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ÉTUDE EN LABORATOIRE DES MÉCANISMES DE RÉCUPÉRATION DU TRICHLOROÉTHÈNE (TCE) EN PHASE RÉSIDUELLE LORS DE L'INJECTION DE SOLUTIONS MICELLAIRES DANS DES SABLES

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RÉSUMÉ

La récupération de la phase résiduelle des liquides immiscibles denses (LID) dans la zone saturée des sols est très complexe. L'injection de solutions de lavage est une méthode chimique récemment mise au point principalement pour extraire les contaminants récalcitrants à saturation résiduelle dans des aquifères. Des solutions de lavage composées d'alcool, d'une combinaison alcool/tensioactif anionique ou d'une combinaison tensioactif nonionique/tensioactif anionique ont été développées pour récupérer le trichloroéthène (TCE) en phase résiduelle. L'utilisation de diagrammes de phases pour la sélection des solutions de lavage s'est avérée une méthode simple, rapide et efficace. Les courbes de distribution tracées à l'intérieur des diagrammes de phases ont permis de prédire le principal mécanisme responsable de la récupération du TCE (solubilisation ou mobilisation) pour chaque solution retenue.

Ces solutions ont par la suite été injectées en colonne de sable. L'analyse des effluents récupérés lors de ces essais a permis d'évaluer l'efficacité de récupération des solutions. Les essais en colonne de sable ont également permis de confirmer la validité de la méthode de prédiction des mécanismes de récupération par le biais des courbes de distribution. Les solutions injectées en colonnes de sable ont permis de récupérer de 1% à près de 100% de TCE à saturation résiduelle. Les solutions qui ont récupéré le TCE par mobilisation sont généralement plus efficaces, c'est-à-dire qu'elles ont récupéré davantage de TCE en injectant moins de solution, que celles qui ont extrait le TCE par solubilisation. La combinaison de deux types de solutions est l'une des stratégies d'injection qui pourraient accroître la récupération du TCE. Une solution qui solubilise le TCE serait injectée à la suite d'une autre qui récupère la majorité du TCE par mobilisation. Évidemment cette approche nécessite des conditions hydrogéologiques favorables comme la présence d'un aquitard au-dessous de l'aquifère restauré. Même pour ces conditions, il peut être difficile de contrôler la migration verticale d'un banc de TCE. La dissolution *in situ* s'avère un mécanisme de récupération mieux adapté. Si la récupération n'est pas totale, une technique de biorestauration *in situ* pourrait également dégrader le TCE restant dans les aquifères suite à l'injection d'une solution nettoyante.

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INTRODUCTION GÉNÉRALE

Au cours des dernières années, la technique d'injection de solutions de lavage dans les aquifères visant à récupérer la phase résiduelle des liquides immiscibles denses (LID) a connu d'importants progrès (Simpkin et al., 1999; Brandes et Farley, 1993; Brown et al., 1996; Falta et al., 1998; Fountain et al., 1996; Martel et Gélinas, 1996; Martel et al., 1998b; Martel et al., 1998c; Penell et al., 1994; Rao et al., 1997; Sabatini et al., 1997). Toutefois, il existe encore peu d'information sur les mécanismes responsables de la récupération de cette phase résiduelle. La présente étude a pour but de transférer les connaissances acquises dans le domaine pétrolier (Larson, 1979; Larson et Hirasaki, 1978) sur la prédiction du comportement des hydrocarbures en présence de tensioactif et d'alcool au domaine de la restauration des aquifères. L'objectif principal de ce projet de maîtrise est d'approfondir les connaissances entourant la technique de lavage de sol pour améliorer l'efficacité de récupération des liquides immiscibles denses en phase résiduelle, plus particulièrement le trichloroéthène (TCE), dans les aquifères.

Ce mémoire de maîtrise est divisé en quatre chapitres. Le premier chapitre présente une revue de la problématique entourant les LID, certaines notions de bases de l'écoulement multiphase et de façon générale les objectifs et la méthodologie. Le deuxième et le troisième chapitre contiennent chacun un article rédigé en anglais. Le premier traite particulièrement de la sélection des solutions de lavage à l'aide des diagrammes de phases et de la prédiction des mécanismes de récupération. Le second étudie, à l'aide d'essais en colonne de sable, la récupération du TCE par l'injection des solutions de lavage sélectionnées précédemment. Il permet également d'étudier les mécanismes de récupération associés à ces solutions de lavage. Finalement, les recommandations seront précédées d'une conclusion générale.

CHAPITRE 1

INTRODUCTION

1.1 Problématique

1.1.1 Historique

C'est en Allemagne au 19^e siècle que la production de solvants chlorés a commencé et c'est en 1906 que l'utilisation de ces produits s'est étendue aux États-Unis. Durant la deuxième guerre mondiale, l'usage des solvants chlorés s'est répandu dans les industries et cette augmentation s'est accrue dans les années suivantes. Jusqu'aux années 1970, les méthodes analytiques ne permettaient pas de détecter la présence de ces solvants dans les eaux souterraines. Les méthodes d'élimination recommandées par les manufacturiers à cette époque étaient l'épandage des solvants à la surface du sol pour faciliter leur évaporation dans l'atmosphère. Ce n'est qu'au début de l'année 1975 que l'EPA (Environmental Protection Agency) débuta un vaste programme de reconnaissance de la présence de composés organiques dans les eaux de surface et souterraines (Pankow and Cherry, 1996). Le début des années 1980 fut marqué par un intérêt accru pour la contamination des eaux souterraines, ce qui entraîna des règlements plus sévères qui exigeaient la protection et la surveillance de la qualité des eaux souterraines. Au Québec, en 1988, la politique de réhabilitation des terrains contaminés du Ministère de l'Environnement reconnaissait les possibilités de contamination des eaux souterraines par les composés organiques.

