure 27: Pressure development in reactors after 20/80 chitosan injection

Pure chitosan was applied to assess if there could be any differences in pressure development due to the concentration increase. The results showed an enhanced permeability contrast developing an increased pressure in the coarse sand reactor (Figure 28). But, it was still not high enough to overcome the pressure differentials between high and low permeability reactors.

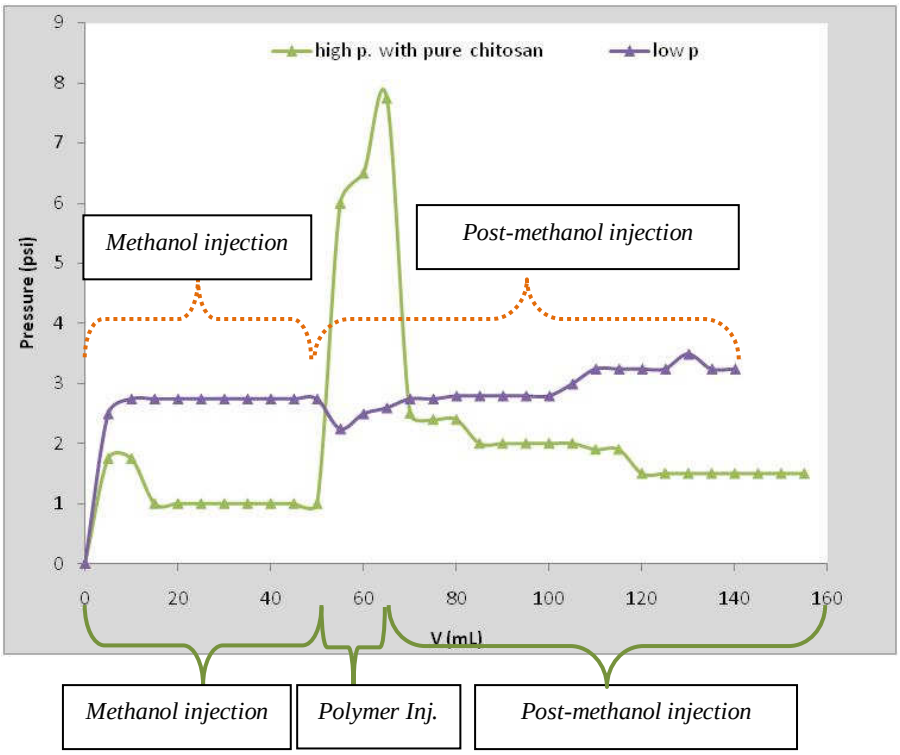


Figure 28: Pressure development in reactors after pure chitosan injection

Alginic acid with an aqueous concentration of 1% was the second natural polymer evaluated in the current study. The results were better with alginic acid than chitosan. The high permeability reactor achieved a greater pressure development than low permeability reactor. This behavior could be caused by a higher viscous effect and adhesion with porous medium in comparison to chitosan.

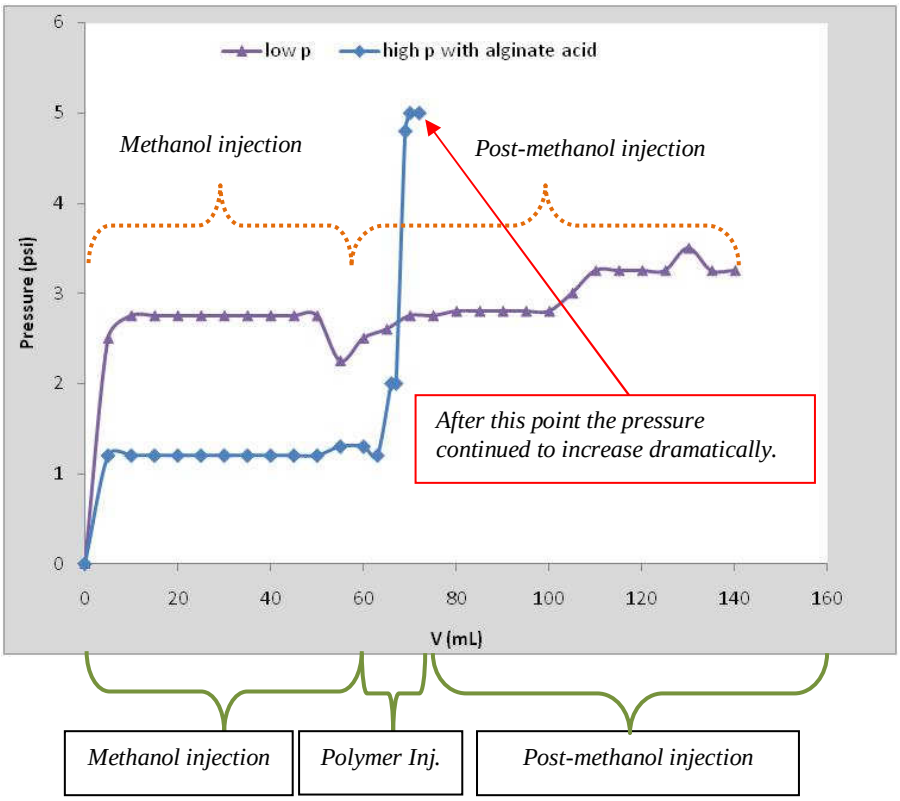


Figure 29: Pressure development in reactors after alginic acid injection

4.4.2 Synthetic polymers

Synthetic polymers were also tested with the same procedure used for the natural polymers. As shown in Figure 30, the synthetic polymers worked similar to alginic acid. Among the synthetic polymers, a greater pressure development in the high permeability reactor was achieved with POL EZ 8736 followed by POL EZ 675.

Both the ionicity (i.e., ionization capacity) and the high molecular weight polymers are key factors in the pressure development in the reactor. The higher ionicity of the polymer increases the repulsive interactions between molecules. As a result, the increase in the viscosity is observed (Rattanakawin and Hogg, 2007). On the other hand, the increase in molecular weight is directly related with the increase in polymer viscous effect on porous medium. POL EZ 8736 has higher ionicity and greater molecular weight than POL EZ 675.

The experiments had so far focused on the pressure development in the high permeability reactor due to polymer injections to it. Based on the results from those studies, it is construed that polymer injection could reverse permeability contrast by blocking a high permeable zone so as to enhance overall TCE remediation by inducing alcohol flushing toward a low permeable zone.

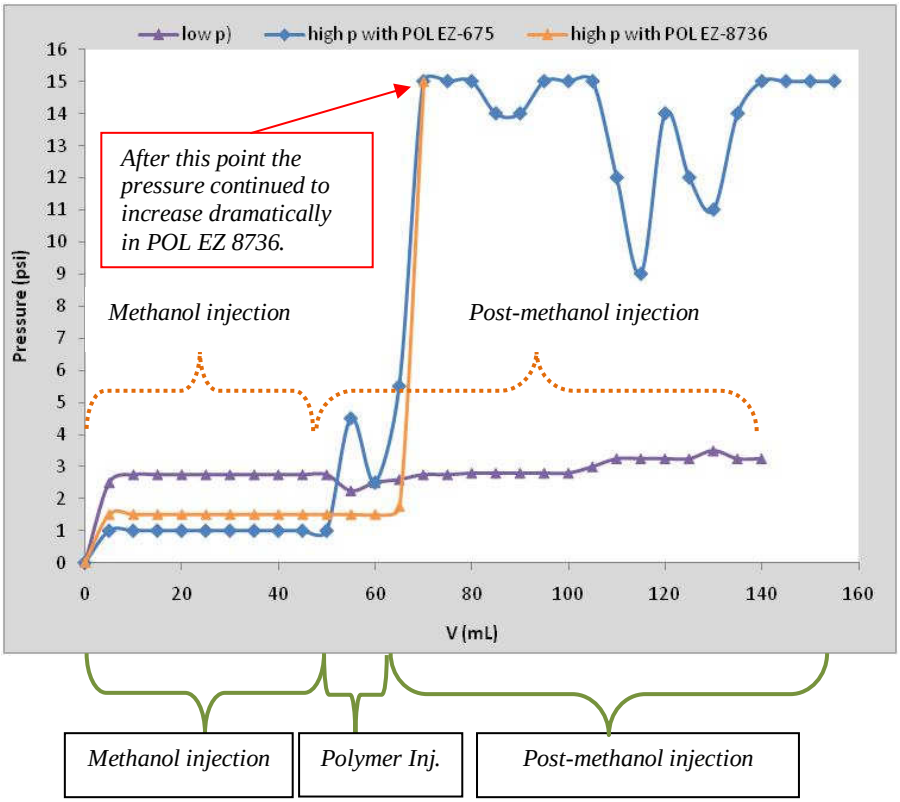


Figure 30: Pressure development in reactors after synthetic polymers injection

TCE was injected to the systems which were set up in accordance to the methodology developed previously. Two natural polymers, chitosan and alginic acid, and a synthetic polymer, POL EZ 8736, were chosen as the model polymers based on the previous results. Effluent TCE concentration in conjunction with the polymer injection was analyzed and results are presented in the next section.

4.5 Effects of polymer types on TCE removal

The natural and synthetic polymers selected in the previous section were studied with PAAF methodology. Methanol concentration and injection method were chosen based on the results obtained in section 4.3. A methanol concentration 5% (v/v) with continuous flushing (MC5CF) and a methanol concentration 10% (v/v) with intermittent flushing (MC10IF) had the lower and higher TCE removal percentage, respectively. The purpose was to use PAAF in the worst scenario (MC5CF) to compare it with the best scenario (MC10IF).It is noteworthy to mention that, for these experiments, individual reactors arrangement was used, where separated injections of reagents were done to each reactor.

4.5.1 Natural polymers

. Permeability contrast was found after injecting the alginic acid. This behavior was evidenced in the point when no more effluents were coming out of the system. Therefore, with alginic acid injection, the high permeability reactor decreased its permeability lower than the low permeability reactor (Figure 31).