1.1.2 Causes de la contamination par les liquides immiscibles

Les causes habituelles de la contamination des eaux souterraines sont les déversements accidentels ou intentionnels, les fuites dans les réservoirs d'entreposage ou les conduites et les sites d'enfouissement de déchets industriels et municipaux inadéquats. Ces produits peuvent aussi être perdus lors du lavage de machineries et du rinçage de réservoirs. Les solvants chlorés tels que le TCE (trichloroéthène) et le PCE (tetrachloroéthène) sont utilisés principalement comme produits de nettoyage à sec et de dégraissage. Ces deux produits sont en tête de liste des contaminants les plus fréquemment rencontrés dans les eaux souterraines sous les sites d'enfouissement industriels (NRC, 1994).

1.1.3 Propriétés physiques et chimiques des liquides immiscibles denses

Les solvants chlorés qui constituent les principaux liquides immiscibles denses (LID) sont souvent rencontrés dans les eaux souterraines des sites industriels contaminés. Ces produits sont faiblement solubles dans l'eau et leur phase organique libre tend à migrer verticalement pour atteindre la base des aquifères (Tableau 1.1). Ce déplacement est rapide à cause de leur forte densité et leur faible viscosité. Les LID sont aussi très mobiles car ils peuvent se propager sous forme de gaz, en phase organique liquide et dissous dans l'eau. La tension interfaciale entre ces produits et l'eau engendre des saturations résiduelles importantes (25% à 30% du volume des pores). Par contre, leur adsorption au sol est négligeable à cause de leur faible partition sur les solides. Les liquides immiscibles denses sont des composés persistants dans l'environnement car leur dégradation est habituellement lente. La solubilité relative de ces produits est élevée par rapport aux concentrations maximales permises dans l'eau. La toxicité des solvants chlorés est aussi très importante comme le démontre les valeurs de doses létales. Le tableau 1.1 résume les propriétés physiques et chimiques de trois solvants chlorés qui constituent les principaux LID.

Tableau 1.1 - Propriétés physiques et chimiques des principaux solvants chlorés

Composé	Densité [a] (kg/m^3)	Viscosité [a] dynamique (mPa·s)	Pression [a] de vapeur (kPa)	H [a] ($atm{\cdot}m^3$ /mole)	Solubilité [a] dans l'eau (mg/L)	Tension [a] interfaciale (mN/m)	Critère de potabilité [b] (µg/L)	LD_{50} [c] Oral rat (mg/kg)
PCE	1623	0.89	1.9	0.0153	150	44.4	5	2629
TCE	1464	0.57	7.7	0.0091	1100	34.5	5	5650
1,1,1-TCA	1339	1.20	13.3	0.0180	1360	45.0	200	9600

[a] Cohen & Mercer, 1993
[b] EPA, National Primary Drinking Water Regulations, revised 1998
[c] MSDS databases
H : constante de Henry
LD_{50} : dose mortelle chez 50% des organismes testés
PCE (tetrachloroéthène), TCE (trichloroéthène) et 1,1,1-TCA (1,1,1-trichloroéthane)

1.1.4 Méthodes de restauration des aquifères

Les différentes caractéristiques des LID restreignent les méthodes de restauration applicables à ce type de contamination (NRC, 1994). La méthode de pompage et traitement traditionnelle qui consiste à pomper l'eau de l'aquifère ainsi que le contaminant qu'elle contient n'est pas assez efficace et est très lente. En général, l'excavation des sols n'est également pas praticable étant donné la profondeur à laquelle un contaminant sous forme de LID peut se loger. Certaines techniques de restauration *in situ* inspirées du génie pétrolier ont été développées à partir de la méthode de base de pompage et traitement et sont appliquées à la décontamination des aquifères (Fountain, 1998).

Les principales méthodes de restauration appliquées à la contamination par les LID et utilisant une variante de la technique de pompage et traitement sont la bioventilation, la ventilation forcée et la biodégradation *in situ* des hydrocarbures. La bioventilation peut améliorer la récupération de certains solvants chlorés. Cette méthode consiste à injecter un faible débit d'air dans la zone contaminée partiellement saturée pour favoriser la biodégradation en fournissant de l'oxygène aux micro-organismes. La ventilation forcée est semblable à la précédente technique à l'exception que l'air est injecté avec un plus grand débit. Cette méthode favorise l'évaporation des contaminants volatils pour ainsi les extraire sous forme de gaz et les acheminer vers la surface où ils sont traités. Cette méthode favorise également la biodégradation en imposant une circulation d'oxygène dans le sol contaminé, mais ce n'est pas le but premier de la ventilation forcée. La biodégradation *in situ* des hydrocarbures, contrairement à la bioventilation, s'effectue dans la zone saturée et c'est l'eau contenant des nutriments et de l'oxygène qui est injectée.

Le confinement est également une méthode appliquée aux LID mais cette technique est un moyen de contrôler la source et de limiter la propagation de la contamination. Il ne s'agit pas d'une méthode de décontamination. Cette méthode est inutilisable si l'aquifère ne possède pas de base imperméable.

Il existe aussi d'autres méthodes qui sont encore en développement (Fountain, 1998). Parmi celles-ci, se retrouvent, le barbotage et le lavage de sol. La technique de barbotage consiste à injecter un grand débit d'air dans la zone saturée d'un sol. Une partie des contaminants dissous se volatilise pour ensuite être captée par un puits d'extraction de vapeur pour être traitée. Certains endroits sont moins accessibles que d'autres (ex. contamination sous bâtiment) et lorsque cette situation se produit, l'injection de solutions de lavage est une méthode envisageable. La solution de lavage composée d'alcool et/ou de tensioactif est introduite dans le sol par un puits d'injection et récupérée en aval par un puits d'extraction. Cette technique favorise la récupération des solvants chlorés car elle solubilise et/ou mobilise la contamination sous forme résiduelle et libre facilitant ainsi son extraction. La méthode de lavage de sol est présentement appliquée seulement sur de petites surfaces car elle est encore trop coûteuse à grande échelle. Les principes de cette technique seront analysés plus en détail tout au long de ce mémoire.

1.2 Principes de l'écoulement multiphase immiscible

La compréhension des principes de l'écoulement multiphase immiscible est essentielle pour procéder à la surveillance, à l'échantillonnage, au contrôle de la contamination et à la restauration des sites contaminés par des liquides immiscibles. Dans cette section, il sera question de la répartition des fluides immiscibles dans les milieux poreux et de l'écoulement simultané des fluides immiscibles (Cohen et Mercer, 1993).

1.2.1 Hydrostatique

La tension interfaciale, la mouillabilité et la capillarité sont les facteurs qui contrôlent la distribution des liquides immiscibles dans les milieux poreux. La distribution à l'échelle des pores est influencée par la tension interfaciale qui existe entre deux fluides immiscibles. L'interface formée entre deux liquides résulte du déséquilibre des forces d'attraction entre les molécules différentes des deux fluides.

La mouillabilité est l'affinité des deux fluides immiscibles en présence d'un solide. Celle-ci dépend des propriétés chimiques des deux fluides, de la composition de la surface solide et des conditions de température et de pression. Lorsque deux fluides sont en contact avec un solide, il y a habituellement un fluide mouillant et un non mouillant. Le fluide mouillant est celui qui a le plus d'affinité avec le solide tandis que l'autre fluide est appelé non mouillant. Le fluide mouillant aura donc tendance à se distribuer à travers le solide et il se concentrera plus particulièrement dans les pores les plus fins et près des surfaces solides tandis que le fluide non mouillant est localisé au centre des pores. Les solvants organiques comme le TCE sont habituellement des fluides non mouillants tandis que l'eau est le fluide mouillant. Le TCE se distribue donc dans les grands pores tandis que l'eau englobe les solides et occupe les pores les plus petits. Lorsqu'un gaz est présent dans le milieu poreux, il se situera toujours au centre des pores parce que sa tension interfaciale par rapport aux surfaces solides est plus grande que celle de la majorité des liquides.

La différence de pression entre le fluide mouillant et non mouillant est appelée la pression capillaire (P_c). La relation entre la pression capillaire et la saturation en eau (S_w) permet de tracer la courbe de drainage et d'imbibition et de déterminer la saturation résiduelle en TCE (S_{rnw}). Ces relations sont présentées à la Figure 1.1. La courbe de drainage est obtenue en appliquant une pression à un fluide non mouillant (TCE) pour qu'il déplace le fluide mouillant (eau) qui sature l'échantillon ou une colonne de sable par exemple. La pression de déplacement (P_d) est la pression capillaire nécessaire à laquelle le fluide non mouillant peut commencer à déplacer le fluide mouillant. La pression capillaire de la courbe de drainage augmente jusqu'à atteindre un plateau qui correspond à la saturation irréductible ou la saturation en eau résiduelle (S_{rw}). L'eau est ensuite injectée dans la colonne déplaçant ainsi l'huile. Les valeurs de pression obtenues de ce déplacement permettent d'obtenir la courbe d'imbibition. La courbe d'imbibition ne rejoint pas le début de la courbe de drainage car une certaine quantité de TCE est demeurée dans le milieu poreux ce qui s'appelle la saturation résiduelle en TCE (S_{mw}). C'est cette méthode qui est appliquée lors des essais en colonne pour obtenir une saturation résiduelle en TCE.

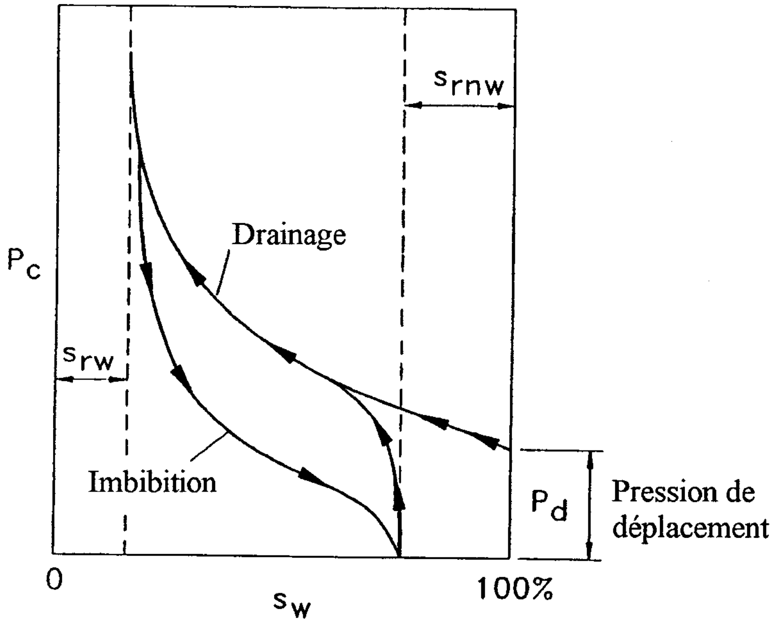

Figure 1.1 - Courbes de drainage et d'imbibition (adapté de Cohen et Mercer, 1993)

1.2.2 Hydrodynamique

La distribution de la saturation en eau et en liquide immiscible dense dans le sol dépend de la capillarité. S'il est en quantité suffisante, le LID s'infiltre en phase libre jusqu'à la base de l'aquifère. La saturation en LID diminue graduellement à la surface de cette phase libre et forme la frange capillaire. Au-dessus de cette frange capillaire se trouve la saturation résiduelle en LID qui correspond à la zone d'infiltration de celui-ci dans l'aquifère.