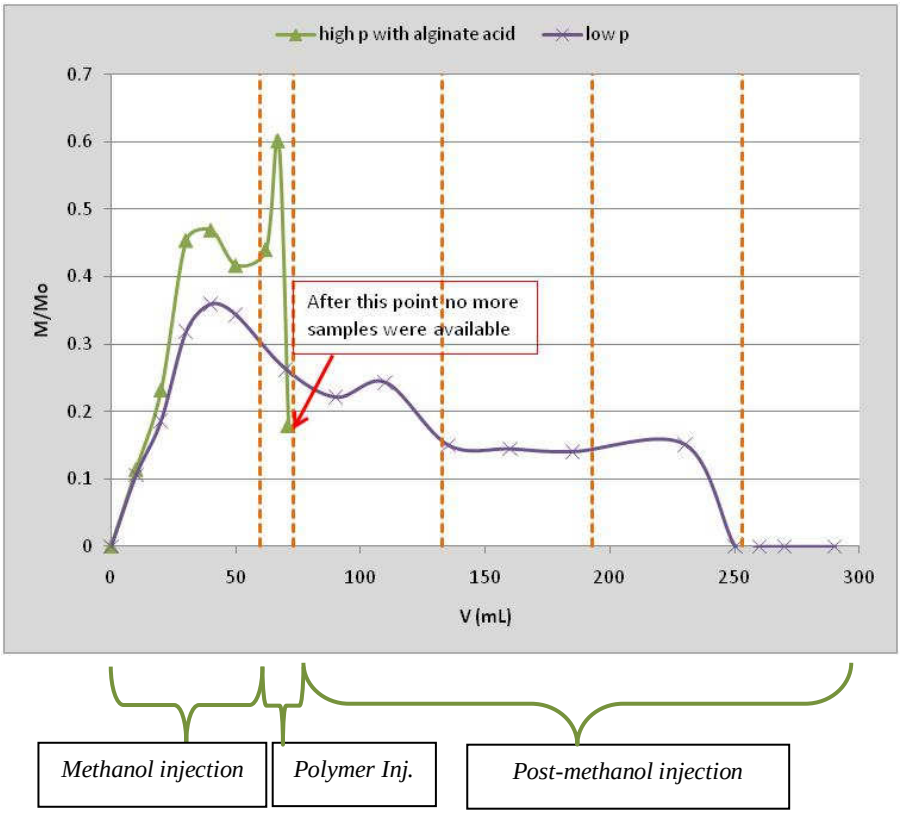


Figure 31: Breakthrough curve in reactors after alginic acid injection

4.5.2 Synthetic polymer

POL EZ 8736 was also tested with the same procedure used for the natural polymers. As shown in Figure 32, the synthetic polymer worked similar to alginic acid. This means that a permeability contrast was also produced by this synthetic polymer, reducing the permeability of the high permeable reactor lower than that of the low permeability reactor.

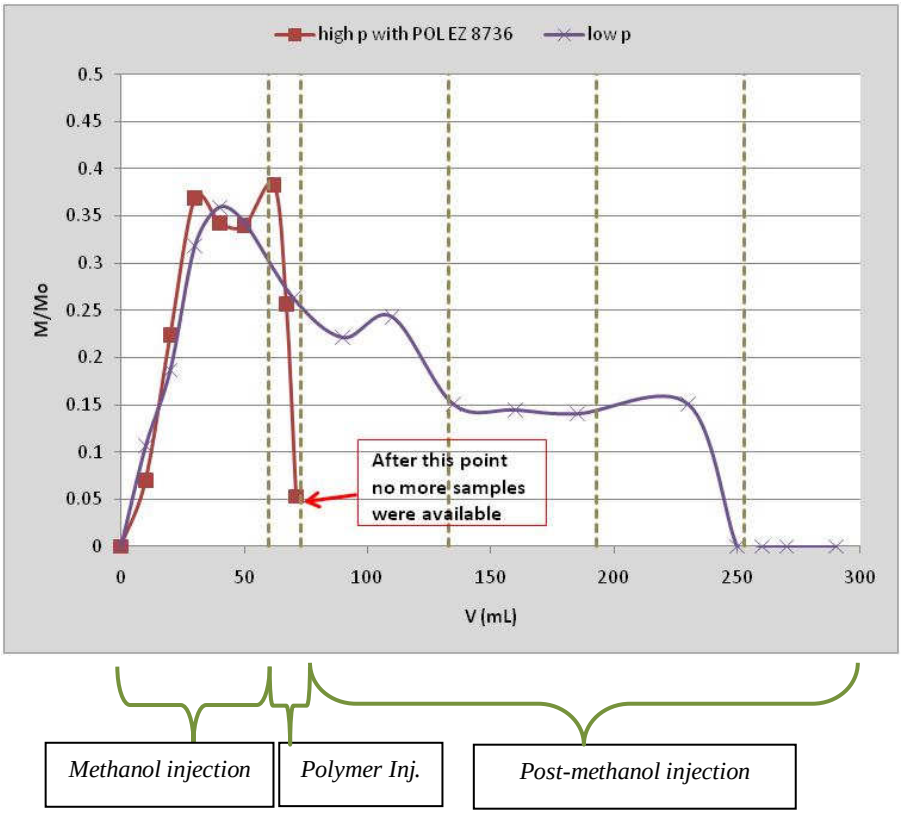


Figure 32: Breakthrough curve in reactors after POL EZ 8736 injection

As shown the Figure 31 and Figure 32, only alginic acid (natural polymer) and POL EZ 8736 achieved a permeability contrast. This behavior was the result of the polymer occupying the pores in higher permeability zones that resulted in hydraulic short circuiting and subsequently sealing in the reactor. For this reason, the permeability decreased drastically and no more effluent samples were available Alginic acid has advantages over POL EZ 8736. Advantages include safety to human health, biodegradability, and treatability. Also, alginic acid is safer because it is not toxic, ecologically acceptable, and

environmentally friendly (Renault et al., 2009). Therefore, alginic acid was selected for further PAAF analysis in a parallel configuration.

4.6 Effects of natural polymer on permeability modification

Alginic acid was tested with PAAF methodology (configuration 4) in a parallel arrangement to validate the application of this polymer in PAAF technology.

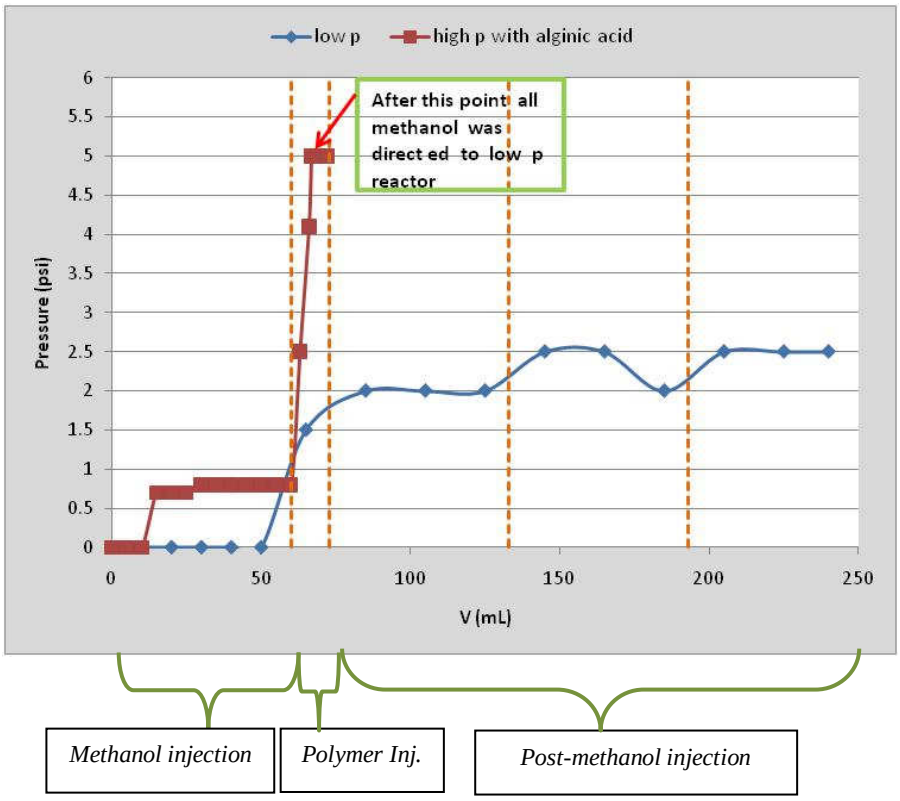


Figure 33: Pressure development in both reactors after natural polymer injection

As shown in the Figure 33, alginic acid achieved a permeability contrast between high and low permeability reactors. In the initial alcohol flushing, the alcohol solution transported more rapidly through larger pore spaces producing greater pressure. In contrast, the alcohol solution affected less on those TCE present in the low permeability reactor. The injected polymer occupied pores in the higher permeability zones, resulting in the reverse of flow velocities between low and high permeability zones. Consequently, post-alcohol flushing enhanced removal efficiency by directing all methanol solutions to the low permeability reactor.

4.7 Effects of natural polymer on TCE removal

In the initial alcohol flushing, the alcohol solution transported more rapidly through larger pore spaces and solubilize/mobilize TCE contained in such zones (Figure 34). On the contrary, the alcohol solution affected less on those TCE present in the low permeability zones. As mentioned before, polymer injected resulted in the reverse of permeability contrast between low and high permeability zones.