La capacité d'un milieu à transmettre un fluide en même temps qu'un autre fluide est la perméabilité relative (k_r). La Figure 1.2 présente la courbe de perméabilité relative à l'eau k_{rw} (fluide mouillant) et à l'huile k_{rnw} (fluide non mouillant) en fonction de la saturation en eau (S_w). La perméabilité relative à l'huile augmente avec la saturation en huile tandis que la perméabilité relative à l'eau augmente avec la saturation en eau. C'est-à-dire que plus il y a d'huile dans le sol, plus le milieu a la capacité de transmettre ce fluide. Toutefois, lorsque la saturation en huile diminue, la tortuosité de son cheminement augmente causant ainsi une diminution de la perméabilité relative à l'huile. Le même concept s'applique pour l'eau.

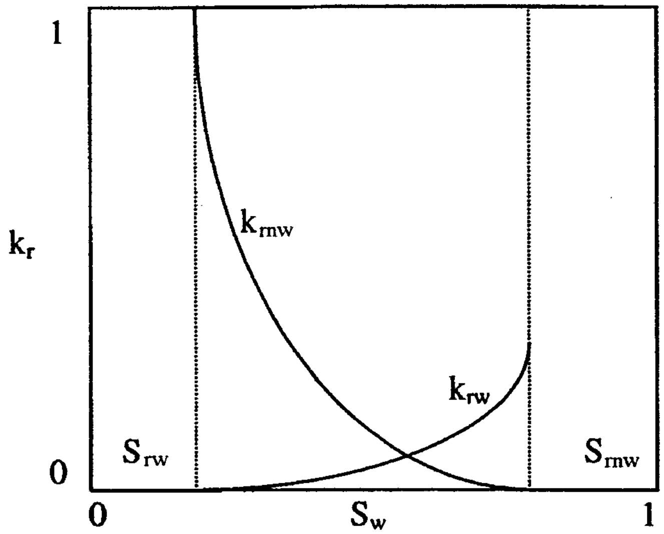

Figure 1.2 - Perméabilité relative de l'eau et de l'huile en fonction de la saturation en eau (adapté de Cohen et Mercer, 1993)

Le graphique montre aussi que la perméabilité relative à l'eau est inférieure à celle de l'huile. Ce fait est dû aux propriétés capillaires des milieux poreux. Lorsque deux fluides sont présents en même temps dans le sol, le fluide mouillant occupe les plus petits pores tandis que le fluide non mouillant occupe les grands pores. Le TCE occupant les pores les plus gros aura donc une perméabilité relative plus élevée.

Lorsque le TCE s'infiltre dans un sol, une certaine quantité de ce fluide se retrouve piégé dans les pores sous la forme résiduelle par différents phénomènes de piégeage et la remobilisation de ces globules est très complexe. L'enlèvement de cette saturation résiduelle est l'objectif de la méthode de lavage des sols. Il existe principalement deux mécanismes pour réduire la saturation résiduelle des liquides immiscibles. L'une des méthodes est de diminuer la tension interfaciale en utilisant des solutions tensioactives pour ainsi déplacer le TCE dans une phase distincte lors de l'écoulement. Ce dernier mécanisme déplace le fluide par mobilisation. Il est aussi possible de solubiliser le TCE pour mieux l'extraire. Il suffit de le transférer dans une autre phase mobile qui sera ensuite extraite. Ces mécanismes seront analysés plus en détail dans les chapitres suivants.

1.3 Objectifs

Le plus grand défi posé par la restauration des sites contaminés par les LID demeure la récupération de la phase résiduelle. Si cette contamination sous forme résiduelle est présente uniquement dans la zone non saturée, la décontamination pourra se faire par extraction de vapeur ou par bioventilation des sols et en traitant l'effluent gazeux généré. Toutefois, l'enlèvement de la contamination sous forme résiduelle dans la zone saturée pose un problème plus sérieux qui n'est pas résolu. L'objectif de ce projet de recherche est donc d'approfondir les connaissances entourant la technique de lavage de sol pour améliorer l'efficacité de récupération des liquides immiscibles denses en phase résiduelle dans les aquifères. C'est en développant des solutions de lavage et en analysant les différents mécanismes impliqués lors de la récupération du LID qu'il est possible d'atteindre cet objectif. Le TCE a été choisi comme LID modèle dans cette recherche. Les diagrammes de phases serviront à sélectionner les solutions de lavages et à prédire leur principal mécanisme de récupération du TCE. Les essais en colonne, quant à eux, serviront à classer les solutions selon leur efficacité et à vérifier les mécanismes de récupération du TCE associés à ces solutions. Cette recherche a aussi pour but de vérifier certaines observations émises par Falta (1998) concernant la concentration et la composition des solutions injectées dans des milieux poreux contaminés et leur position par rapport à la courbe de distribution critique dans les diagrammes de phases.

Des essais en laboratoire ont déjà été réalisés par Martel et al., (1993; 1996; 1997; 1998a; 1998b; 1998c) pour la récupération de diesel, d'huiles complexes et de BPC. Des essais à l'échelle pilote sur le terrain ont aussi été réalisés avec les solutions développées pour récupérer ces contaminants. Toutefois, pour augmenter l'efficacité de la technique de lavage des sols, il faut accroître les connaissances en matière de mécanismes de récupération pour appliquer cette technique de façon encore plus efficace.

1.4 Méthodologie

Les essais en laboratoire consistent à réaliser des diagrammes de phases ternaires et des essais en colonnes de sable. Les diagrammes servent à développer et sélectionner les solutions de lavage. Les courbes de miscibilité des alcools et des solutions micellaires (tensioactif dans l'eau) sont tracées à l'intérieur des diagrammes de phases ternaires. Certaines solutions sont alors sélectionnées à l'aide de la position des enveloppes de miscibilité à l'intérieur du diagramme. Cette technique de sélection des solutions de lavage a été développée par Martel et al. (1993) et Desnoyers et al. (1983). Les courbes de distribution des solutions retenues sont tracées pour prédire le mécanisme avec lequel le TCE sera extrait des sols (solubilisation ou mobilisation). Les essais en colonne, quant à eux, ont pour but d'étudier les mécanismes de récupération mais aussi d'évaluer l'efficacité de récupération des solutions injectées. Des stratégies d'injection sont ensuite proposées dans le but d'atteindre une récupération maximale du TCE en phase résiduelle dans les sols.