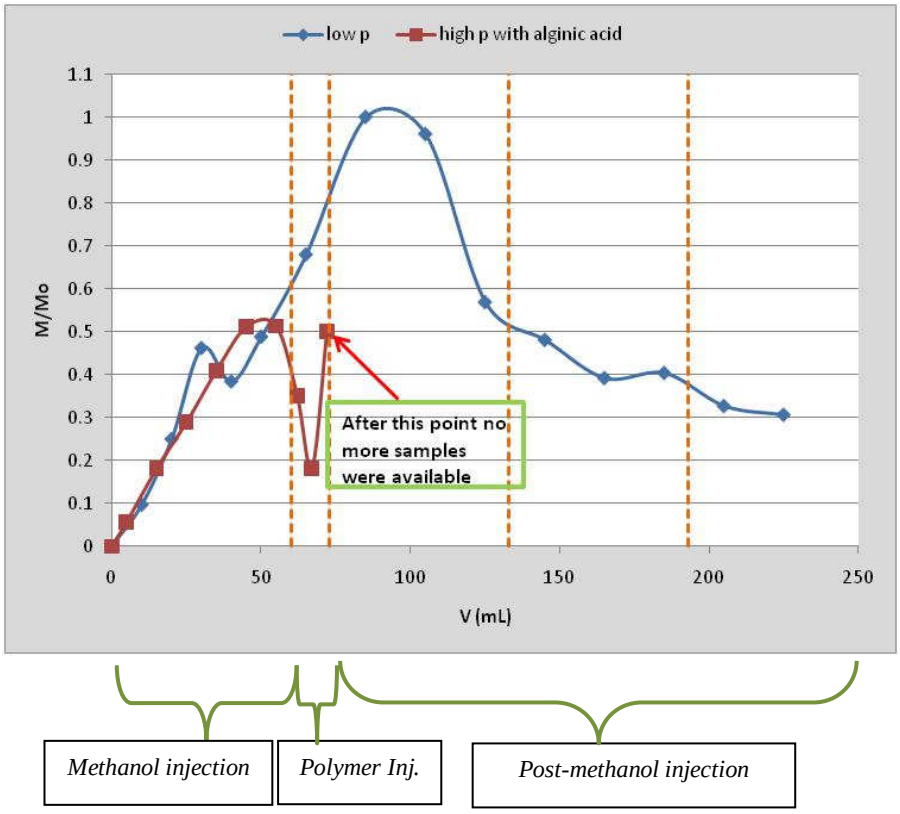


Figure 34: Breakthrough curve in both reactors after natural polymer injection

Consequently, post-alcohol flushing enhanced efficiency for TCE removal from 32.4% (MC5CF) to 51.8% in the lower permeability reactor, leading to the improvement of overall TCE reduction (Giese and Powers, 2002). This behavior is shown in Figure 35. The blue line represents the low permeability reactor. The reactor increased the TCE removal percent after injecting polymer in comparison to continuous alcohol flushing (violet line).

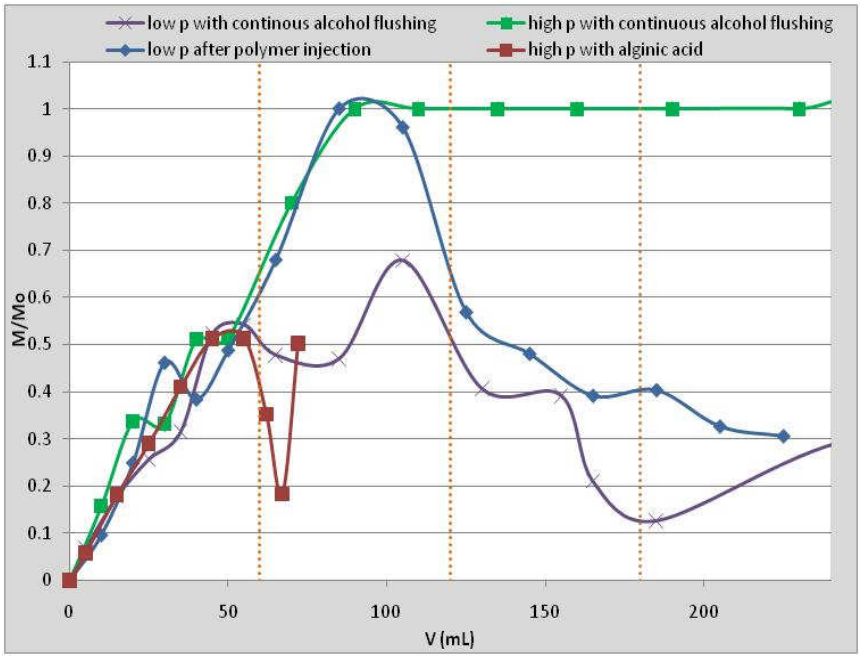


Figure 35: Comparison between alcohol flushing and PAAF

4.8 Effects of TCE aging on alcohol flushing performance (parallel)

Limitations of the alcohol flushing in low permeability zones were evidenced (Figure 36). The reduction percents were: 33% (standard experiment) and 37% (aging experiment). These preliminary results showed that the TCE removal from the low permeable zones was restricted independently of contaminant age. The initial behavior in the reactor with aged TCE can be attributed a preferential flux generated in that reactor.

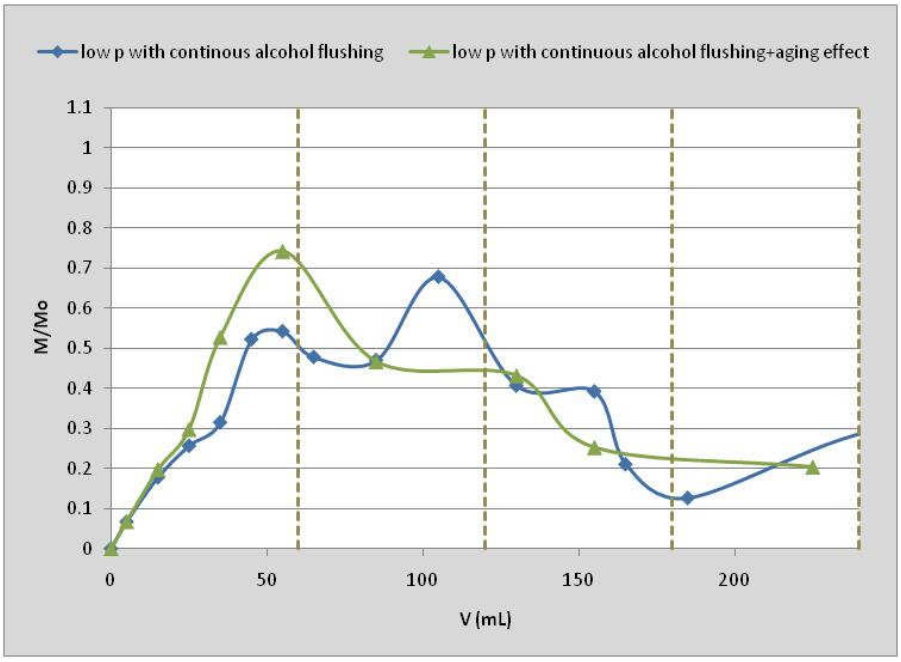


Figure 36: TCE aging on alcohol flushing performance effect

On the other hand, in high permeability zones, the TCE reduction percent was greater in the standard experiments (83%) in comparison to the aging experiment (62%) (Figure 37). This behavior was produced by less interaction time of TCE and the porous medium in the standard experiment. The greater flushing volume required to remove the TCE for the "aging" experiments suggest that there was more time for TCE to diffuse into immobile zones or sorbs during aging, and therefore it took longer to diffuse not or desorb.

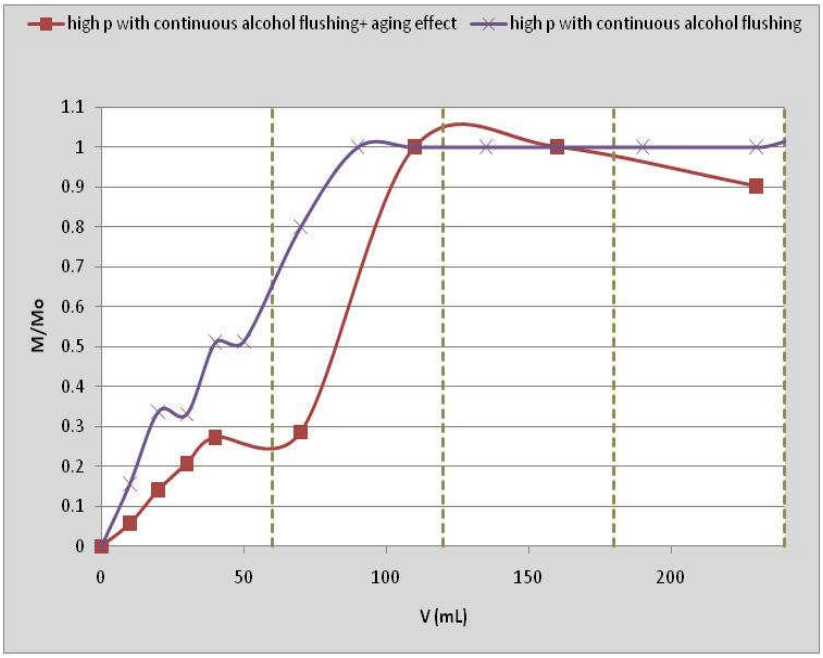


Figure 37: Effects of TCE aging on alcohol flushing performance (parallel)

4.9 Effects of soils types on PAAF

A natural sandy soil was also used to compare the results with those obtained with the natural clayey soil that had been presented in the previous sections. Two different configurations were tested for this purpose. The first one was a reactor with coarse sand and natural sandy soil (high permeability reactor) set up in parallel to another reactor with fine sand and natural sandy soil (low permeability reactor). On the other hand, for the second configuration, the high permeability reactor was composed of coarse sand and natural sandy soil and the low permeability reactor of clay and fine sand.

4.9.1 PAAF with natural sandy soil

Configuration five (5) was used for this experiment. The specifications of packing method are showed in Table 13.

Table 13: Specification in the packing method with natural soil

Compact energy		
Variable	High permeability reactor	Low permeability reactor
# Layers	19	17
# Knocks	20	30
Hammer weight (grams)	79.83	79.83
Fall height (cms)	6.35	6.35
Mold volume (cm^{-3})	113	113
Energy (gr-cm.cm^3)	**1,703.4**	**2,286.2**
Resultant density ($gr.cm^{-3}$)	**1.68**	**1.5**

As shown in Figure 38, PAAF methodology also worked with this natural soil. Permeability contrast was found after injecting alginic acid. This behavior was evidenced in the point when no more effluents were coming out of the system. Therefore, with alginic acid injection, the high permeability reactor also decreased its permeability lower than the low permeability reactor. Consequently, post-alcohol flushing enhanced efficiency by all methanol was directed to low permeability reactor. The overall TCE reduction was of 57%.

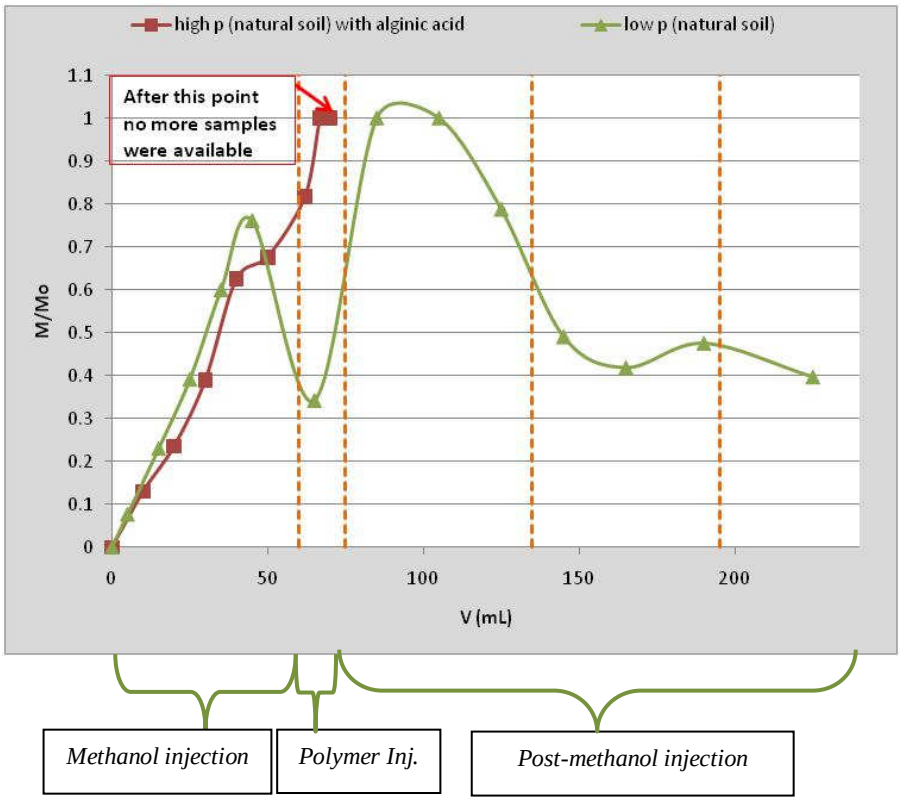


Figure 38: Breakthrough curve in both reactors (natural soil) after natural polymer injection

Figure 39 shows that this last configuration with the natural sandy soil had a higher TCE reduction (57%) than the arrangement with the natural clayey soil (51.8%) of the section 4.7. The difference can be explained by the composition of the soils in the reactor: one (57% removal) had sand predominantly, and the other (32.4% removal) was composed mainly with clay. The reactor with the clayey soil produced more restrictions in the transport of methanol and TCE than the one with sandy soil. Also, TCE would bind more tightly with

the clay fractions than the sands, which can results in lower TCE desorption, subsequently lower dissolution in the methanol.

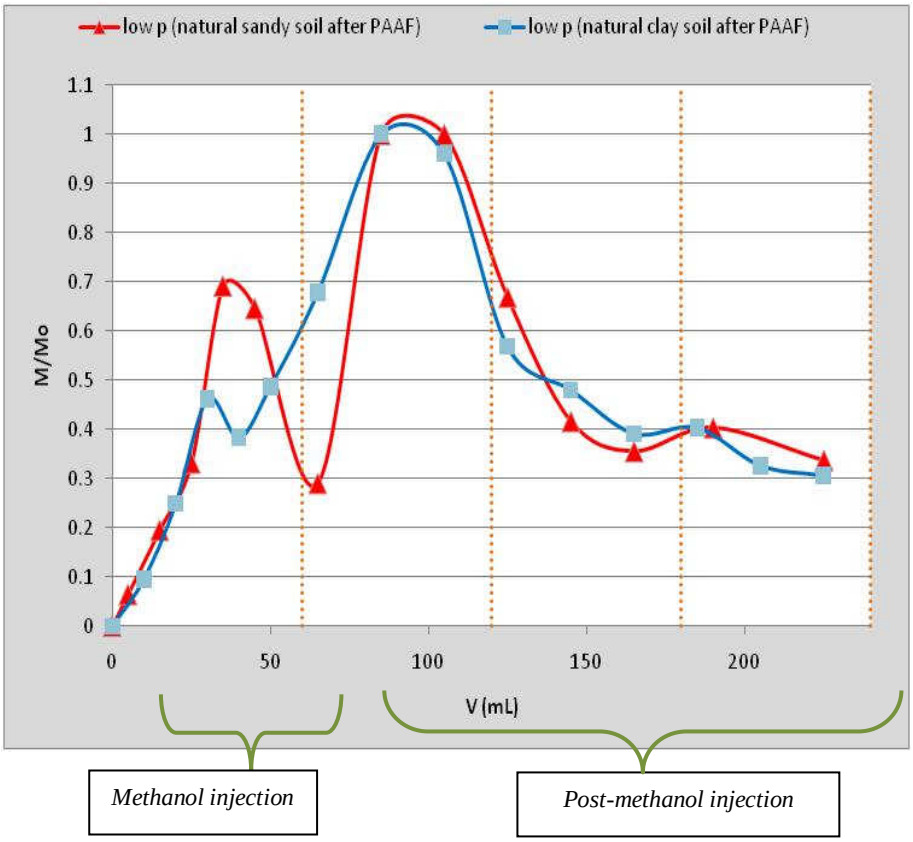


Figure 39: Breakthrough curve with natural soils using PAAF methodology

4.9.2 Effect of soil properties on PAAF

Configuration six (6) was used for this experiment. . This experiment simulated a more realistic case scenario which would occur in field.

4.9.2.1 Without manipulation of polymer flow

This configuration presented a TCE removal percent from 49.4 and 5.6% for high and low permeability reactors, respectively. This result (Figure 40) showed that the amount of polymer was not enough to generate contrast permeability in high permeability reactor. Moreover, it seemed that a small volume of the polymer solution entered the low permeability reactor forced the alcohol solution to flush the high permeability reactor so as to decrease the TCE removal percent in the low permeability reactor.

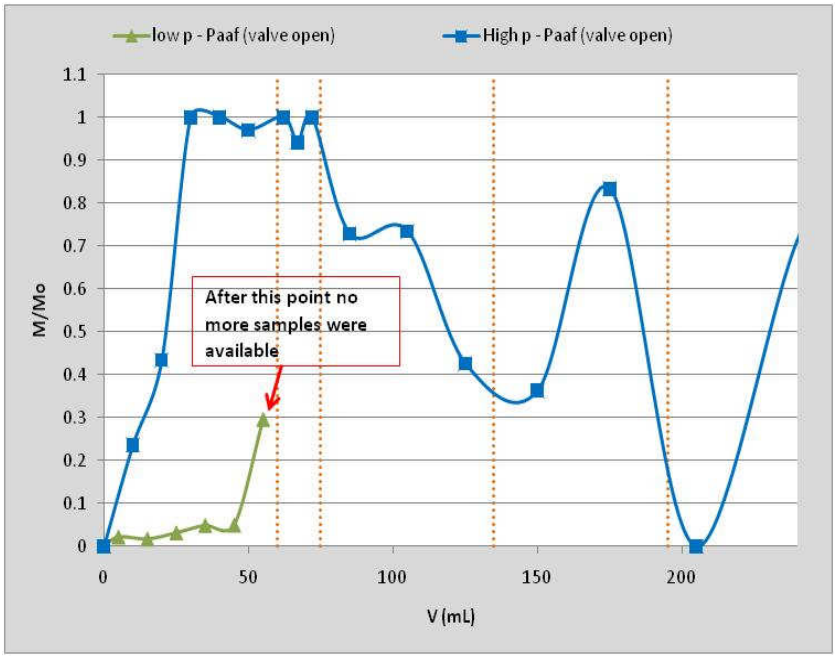


Figure 40: Breakthrough curve in both reactors (natural soil and clay soil) after natural polymer injection (without manipulation of polymer flow)

4.9.2.2 With manipulation of polymer flow

This configuration presented a TCE removal percent of 15.5 and 11.3% from the high and low permeability reactors respectively. The removal percent of 11.3% represents almost twice more the TCE removal percent in low permeability reactor in comparison with the previous experiment (5.6%) using PAAF technology. The difference can be explained by the higher volume of methanol that flushed into the low permeability reactor during the post-alcohol flushing.