CHAPITRE 2

TCE RECOVERY MECHANISMS USING MICELLAR AND ALCOHOL SOLUTIONS: 1-DEVELOPMENT AND CHARACTERIZATION OF WASHING SOLUTIONS WITH PHASE DIAGRAMS

2.1 Abstract

Phase diagrams were used to develop washing solutions for the recovery of residual TCE in aquifer and to study their recovery mechanisms. More than 50 phase diagrams were drawn to select the most promising alcohol and micellar solutions to dissolve or mobilize TCE. Based on position of the miscibility curve, the best solutions for TCE recovery by dissolution or mobilization at same injection concentration located below the critical tie line are i-BuOH/SAS=2 > W2722/SAS=2 > EtOH/SAS=2 > n-PrOH > EtOH > i-BuOH. However, for solutions mobilizing TCE located above the critical tie line, it is not possible to rank them without sand column results. The main recovery mechanism of these selected solutions was analyzed based on their tie lines. Negative tie line slopes for EtOH, EtOH/SAS, i-BuOH/SAS and W2722/SAS solutions show a preferential partition into the aqueous phase and a tendency to dissolve TCE. Positive tie line slopes for n-PrOH and i-BuOH show preferential partition of alcohol solution in the organic phase and a tendency to mobilize TCE. Sand column experiments (Chapter 3) are necessary to evaluate the recovery efficiency of solutions and to confirm the recovery mechanisms predicted from tie line slopes.

2.2 Introduction

Chlorinated solvents are common constituents of dense non-aqueous phase liquids (DNAPL) often present in groundwater at contaminated industrial sites (Pankow and Cherry, 1996). Among this group, trichloroethene (TCE) is the most ubiquitous volatile organic compound (VOC) detected in groundwater (NRC, 1994). TCE has a low water solubility and tends to migrate vertically even through the saturated zone. This vertical migration tends to be rapid due to TCE's high density and low viscosity. Chlorinated solvents are also persistent in the environment because of their generally slow degradation rates (Cohen and Mercer, 1993).

The traditional pump and treat method is not efficient for the recovery of residual DNAPL. The generally low aqueous solubility and high interfacial tension of this contaminant reduces the efficiency of this method. The petroleum industry developed numerous techniques for the recovery of organic liquids from petroleum reservoirs. One technique involves the injection of an aqueous solution containing either surfactants (also called a micellar solution) and alcohols (Lake, 1989). Recently, similar chemical systems were adapted for aquifer remediation (Simpkin et al., 1999). Surfactant or alcohol solutions, or a combination of both, can be injected in porous media by wells or trenches to remove DNAPL. Surfactants and alcohols are used both to increase the total aqueous solubility of a NAPL and to decrease the NAPL-water interfacial tension. The contaminant is removed either by dissolution, mobilization or by both mechanisms. The effluents are then recovered in an extraction well.

This chapter presents the results of a laboratory study aiming to develop and characterize washing solutions for the extraction of TCE at residual saturation in soils. Phase diagrams are used to select the most promising washing solutions. The position of the miscibility curve of micellar and alcohol solutions in phase diagrams indicates their relative efficiency. Tie lines on phase diagrams further allow the prediction of the dominant recovery mechanism; dissolution or mobilization (Falta, 1998). Sand column experiments were also conducted with selected solutions to evaluate their recovery efficiency and to confirm the recovery mechanisms predicted by the tie lines in phase diagrams (Chapter 3).

TCE was used mostly in the dry cleaning and metal degreasing industry. Common causes of ground water contamination by TCE are accidental spills, intentional dumping, leaks in storage tanks, industrial waste pits and municipal or industrial landfills. Physical and chemical characteristics of TCE and water are presented in Table 2.1.

Table 2.1 - Properties of TCE and water at 20 °C (from Cohen and Mercer, 1993)

Properties	Trichloroethene	Water
Molecular weight (g/mol)	131.5	18.0
Density (kg/m³)	1464	1000
Absolute viscosity (mPa·s)	0.57	1.00
Water solubility (mg/L)	1100	-
Henry's constant (atm·m³/mol)	0.0091	-
Vapor pressure (kPa)	7.7	2.3
Drinking water standard (μg/L) [a]	5	-

[a] EPA, National Primary Drinking Water Regulations, revised 1998

2.3 Washing solutions used to extract NAPL from porous media

2.3.1 Alcohol solutions

Alcohol flooding is a promising method which could enhance the removal of residual DNAPL from aquifers. This technique is not commonly used commercially due to the relatively high cost of alcohols. Some alcohols that preferentially partition into the aqueous phase can reduce the interfacial tension between the DNAPL and the aqueous phase and remove the contaminant by dissolution. The DNAPL phase is partially reduced through dissolution as the alcohol concentration increases. In addition, others alcohols are expected to remove the contaminant mainly by mobilization because they preferentially partition into the DNAPL phase. These alcohols cause oil swelling and form an oil bank. The control of phase behavior on the process responsible for NAPL recovery by alcohols is discussed by Falta (1998).

Rao et al. (1997) and Falta et al. (1998) have done a field experiment in a confined test cell to evaluate the recovery of NAPL with alcohol flushing. Rao et al. (1997) used a cosolvent mixture (70% ethanol, 12% n-pentanol and 18% water) for the recovery of jet fuel and chlorinated solvent. After the injection of 9 pore volumes of the solution, almost 85% of the contaminant was removed. Falta et al. (1998) injected 4 pore volumes of a combination of 80% tert-butanol and 15% n-hexanol and removed nearly 90% of the most soluble contaminant (TCA, toluene, ethylbenzene, xylenes, trimethylbenzene, naphthalene) and 70% to 80% of the less soluble compounds such as decane and undecane.