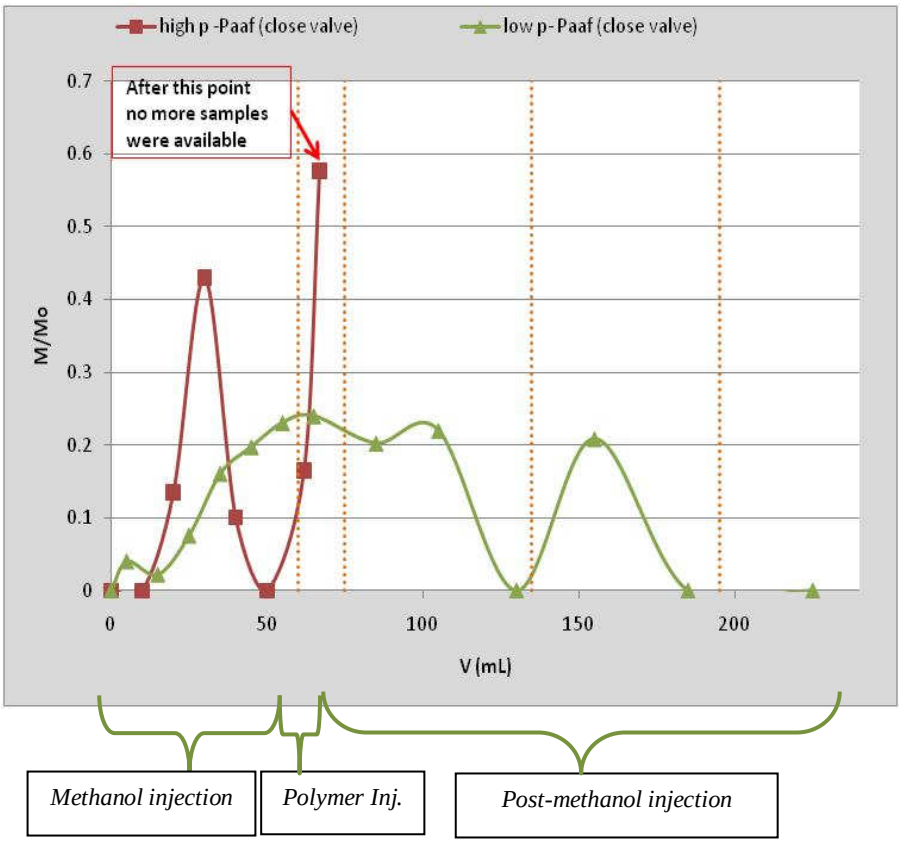


Figure 41: Breakthrough curve in both reactors (natural soil and clay soil) after natural polymer injection (with manipulation of polymer flow)

5 CONCLUSIONS

A laboratory-scale PAAF was conducted to (1) determine the effect of alcohol injection on TCE remediation, from different soil permeability configurations; (2) assess feasibility and design parameters for enhanced remediation TCE with permeability modification by PAAF in saturated soils; (3) evaluate natural biopolymers for their feasibility to be used as the main polymers in an in situ remediation technology, PAAF; and (4) study the PAAF performance in TCE contaminated soils having different characteristics with natural and synthetic polymers.

The following conclusions were derived from various PAAF experiments:

- An increase of contact time between methanol solution and TCE enhanced overall TCE remediation effectiveness. For example, a 16% TCE removal was achieved by the continuous injection of 5% methanol injection, whereas the removal percentage of TCE increased to a 32% of overall TCE remediation effectiveness in intermittent methanol flushing.
- When the methanol concentration increased from 5% to 10% in continuous flushing, the removal percent improved from 17% to 27%. That behavior was due to increased TCE solubility in higher methanol concentration.
- Natural biopolymer, alginic acid, was capable of making relative permeability reversal. This behavior was attributed to polymer blocking of high permeability

pores, thus reversing the relative permeability of the “higher” and “lower” permeability zones, which, in turn, resulted in an induced TCE flushing by methanol solution in tight zones. Alginic acid was the best candidate among the polymers tested, natural and synthetic for the PAAF experiment.

- TCE aging in the system showed a reduction effect in removal efficiency from the high permeable reactor. This behavior can be produced by more interaction time of TCE and the porous medium, thereby tighter sorption of TCE.
- Soil characteristics apparently influenced the PAAF performance, resulting in overall 57% TCE removal from a sandy soil system and 52% from a clayey soil system, both with alginic acid and 5% continuous methanol flushing.
- Twice more the TCE removal percent from low permeability reactor of natural soils can be achieved using PAAF technology. Consequently, post-alcohol flushing enhanced efficiency by more methanol flushing to the low permeability zones.

Therefore, a natural polymer injection for modification of permeability contrast in porous media in conjunction with alcohol flushing has good potential to enhance overall TCE remediation.

6 RECOMMENDATIONS

Most of the experiments have neither been duplicated, nor replicated, except for the two runs indicated in the chapter 4.3. Therefore, it is recommended to run the experiments in duplicate/replicate to ensure the data quality to confirm the results obtained from this study.

Further research is also recommended to assess the impacts of operating parameters of the PAAF with the different types of soils on overall performance and biodegradability of residual TCE.

7 REFERENCES

1. Bailey, S. E., T. J. Olin, R. Bricka, and D. D. Adrian. "A review of potentially low-cost sorbents for heavy metals." *Water Research, 33 (11)*, 1999: 2469-2479.

2. Ben Hur, M., M. Malik, J. Letey, and U. Mingelgrin. "Soil Science." 153, 349. 1992.

3. Boyd, G.R., and K.J. Farley. *Factors influencing nonaqueous phase liquid removal from groundwater by the alcohol flooding technique.* Summary Report, Manteo, NC: Concepts in Manipulation of Groundwater Colloid for Environmental Restoration, 1990.

4. Brandes, D., and K.J. Farley. "Importance of phase behavior on the removal of residual DNAPLs from porous media by alcohol flooding." *Water Environmental Resource, 65 (7)*, 1993: 869-878.

5. Chawla, R. C., K. F. Doura, and D. McKay. "Effect of Alcohol Cosolvents on the Aqueous Solubility of Trichloroethylene." *Proceedings of the 2001 Conference on Environmental Research.* 2001. 52-66.

6. Christ, J.A., C.A. Ramsburg, L. M. Abriola, K. D. Pennell, and F. E. Lőffler. "Coupling Aggressive Mass Removal with Microbial Reductive Dechlorination for Remediation of DNAPL Source Zones: A Review and Assesment." *Environmental Health Perspectives, 113 (4)*, 2005: 465-477.

7. Darwish, M. I. M., J. E. McCray, P. K. Currie, and P. L. J. Zitha. "Polymer-enhanced DNAPL fllushing from low permeability media: An experimental study." *Ground Water and Monitoring Remediation, 23 (2)*, 2003: 92-101.

8. Delinsky, A.D., J. V. Bruckner, and M. G. Bartlett. "A review of analitical methods for the determination of trichloroethylene and its major metabolites chloral hydrate,

trichloroacetic acid and dichloroacetic acid." *Biomedical Chromatography, 19*, 2005: 617-639.

9. Delshad, M., G. Pope, and K. Sepehrnoori. "A composital simultor for modeling surfactant enhanced aquifer remediation, 1. Formulation ." *Journal of Contaminant Hydrology, 23* , 1996: 303-327.

10. Ding, Y., Y. Zhoa, and X. Toa. "Assembled alginate/chitosan micro-shells for removal of organic pollutants." *Journal of Polymer, 50*, 2009: 2841-2846.

11. Elfarissi, F., L. Nabzar, E. Ringenbach, and E. Pefferkorn. *Colloids Surfactants A.* 131, 281, 1998.

12. Falta, R. W., S. M. Hassanizadeh, T. H. Illangasekare, I. Javandel, K. H. Jensen, A.S. Mayer, and M. Oostrom. *Soil and Groundwater Contamination: Nonaqueous Phase Liquids - Principles and Observations.* Washington: AGU Books Board, 2005.

13. Giese, S. W., and S. E. Powers. "Using polymer solutions to enhance recovery of mobile coal tar and creosate DNAPLs." *Journal of Contaminant Hydrology, 58*, 2002: 147-167.

14. Ground-Water Remediation Technologies Analysis Center (GWRTAC). "In situ flushing." 1997.

15. Harmsen, E., J. Colon, C. Lis, and D. Cadiz. "Evaluation of Percolation and Nitrogen Leaching from a Sweet Pepper Crop Grown on an Oxisol Soil in Northwest Puerto Rico." Grenada: Annual Meeting of the Caribbean Food Crops Society, 2003.

16. Hernandez, I. *Phyto-viability on Restored Land with Coal ash Aggregates as Backfilling Amendments.* Dissertation Thesis. University of Puerto Rico at Mayaguez, 2009.

17. Huang, C., S. Chen, and J. R. Pan. "Optimal condition for modification of chitosan: a biopolymer for coagulation of colloidal particles." *Water Research, 34(3),* 2000: 1057-1062.

18. Jeong, S.W., A. Lynn Wood, and T. R. Lee. "Enhanced removal of DNAPL trapped in porous media using simultaneous injection of cosolvent with air: Influencing factors and removal mechanisms." *Journal of Hazardous Materials, 101*, 2003: 109-122.

19. Kawamura, S. "Effectiveness of natural polyelectolytes in water treatment." *Journal of American Water Works Association, 10*, 1991: 88-91.

20. Kueper, B.H., G.P. Wealthall, J.W.N. Smith, S.A. Leharne, and D.N. Lerner. *An Illustrated Handbook of DNAPL Transport and Fate in the Subsurface.* Bristol U.K.: Environment Agenty, 2003.

21. Lake, L.W. *Enhanced Oil Recovery, Chapter 8.* Englewood Cliffs, New Jersey : Prentice Hall, 1989.

22. Martel, K.E., R. Martel, R. Lefebvre, and P.J. Gelinas. "Laboratory study of polymer solutions used for mobility control during in situ Napl." *Ground Water Monitoring and Remediation*, 1998: 103-113.

23. Molina, G. M., I. Padilla, M. Pando, and D. D. Perez. "Field Lysimiters for the study of Fate and Transport of Explosive Chemical in Soils under Variable Environmental Conditions." Proc. of SPIE Vol. 6217,, 2006.

24. Moran, M.J., J.S. Zogorski, and P. J. Squillance. "Chlorinated solvents in groundwater of the United States." *Environmental Science and Technology, 41*, 2007: 74-81.

25. Nalco. *Material Safety Data Sheet of POL EZ 675 and 8736.* http://www.nalco.com (accessed June 15, 2008).

26. NRC, National Research Council. "Research Needs in Subsurface Environments." 2000.

27. O'Niell, W. L., V.A. Nzengung, J.E. Noakes, J. Bender, and P.C. Phillips. "Biosorption and transformation of tetrachloroethylene and tricholoroethylene using mixed-species Microbial Mats." *Journal of Hazardous Substance Research, 2.,* 1999: 1-15.

28. Oostrom, M., C. Hofstee, R.C. Walker, and J.H. Dane. "Movement and remediation of trichloroethylene in a saturated, heterogeneous porous medium 2. Pump-and-treat and surfactant flushing." *Journal of contaminant Hydrology, 37,* 1999: 179-197.

29. Osada, Y., and K. Kajiwara. "Environment: Earth Environment and Gels." *Gels Handbook. Vol 4.* San Diego, California, 2001.

30. Padget, P.K., and N. J. Hayden. "Mobilization of residual tetrachloroethylene during alcohol flushing of clay containing porous media." *Journal of Contaminant Hydrology, 40,* 1999: 285-296.

31. Padilla, I.Y. "Transport of Nonreactive and Voaltile Solutes in Unsaturated Porous Media under Wetting and Draining Conditions." (Dissertation Thesis. University of Arizona) 1998.

32. Pefferkorn, E. "Polyacrylamide at solid/liquid interfaces." *Journal of Colloid and Interface Science, 216,* 1999: 197-220.

33. Penell, K.D., A. M. Adinolfi, L. M. Abriola, and M. S. Diallo. "Solubilization of dodecane, tetrachloroethylene, and 1,2- dichlorobenzene in micellar sollutions of ethoxylated nonionic surfactants." *Environmental Science and Technology, 31,* 1997: 1382-1389.

34. Powers, S.E., I.M. Nambi, and G.W. Curry. "Napl dissolution in heterogeneous systems: Mechanisms and a local equilibrium modeling approach." *Water Resources Research, 34 (12),* 1998: 3293-3302.

35. Rattanakawin, C., and R. Hogg. "Viscocity behavior of polymeric flocculant solutions." (Journal of Minerals Engineering) 20 (2007).

36. Renault, F., B. Sancey, P. M. Badot, and G. Crini. "Chitosan for coagulation/flocculation processes - An eco-friendly approach ." *European Polymer Journal, 45,* 2009: 1337-1348.

37. Rodriguez, S., I. Padillla, and S. Hwang. "Development of a multi-scale packing methodology for evaluating fate and transport processes of explosive-related chemicals in clayey soils." Proc. of SPIE, Vol 6553, 2007.

38. Serrano, M.F. *Detection and Monitoring of DNAPLs in the Subsurface under trasient conditions using cross well radar.* Dissertation Thesis. University of Puerto Rico at Mayaguez, 2008.

39. Sorbie, K.S. "Polymer-Improved Oil Recovery ." *CRC Press.* Boca Raton, Florida, 1991. 274-287.

40. Standard Sand. http://standardsand.com (accessed March 15, 2009).

41. Tood, D.K,. and L. W. Mays. *Groundwater Hydrology.* Thd Edition. John Wiley and Sons, Inc., 2005.

42. United States Department of Health and Human Services (USDHHS). "Toxicological profile for Trichloroethylene, Public Health Service, Agency for Toxic Substances and Disease Registry." 1997.

43. United States Environmental Protection Agency (US EPA). "Handbook on the Managament of Munitions Response Actions, Office of Solid Waste and Emergency Response." 2005.

44. Urynowicz, M.A., and R. L. Siegrist. "Interphase mass transfer during chemical oxidation of TCE DNAPL in an aqueous system." *Journal of Contaminant Hydrology, 80*, 2005: 93-106.

45. Xu, N., S. Vandegrift, and G. W. Sewell. "Determination of chloroethenes in environmental biological samples using gas chromatography coupled with solid Phase micro extraction." *Chromatographia, 42 (5)* (Chromatographia Vol. 42, No 5/6, March 1996), 1996: 313-317.

8 ANNEXES (Mass Balance)

List of Symbols and Abbreviations

Co=	initial concentration
Ceff=	effluent concentration
Vo=	initial volume before TCE recirculation
Vout=	final volume after TCE recirculation
PV=	pore volume
Mass soil =	Total mass soil in the reactor
Kd =	TCE desorption coefficient
Koc =	Partitioning coefficient
foc =	fraction organic carbon
TTCE =	Total TCE present in the reactor
M/Mo =	normalized mass = sample mass / total mass

EXAMPLE OF CALCULATION (Continuous flushing 5% high permeability reactor)

DATA

Co= 1100 $mg.L^{-1}$

Ceff= 41.53 $mg.L^{-1}$

Vo= 100 mL

Vout= 57 mL

Mass soil = 170gr

Calibration curve slope= 42.2

TOTAL TCE PRESENT IN THE REACTOR

PV= Vo- Vout = (100-57)mL = 43 mL

Total TCE present in reactor = TCE in pores + qe*(mass soil)

TCE in pores= C*PV = 41.53(mg. L-1)(1L. 1000 mL-1) * 43mL = 1.78 mg TCE

qe*(mass soil) = Kd * C * (mass soil)

Kd = Koc*foc =

Log Koc = 1.81 (Chawla, et.al 2001)

foc = (% clay in the reactor)*(foc clay) + (% coarse sand in the reactor)* (foc coarse sand)
foc = (0.4)*(0.67) + (0.6)* (0.01)= 0.274

Kd = Koc*foc = 10^1.81L. Kg-1 * 0.274= 0.18 L. Kg-1

qe*(mass soil) = Kd * C * (mass soil) = 0.18 L. Kg-1* 41.53 mg.L-1 * =1.25 mg TCE

TTCE = TCE in pores + qe*(mass soil) = 1.78+1.25 = 3.03 mg TCE

MOMENTS METHOD

C = Area / calibration curve slope = 1505.37 / 42.2 = 35.68 mg L-1

M/Mo = C * V / Ceff = 57.53 mg.L-1 *5 mL *(1L/1000mL) / 41.53 mg.L-1 = 0.07189

(M/Mo)*100 = 0.07189 *100 = 7.19

((M/Mo)1+(M/Mo)2)*(v2-v1)/2 = (0.116598 + 0)*(0+10)/2 = 0.0005829992

Σ ((M/Mo)1+(M/Mo)2)*(v2-v1)/2 = 0.071349585

Normalized Σ = [Σ ((M/Mo)1+(M/Mo)2)*(v2-v1)/2] * TTCE/ Vinj =
= 0.071349585* 3.03 mg *(1L/1000mL)/ 295 mL = 0.733 mg

% remotion = Normalized Σ/ TTCE = 0.733 / 3.03 = 24.19%

Continuous flushing 5% high permeability						
No	Area	C(mg/L)	M/Mo	(M/Mo)*100	((M/Mo)1+(M/Mo)2)*(v2-v1)/2	V(ml)
0	0	0	0	0	0	0
1	2057.23	35.38436	0.116598	11.65984949	0.000582992	10
2	2002.45	34.44214	0.226987	22.69874113	0.00171793	20
3	1747.74	30.06113	0.297172	29.71721977	0.002620798	30
4	1563.38	26.89014	0.354433	35.44333982	0.003258028	40
5	1336.73	22.99176	0.378812	37.88120581	0.003666227	50
6	949.09	16.32435	0.376544	37.65438277	0.007553559	70
7	667.5	11.481	0.34049	34.04896186	0.007170334	90
8	480.73	8.268556	0.299712	29.97119131	0.006402015	110
9	322.68	5.550096	0.246897	24.68970565	0.006832612	135
10	272.06	4.679432	0.246715	24.67145552	0.006170145	160
11	201.6	3.46752	0.217097	21.7097201	0.006957176	190
12	141.91	2.440852	0.184991	18.49911412	0.008041767	230
13	114.57	1.970604	0.162338	16.23383088	0.003473294	250
14	125.12	2.152064	0.198561	19.85614166	0.005413496	280
15	0	0	0	0	0.001489211	295
				Σ	0.071349585	
				normalized Σ	0.733986022	
				% remotion	24.19	

tce out	2414.48	41.52906	mg/L
PV		43	mL
soil mass		170	gr

TCE in the pores	1.785749	mgr
% clay in column	0.4	
% sand in column	0.6	
foc clay	0.67	%
foc sand	0.01	%
foc total	0.274	%
log Koc	1.81	
Kd	0.18	
qe*total mass	1.248969	mgr

total TCE in column	3.03	mgr

Continuous Flushing 5% low permeability						
No	Area	C(mg/L)	M/Mo	(M/Mo)*100	((M/Mo)1+(M/Mo)2)*(v2-v1)/2	V(ml)
0	0	0	0	0	0	0
1	2466.68	42.4269	0.110714	11.07140552	0.00055357	10
2	2166.76	37.26827	0.194505	19.45049916	0.001526095	20
3	2464.17	42.38372	0.331804	33.18041904	0.002631546	30
4	2085.9	35.87748	0.374493	37.44927559	0.003531485	40
5	1594.58	27.42678	0.357854	35.78543187	0.003661735	50
6	871.6	14.99152	0.273845	27.38452469	0.006316996	70
7	571.1	9.82292	0.230698	23.06984175	0.005045437	90
8	513.37	8.829964	0.253462	25.34621515	0.004841606	110
9	258.83	4.451876	0.156833	15.68333166	0.005128693	135
10	210.22	3.615784	0.150968	15.09676727	0.003847512	160
11	176.63	3.038036	0.146665	14.6664884	0.003720407	185
12	152.44	2.621968	0.157368	15.73681074	0.006840742	230
13	0	0	0	0	0.001573681	250
14	0	0	0	0	0	260
15	0	0	0	0	0	270
16	0	0	0	0	0	290
				Σ	0.049219506	
tce out	2732.49	46.99883	mg/L	normalized Σ	0.650395833	
PV		55	mL	% remotion	16.97	
soil mass		150	gr			