Based on his previous column studies and batch equilibration results, Farley et al. (1993) tried to mix two alcohols in a quaternary system. Alcohol such as methanol was added to n-butanol which create a TCE-rich NAPL phase. This combination enhances the aqueous solubility of n-butanol which is not miscible with water and creates a single phase flooding mixture. The residual TCE recovery with upward flow of this solution in glass beads was approximately 85%.

Falta (1998) used phase diagrams to predict the performance of cosolvent flooding for TCE and PCE remediation. This researcher summarized most of the experiments done with alcohols (methanol, iso-propanol and tert-butanol) in soil or glass bead columns for the recovery of residual TCE and PCE. Every experiment with alcohol concentration above the critical tie line results in significant NAPL mobilization. The NAPL recovery after one pore volume varied from 76% to 100% in these cases. The experiments in which the injection concentration was below the critical tie line resulted in much lower NAPL recovery also after one pore volume. The recovery efficiency ranged from less than one to 40% and dissolution was the dominant NAPL removal mechanism. Since enhanced dissolution is slower than NAPL mobilization, the recovery rate is better with the mobilization recovery mechanism after one pore volume injection.

2.3.2 Surfactant solutions

Surfactants are chemical agents which alter the interfacial properties of solutions. Surfactant molecules have both a hydrophilic and a hydrophobic portion, and are generally classified as anionic, nonionic, cationic and amphoteric (Rosen, 1978). The hydrophile-lipophile balance (HLB) number characterizes the relative influence of the hydrophilic and hydrophobic portions of the surfactant molecule. When the surfactant concentration in aqueous solution reaches the critical micelle concentration, aggregations of surfactant monomers, called micelles, appear and NAPL is trapped inside the micelles as shown in Figure 2.1.

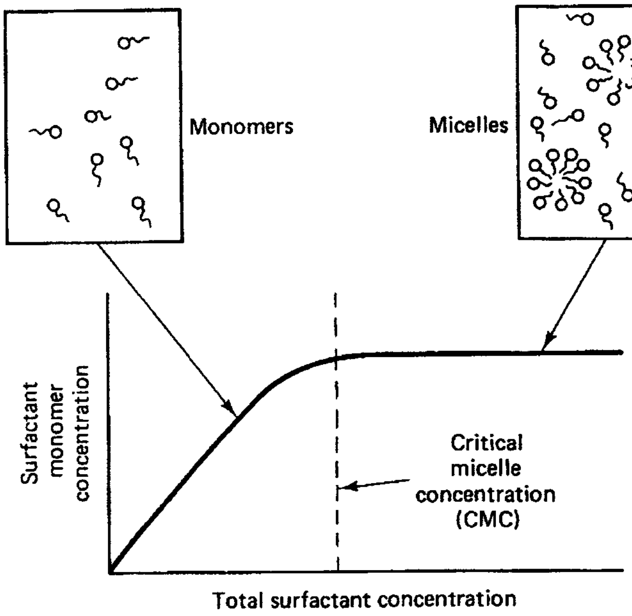

Figure 2.1 - Formation of micelles at the critical micelle concentration (from Lake, 1989).

Like alcohols, surfactants have the capacity to increase the apparent solubility of NAPL and reduce the interfacial tension between the aqueous and organic phases sufficiently to mobilize residual organic liquids. However, surfactants cannot be used at high concentrations due to their high viscosity. Numerous studies have been carried on surfactants. Larson and Hirasaki (1978) and Larson (1979) studied the fractional flow theory and the mobilization efficiency of oil with surfactant for petroleum industry applications. Recently, Abdul et al. (1990) studied ten surfactants to extract automatic transmission fluid from sandy material in batch-washing experiments. Based on their experiment results, three surfactants (Witconol 1206, SN70, SN90) showed good potential for the effective *in situ* washing of automatic transmission fluid. The possibility of using surfactant to enhance remediation of soil columns contaminated by PCE (tetrachloroethene) was studied by Pennel et al. (1994). A 4% solution of POE (20) sorbitan monooleate was injected in two sand columns. More than 90% of the residual contaminant was removed mainly by dissolution. In two other sand columns, the residual PCE was recovered mainly by mobilization with the injection of a solution containing mixtures of sodium sulfosuccinates. The contaminant recovery was over 99%. This study demonstrated that ultra-low interfacial tensions (<0.001 dyne/cm) are not required to achieve significant PCE mobilization when buoyancy forces are important.

Herrin et al. conducted batch studies with their most successful surfactant mixtures (Monawet MM-80/NaCl and Witconol H-31A/NaCl) based on a screening study with soils saturated with DNAPL (mainly TCE) collected from their site. Their results showed that the Monawet/NaCl solution was the most efficient for TCE dissolution. The results of a field test done by Fountain et al. (1996) have demonstrated that surfactant flooding is an effective way to rapidly remove PCE from an aquifer. A mixture of Rexophos 25/97 and Alkasurf NP10 was used in the test cell.

Laboratory batch and column studies conducted by Sabatini et al. (1997) demonstrated that Dowfax 8390 was capable of significantly enhancing NAPL elution while experiencing minimal losses. Thus, a field demonstration study was conducted with the same surfactant. Of the total PCE mass removed from a shallow unconfined aquifer, over 80% is attributable to enhanced dissolution by Dowfax 8390 in the treated zone around the vertical circulation well used.

Peters et al. (1997) demonstrated the efficiency of combining two complementary technologies, surfactant foams and bioaugmentation, to remediate TCE in sand columns. The injection of foam (Steol CS-330) resulted in 90% to 95% mobilization and after the addition of specialized degradative micro-organisms approximately 1% of TCE was left in the sand columns.

2.3.3 Extraction with alcohol/surfactant solutions

When used in combination with chemical surfactant, alcohol allows an increase in surfactant concentration in water without increasing the solution viscosity. This combination also decreases the sorption of surfactant on aquifer solids (Martel et al., 1998a). Furthermore, adding surfactant to an alcohol solution increases the solution's density and avoids the overriding of the solution in the soil. Finally, the recovery efficiency can be increased using an alcohol and a surfactant combination instead of using them separately at equivalent concentration.

Brown et al. (1996) choose Aerosol MA-801 (sodium dihexyl sulfosuccinate) from screening studies of many systems for a field test. A mixture of 7.55 % aerosol MA-801, 3.75 % iso-propanol and 7000 mg/L NaCl was used to remove nearly 99% of a residual mixture of TCE, PCE and TCA.

Martel et al. (1993) made phase diagrams to select micellar solutions able to efficiently recover residual DNAPL in an aquifer. For such a complex DNAPL, the alcohol and surfactant combination is more efficient than the use of alcohol or surfactant separately. The optimal surfactant solutions were n-amyl alcohol/Genapol LRO, n-butanol/Hostapur SAS and n-butanol/PHENYL and the systems tested were especially efficient to dissolve chlorinated solvents (TCE and PCE) and light oils (gasoline and diesel oil). Martel and Gélinas (1996) also carried more than 50 sand column experiments to study the dissolution of diesel. The washing solution n-amyl alcohol:n-butanol/Hostapur SAS was found to be efficient for that purpose. The influence of concentration, temperature, flow direction, velocity, salinity and sand characteristics were some of the factors studied in more than 90 sand columns experiments contaminated with complex DNAPL (Martel et al., 1998a). The same contaminant was also used in a large sand column to illustrate the recovery mechanisms with a solution of n-butanol, Hostapur SAS, D-limonene and toluene. Mobilization (oil swelling) and dissolution were observed and more than 89% of the initial residual DNAPL saturation was recovered with the injection of 0.8 pore volume of washing solution (Martel et al., 1998b). A quite similar solution was injected in a field test (Martel et al., 1998c) and 86% of residual DNAPL was recovered using only 0.9 pore volume of a surfactant solution. Recently, Martel et al. (1997) and Foy (1999) have shown that up to 99% of an initial Aroclor 1248 concentration can be recovered by dissolution after the injection of less than 8 pore volumes of alcohol/surfactant solution in soil columns.

Polymer solutions can be used for mobility control during *in situ* NAPL recovery (Martel et al., 1998b and 1998c). Martel, K.E., et al. (1998) have shown that among several polymers, xanthan gum is the most suitable for aquifer remediation. The polymer solutions are injected following a surfactant solution slug to act as a mobility buffer. Laboratory tests in sand box have shown that the xanthan gum solution increases surfactant solution's sweep efficiency and limits viscous fingering. A field test has also shown these effects (Hébert, 1998).

TCE recovery with an alcohol solution is well documented but its behavior in the presence of a micellar solution is almost unknown. This study will increase the understanding on the DNAPL behavior in presence of different concentrations of alcohol and micellar solutions. To facilitate the understanding of recovery mechanisms of DNAPL by the washing solution technique, a single component product (TCE) was used rather than a mixture of many components. Washing solution formulations will be proposed for sand column tests and TCE recovery mechanisms of these solutions will be studied.

2.4 Methods

2.4.1 Hypothesis

Some basic assumptions were made in this project before the construction of phase diagrams. The selection of the washing solutions was based on the premise that the lower the miscibility curve in phase diagrams, the better is the recovery (Martel and Gélinas, 1996). Also, the efficiency of the recovery can be increased using a combination of an alcohol and a surfactant instead of using them separately (Martel et al., 1993). Furthermore, the washing solution optimization and selection process using phase diagrams is considering variables such as the type of alcohol or surfactant and their ratio in the solution as independent.

Studies were done mainly to develop solutions which would dissolve TCE in soil. This is required in many cases where the contaminated zone is not underlain by an impermeable material. In such a case, TCE mobilization is not suitable because its high density would lead to its vertical migration into uncontaminated portions of the aquifer. Mobilization must be used only when an impermeable layer is underlying the contaminated zone. Even in such a case, it may be difficult to control the migration of the mobilized TCE bank. Dissolution may thus be considered a more generally applicable recovery mechanism.

2.4.2 Phase diagrams

Phase diagrams are required to evaluate the mechanisms involved in TCE recovery. At first, the miscibility curve must be drawn in a ternary diagram (Figure 2.2). This diagram is composed of 3 end-points representing water, TCE and active matter (a.m.) which includes alcohol, surfactant or both. Only the lower left part of the diagram is useful for the prediction of TCE recovery in aquifers. This section depicts the water-rich phase representative of *in situ* conditions where TCE is present at residual saturation. The miscibility curve separates two regions in phase diagrams: the region within which components are miscible is located above the miscibility curve whereas below the curve the components are not miscible and form two separate phases. Tie lines and plait points will be discussed later.

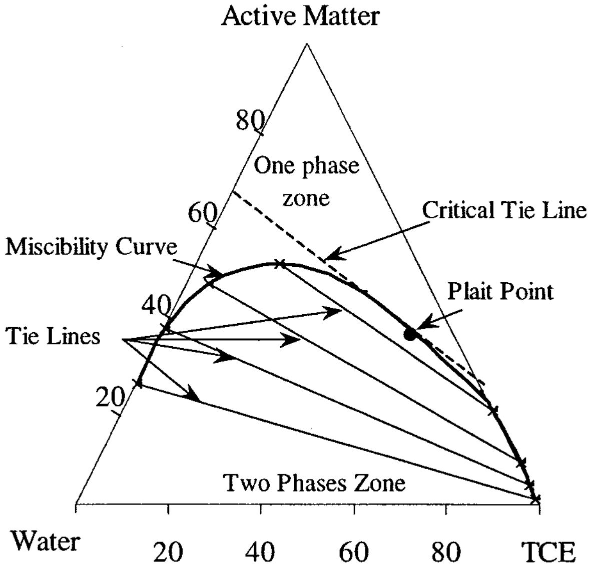

Figure 2.2 - Ternary phase diagram.