TCE in the pores	2.584936	mgr
% clay in column	0.4	
% sand in column	0.6	
foc clay	0.67	%
foc sand	0.01	%
foc total	0.274	%
log Koc	1.81	
Kd	0.18	
qe*total mass	1.247179	mgr

total TCE in column	3.83	mgr

Continuous Flushing 10% low permeability						
No	Area	C(mg/L)	M/Mo	(M/Mo)*100	((M/Mo)1+(M/Mo)2)*(v2-v1)/2	V(ml)
0	0	0	0	0	0	0
1	1505.37	35.67727	0.118143	11.81432734	0.000590716	10
2	1234.64	29.26097	0.193792	19.37921057	0.001559677	20
3	1829.85	43.36745	0.430827	43.08265785	0.003123093	30
4	1344.6	31.86702	0.422103	42.2103391	0.00426465	40
5	1637.44	38.80733	0.642541	64.25414403	0.005323224	50
6	748.06	17.72902	0.410961	41.09606274	0.010535021	70
7	721.15	17.09126	0.509371	50.9370583	0.009203312	90
8	298.86	7.082982	0.258004	25.80038699	0.007673745	110
9	226.1	5.35857	0.239552	23.95521504	0.00621945	135
10	96.35	2.283495	0.120987	12.0986648	0.004506735	160
11	161.81	3.834897	0.234932	23.49323534	0.004448988	185
12	0	0	0	0	0.005285978	230
13	0	0	0	0	0	250
14	0	0	0	0	0	280
15	0	0	0	0	0	310
				Σ	0.062734589	
				normalized Σ	0.823686261	
				% remotion	27.28	

tce out	2370.2	40.76744	mg/L
PV		44	mL
soil mass		170	gr

TCE in the pores	1.793767	mgr
% clay in column	0.4	
% sand in column	0.6	
foc clay	0.67	%
foc sand	0.01	%
foc total	0.274	%
log Koc	1.81	
Kd	0.18	
qe*total mass	1.226063	mgr

total TCE in column	3.02	mgr

Intermittent Flushing 10% low permeability						
No	Area	C(mg/L)	M/Mo	(M/Mo)*100	((M/Mo)1+(M/Mo)2)* (v2-v1)/2	V(ml)
0	0	0	0	0	0	0
1	3344.87	57.53176	0.071899	7.189892925	0.000179747	5
2	2941.25	50.5895	0.252892	25.28920115	0.002435932	20
3	2972.85	51.13302	0.383414	38.34135231	0.003181528	30
4	2038.91	35.06925	0.350616	35.06155894	0.003670146	40
5	2504.04	43.06949	0.53825	53.82504994	0.00444433	50
6	1374.47	23.64088	0.324991	32.49908469	0.002158103	55
7	1265.55	21.76746	0.380847	38.08469862	0.005293784	70
8	830.91	14.29165	0.28577	28.57703375	0.003333087	80
9	592.47	10.19048	0.229236	22.92355921	0.00257503	90
10	655.08	11.26738	0.281623	28.16226076	0.002554291	100
11	1094.68	18.8285	0.51767	51.76700551	0.003996463	110
12	598.78	10.29902	0.296032	29.6031756	0.002034255	115
13	674.46	11.60071	0.37694	37.69404334	0.005047291	130
14	553.15	9.51418	0.332923	33.29232514	0.003549318	140
15	390.94	6.724168	0.252101	25.21009851	0.002925121	150
16	334.9	5.76028	0.230361	23.03606553	0.002412308	160
17	471.18	8.104296	0.344357	34.43570227	0.002873588	170
18	603	10.3716	0.492543	49.25429284	0.008369	190
19	458.13	7.879836	0.393905	39.3905371	0.004432241	200
20	285.43	4.909396	0.257687	25.76867495	0.003257961	210
21	297.54	5.117688	0.281411	28.1411094	0.002695489	220
22	276.07	4.748404	0.272973	27.29733354	0.002771922	230
23	643.22	11.06338	0.69131	69.13098158	0.009642832	250
24	183.44	3.155168	0.205041	20.50409308	0.004481754	260
25	277.73	4.776956	0.322374	32.23737961	0.002637074	270
26	141.61	2.435692	0.170461	17.04610382	0.002464174	280
27	152.72	2.626784	0.1904	19.04000632	0.001804306	290

tce out	3000	51.6	mg/L
PV		51	mL
soil mass		150	gr

Σ	0.095221074
normalized Σ	1.313682309
% remotion	32.83

TCE in the pores	2.6316	mgr
% clay in column	0.4	
% sand in column	0.6	
foc clay	0.67	%
foc sand	0.01	%
foc total	0.274	%
log Koc	1.81	
Kd	0.18	
qe*total mass	1.369278	mgr

total TCE in column	4.00	mgr

Intermittent flushing 5% low permeability						
No	Area	C(mg/L)	M/Mo	(M/Mo)*100	((M/Mo)1+(M/Mo)2)* (v2-v1)/2	V(ml)
0	0	0	0	0	0	0
1	2623.47	62.17624	0.130585	13.05847757	0.000652924	10
2	2419.36	57.33883	0.24085	24.08501588	0.001857175	20
3	2346.45	55.61087	0.350388	35.03878227	0.00295619	30
4	2262.82	53.62883	0.450533	45.05328321	0.004004603	40
5	1636.4	38.78268	0.407264	40.72639044	0.004288984	50
6	2194.75	52.01558	0.600847	60.08474086	0.002520278	55
7	1182.91	28.03497	0.41216	41.21603295	0.007597558	70
8	902.98	21.40063	0.359571	35.95709219	0.003858656	80
9	691.66	16.39234	0.30985	30.98500817	0.003347105	90
10	649.34	15.38936	0.323213	32.32128375	0.003165315	100
11	602.58	14.28115	0.329932	32.99315471	0.003265722	110
12	692.18	16.40467	0.396217	39.62172069	0.001815372	115
13	854.44	20.25023	0.552893	55.28933532	0.007118329	130
14	421.44	9.988128	0.293684	29.36839646	0.004232887	140
15	320.91	7.605567	0.239602	23.96022847	0.002666431	150
16	272.3	6.45351	0.216862	21.68623049	0.002282323	160
17	262.97	6.232389	0.222521	22.25212921	0.002196918	170
18	255.62	6.058194	0.222664	22.26636503	0.001112962	175
19	622.19	14.7459	0.588428	58.84276515	0.006083185	190
20	291.44	6.907128	0.290132	29.01319782	0.004392798	200
21	213.06	5.049522	0.222709	22.27089461	0.002564205	210
22	169.17	4.009329	0.185252	18.52518166	0.002039804	220
23	183.52	4.349424	0.210101	21.01007883	0.001976763	230
24	456.01	10.80744	0.567454	56.74542075	0.00777555	250
25	209.13	4.956381	0.270649	27.06488155	0.004190515	260
26	132.68	3.144516	0.178314	17.83140944	0.002244815	270
27	106.58	2.525946	0.148542	14.85423165	0.001634282	280
28	103.31	2.448447	0.149127	14.91271798	0.001488347	290
29	94.3	2.23491	0.138938	13.89376181	0.000864194	296

Σ	0.09419419
normalized Σ	1.515180261
% remotion	31.82

tce out	2404.96	56.99755	mg/L
PV		57	mL
soil mass		150	gr

TCE in the pores	3.24886	mgr
% clay in column	0.4	
% sand in column	0.6	
foc clay	0.67	%
foc sand	0.01	%
foc total	0.274	%
log Koc	1.81	
Kd	0.18	
qe*total mass	1.512509	mgr

total TCE in column	4.76	mgr

High permeability reactor after PAAF technology with alginic acid (configuration 4)						
No	Area	C(mg/L)	M/Mo	(M/Mo)*100	((M/Mo)1+(M/Mo)2)*(v2-v1)/2	V(ml)
0	0	0	0	0	0	0
1	3197.37	49.878972	0.057039819	5.703981884	0.0001426	5
2	3391.72	52.910832	0.181520838	18.15208384	0.001192803	15
3	3247.85	50.66646	0.289701811	28.97018106	0.002356113	25
4	3282.45	51.20622	0.409903287	40.99032872	0.003498025	35
5	3188.62	49.742472	0.511953501	51.19535006	0.004609284	45
6	2616.29	40.814124	0.513409391	51.34093908	0.005126814	55
7	1590.3	24.80868	0.351792022	35.17920217	0.003028205	62
8	762.91	11.901396	0.182374178	18.23741781	0.001335415	67
9	1953.33	30.471948	0.501791562	50.17915619	0.001710414	72
10	no sample	no sample	no sample	no sample	no sample	135
11	no sample	no sample	no sample	no sample	no sample	195
12	no sample	no sample	no sample	no sample	no sample	255

tce out	3324.52	51.862512	
PV		56	mL
soil mass		160	gr

Σ	0.022999675
normalized Σ	1.39668529
% remotion	31.94

TCE in the pores	2.904300672	mgr
% clay in column	0.4	
% sand in column	0.6	
foc clay	0.67	%
foc sand	0.01	%
foc total	0.274	%
log Koc	1.81	
Kd	0.18	
qe*total mass	1.467993369	mgr

total TCE in column	4.37	mgr

Low permeability reactor after PAAF technology with alginic acid (Configuration 4)						
No	Area	C(mg/L)	M/Mo	(M/Mo)*100	((M/Mo)1+(M/Mo)2)* (v2-v1)/2	V(ml)
0	0	0	0	0	0	0
1	1682.69	26.24996	0.096494	9.649436053	0.000482472	10
2	2174.28	33.91877	0.249369	24.93694717	0.001729319	20
3	2683.49	41.86244	0.461657	46.16566061	0.00355513	30
4	1672.95	26.09802	0.383743	38.37432693	0.004226999	40
5	1701.5	26.5434	0.487865	48.7865128	0.004358042	50
6	1822.85	28.43646	0.679457	67.94572043	0.008754917	65
7	2141.11	33.40132	1.043652	104.3652035	0.017231092	85
8	1594.93	24.88091	0.960348	96.03482398	0.020040003	105
9	793.07	12.37189	0.568485	56.84854497	0.015288337	125
10	577.78	9.013368	0.480428	48.04280162	0.010489135	145
11	413.8	6.45528	0.391536	39.15364954	0.008719645	165
12	380.34	5.933304	0.403498	40.34981512	0.007950346	185
13	277.66	4.331496	0.326411	32.64111601	0.007299093	205
14	237.12	3.699072	0.305949	30.59486372	0.006323598	225
tce out	2087.5	32.565		Σ	0.11644813	
PV		57		normalized Σ	1.407916111	
soil mass		150		% remotion	51.75	

TCE in the pores	1.856205	mgr
% clay in column	0.4	
% sand in column	0.6	
foc clay	0.67	%
foc sand	0.01	%
foc total	0.274	%
log Koc	1.81	
Kd	0.18	
qe*total mass	0.864158	mgr

total TCE in column	2.72	mgr

TCE aging on alcohol flushing performance effect in low permeability reactor						
No	Area	C(mg/L)	M/Mo	(M/Mo)*100	((M/Mo)1+(M/Mo)2)* (v2-v1)/2	V(ml)
0	0	0	0	0	0	0
1	2835.95	32.04624	0.067769	6.776878969	0.000169422	5
2	2751.35	31.09026	0.197241	19.72414812	0.001325051	15
3	2492.69	28.1674	0.297831	29.78306817	0.002475361	25
4	3157.29	35.67738	0.528133	52.81334487	0.004129821	35
5	2826.46	31.939	0.742962	74.29621489	0.012710956	55
6	1149.88	12.99364	0.467124	46.71244521	0.018151299	85
7	695.54	7.859602	0.432142	43.21421405	0.020233498	130
8	341.08	3.854204	0.252667	25.26673398	0.008560119	155
9	189.75	2.144175	0.204045	20.40447656	0.015984924	225

tce out	2630.71	29.72702
PV		53
soil mass		150

Σ	0.08374045
normalized Σ	0.879974449
% remotion	37.22

TCE in the pores	1.575532	mgr
% clay in column	0.4	
% sand in column	0.6	
foc clay	0.67	%
foc sand	0.01	%
foc total	0.274	%
log Koc	1.81	
Kd	0.18	
qe*total mass	0.788848	mgr

total TCE in column	2.36	mgr

TCE aging on alcohol flushing performance effect in high permeability reactor						
No	Area	C(mg/L)	M/Mo	(M/Mo)*100	((M/Mo)1+(M/Mo)2)*(v2-v1)/2	V(ml)
0	0	0	0	0	0	0
1	1316.75	14.87928	0.05722	5.721957052	0.000286098	10
2	1619.39	18.29911	0.140742	14.0741675	0.000989806	20
3	1594.8	18.02124	0.207907	20.7906826	0.001743243	30
4	1571.37	17.75648	0.273136	27.31364846	0.002405217	40
5	939.9	10.62087	0.285904	28.59044772	0.008385614	70
6	2457.68	27.77178	1	100	0.02571809	110
7	1652.81	18.67675	1	100	0.05	160
8	902.39	10.19701	0.90191	90.19103623	0.066566863	230

tce out	2873.85	32.47451
PV		50
soil mass		170

Σ	0.15609493
normalized Σ	1.764810738
% remotion	67.87

TCE in the pores	1.623725	mgr
% clay in column	0.4	
% sand in column	0.6	
foc clay	0.67	%
foc sand	0.01	%
foc total	0.274	%
log Koc	1.81	
Kd	0.18	
qe*total mass	0.976657	mgr

total TCE in column	2.60	mgr

Low perm reactor after PAAF technology with alginic acid and without manipulation of polymer flow						
No	Area	C(mg/L)	M/Mo	(M/Mo)*100	((M/Mo)1+(M/Mo)2) *(v2-v1)/2	V(ml)
0	0	0	0	0	0	0
1	471.2	5.560	0.021287	2.128712127	5.32178E-05	5
2	121.66	1.4355	0.016488	1.64884837	0.000188878	15
3	136.85	1.614	0.030912	3.091195401	0.000237002	25
4	152.03	1.7939	0.048077	4.807718023	0.000394946	35
5	120	1.416	0.048791	4.879051564	0.000484338	45
6	593.73	7.0060	0.295048	29.50484457	0.001719195	55
7	0	0	0	0	0	65
8	0	0	0	0	0	85
9	0	0	0	0	0	105
10	0	0	0	0	0	130
11	0	0	0	0	0	155
12	0	0	0	0	0	185
13	0	0	0	0	0	225

tce out	1870.875	22.076325
PV		55
soil mass		140

Σ	0.003077577
normalized Σ	0.07307799
% remotion	5.60

TCE in the pores	1.214198	mgr
% natural soil in column	0.6	
% sand in column	0.4	
foc natural soil	0.07	%
foc sand	0.01	%
foc total	0.046	%
log Koc	1.81	
Kd	0.03	
qe*total mass	0.091794	mgr

total TCE in column	1.31	mgr

HIgh permeability reactor after PAAF technology with alginic acid and without manipulation of polymer flow						
No	Area	C(mg/L)	M/Mo	(M/Mo)*100	((M/Mo)1+(M/Mo)2) *(v2-v1)/2	V(ml)
0	0	0	0	0.0	0	0
1	1139.26	15.4981	0.23673	23.7	0.001183677	10
2	1313.4	14.2275	0.43465	43.5	0.003356941	20
3	1205.72	41.1423	1	100.0	0.007173264	30
4	3486.64	39.039	1	100.0	0.01	40
5	3313.89	12.6949	0.96958	97.0	0.009847901	50
6	1075.84	19.3240	1	100.0	0.011817481	62
7	1637.63	9.20105	0.94166	94.2	0.004854161	67
8	779.75	34.9169	1	100.0	0.004854161	72
9	2959.06	5.61137	0.72857	72.9	0.011235713	85
10	475.54	4.57910	0.73443	73.4	0.014630077	105
11	388.06	2.23256	0.42628	42.6	0.011607187	125
12	189.2	1.58320	0.36275	36.3	0.009862958	150
13	134.17	3.11673	0.83314	83.3	0.014948773	175
14	264.13	0	0	0.0	0.012497211	205
15	0	2.03526	0.76167	76.2	0.015233541	245
16	172.48	0	0	0.0	0.007616771	265
17	0	0	0	0.0	0	285
18	0	0	0	0.0	0	305

tce out	970.74	13.59036
PV		44
soil mass		190

Σ	0.150719816
normalized Σ	0.32350908
% remotion	49.42

TCE in the pores	0.597976	mgr
% natural soil in column	0.4	

% sand in column	0.6	
foc natural soil	0.07	%
foc sand	0.01	%
foc total	0.034	%
log Koc	1.81	
Kd	0.02	
qe*total mass	0.056684	mgr

total TCE in column	0.65	mgr

High permeability reactor after PAAF technology with alginic acid and with manipulation of polymer flow						
No	Area	C(mg/L)	M/Mo	(M/Mo)* 100	((M/Mo)1+(M/Mo)2)* (v2-v1)/2	V(ml)
0	0	0	0	0.00	0	0
1	0	0	0	0.00	0	10
2	378.84	5.30376	0.134527	13.45	0.0006726	20
3	806.5	11.291	0.429586	42.96	0.0028206	30
4	141.93	1.98702	0.1008	10.08	0.0026519	40
5	0	0	0	0.00	0.0005040	50
6	150.09	2.10126	0.165222	16.52	0.0009913	62
7	484.8	6.7872	0.576716	57.67	0.0018548	67
8	0	0	0	0.00	0.0008651	70

tce out	1193.99	16.71586
PV		43
soil mass		190

Σ	0.010360389
normalized Σ	0.121928263
% remotion	15.46

TCE in the pores	0.718782	mgr
% natural soil in column	0.4	
% sand in column	0.6	
foc natural soil	0.07	%
foc sand	0.01	%
foc total	0.034	%
log Koc	1.81	
Kd	0.02	
qe*total mass	0.069721	mgr

total TCE in column	0.79	mgr

Low permeability reactor after PAAF technology with alginic acid and with manipulation of polymer flow						
No	Area	C(mg/L)	M/Mo	(M/Mo)*100	((M/Mo)1+(M/Mo)2)*(v2-v1)/2	V(ml)
0	0	0	0	0	0	0
1	551.85	7.7259	0.040081	4.008132176	0.000100203	5
2	100.43	1.40602	0.021883	2.18829418	0.000309821	15
3	208.27	2.91578	0.075634	7.563411146	0.000487585	25
4	316.11	4.42554	0.160715	16.07153146	0.001181747	35
5	302.58	4.23612	0.19779	19.77897201	0.001792525	45
6	289.16	4.04824	0.231021	23.10212286	0.002144055	55
7	254.43	3.56202	0.240233	24.02329963	0.002356271	65
8	164.14	2.29796	0.202668	20.26676064	0.004429006	85
9	144.39	2.02146	0.22023	22.02304666	0.004228981	105
10	0	0	0	0	0.002752881	130
11	92.68	1.29752	0.208674	20.86741758	0.002608427	155
12	0	0	0	0	0.003130113	185
13		0	0	0	0	225

tce out	1163.685	16.29159
PV		55
soil mass		140

Σ	0.025521615
normalized Σ	0.109320773
% remotion	11.34

TCE in the pores	0.896037	mgr
% natural soil in column	0.6	
% sand in column	0.4	
foc natural soil	0.07	%
foc sand	0.01	%
foc total	0.046	%
log Koc	1.81	
Kd	0.03	
qe*total mass	0.067741	mgr

total TCE in column	0.96	mgr