The data points required to draw a miscibility curve are obtained by the titration of TCE, active matter and water at 8 °C (ground water temperature in Quebec) (Figure 2.3). The presence of single or multiple phases is detected by the transparent or cloudy appearance of liquids (Martel et al., 1993). This way of constructing phase diagrams is very fast and inexpensive because it does not require chemical analysis of phases. The appearance of a cloud point is the boundary between the microemulsion zone (single phase) and the multiple phases zone and represents the miscibility curve. To obtain the first data point (point A) of the curve, TCE is added gradually to the diluted solution with a syringe in a 40 ml glass test tube capped with a Teflon minivalve. This turning point can be observed directly but sometimes its appearance is gradual and this influences the precision of the curve thus defined. During the experiment, the solution is agitated with a Teflon coated magnetic stirrer. Each time a component is added to the test tube, its weight is noted. The proportion (by weight) of each component in the test tube is calculated. After the determination of the first point, adding washing solution moves the mixture out of the cloudy zone to reach a clear zone (point B). The second point (point C) is obtained by adding water to reach again a cloudy zone. Around 5 to 9 points are necessary to draw a miscibility curve.

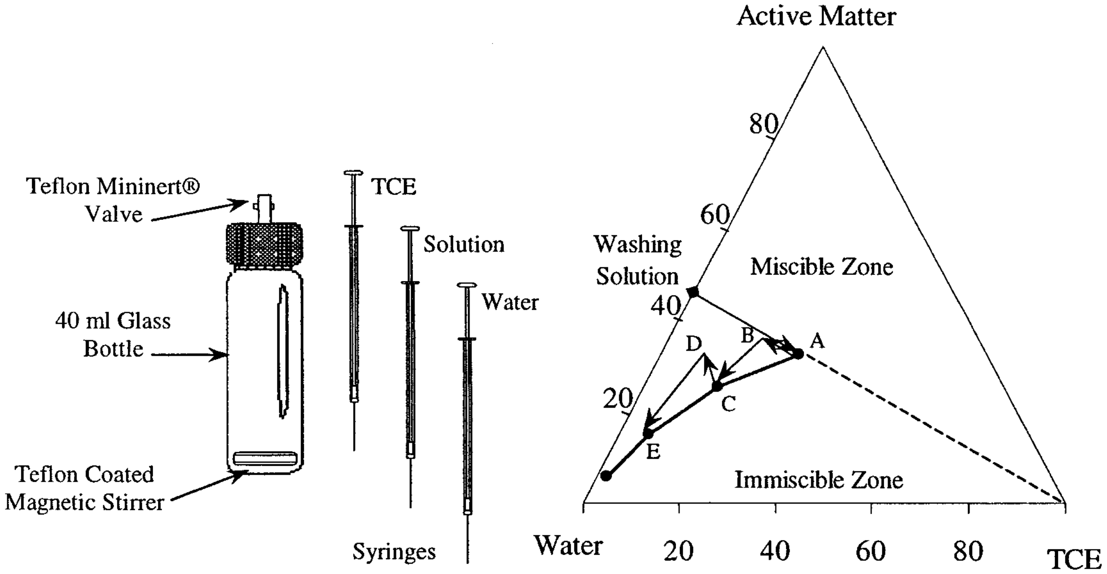

Figure 2.3 - Miscibility curve from the titration method.

Characteristics of alcohols and surfactants studied in phase diagrams are presented in Tables 2.2 and 2.3. The choice of alcohols and surfactants was based on previous works done in aquifer washing studies. Other alcohols and surfactants were added to the list because of their potential efficiency for TCE recovery. For each solution, a miscibility curve with TCE was drawn. Some alcohol and micellar solutions were then selected to proceed with further experiments on TCE extraction in soil.

Table 2.2 - Characteristics of alcohols

Trade name	Abbrev.	Molecular structure	Density 20°C [a] (kg/m³)	Viscosity 20°C [a] (mPa·s)	Aqueous [a] solubility 20°C (mg/L)	LD_{50} [a] oral rat (mg/kg)	Reference
ethanol	EtOH	CH_3CH_2OH	790	1.20	Miscible	7060	Rao et al. (1997)
n-propanol	n-PrOH	$CH_3CH_2CH_2OH$	804	2.2	Miscible	1870	
iso-propanol	i-PrOH	$(CH_3)_2CHOH$	785	2.27	Miscible	5045	Falta (1998)
n-butanol	n-BuOH	$CH_3CH_2CH_2CH_2OH$	810	2.94	77000	790	Farley et al. (1993), Martel et al. (1993, 1996, 1998 a, b, c)
iso-butanol	i-BuOH	$(CH_3)_2CHCH_2OH$	802	4.0	95000	2460	
sec-butanol	s-BuOH	$CH_3CH_2CH(OH)CH_3$	808	4.2	125000	6480	
tert-butanol	t-BuOH	$(CH_3)_2C(OH)CH_3$	786	3.35	Miscible	3500	Falta et al. (1998), Falta (1998)
n-amyl alcohol (n-pentanol)	n-AmOH	$CH_3CH_2CH_2CH_2CH_2OH$	800	4.0	27000 [c]	2200	Rao et al. (1997), Martel et al. (1993, 1996)
iso-amyl alcohol	i-AmOH	$(CH_3)_2CHCH_2CH_2OH$	800	4.3	20000 [d]	1300	
sec-amyl alcohol	s-AmOH	$CH_3CH_2CH_2CH(OH)CH_3$	810	-	166000	-	
tert-amyl alcohol	t-AmOH	$(CH_3)_2C(OH)CH_2\text{-}CH_3$	805	3.7 [b]	120000	1000	

LD_{50} : lethal dose to 50% of the organisms tested

[a] MSDS databases

[b] at 25 °C, [c] at 22 °C, [d] at 14 °C

Table 2.3 - Characteristics of surfactants

Trade name	Abbrev.	Chemical name	Supplier	Reference
Anionic surfactants				
Aérosol OT	AOT	Sodium dioctyl sulfosuccinate	Cytec	Pennel et al. (1994)
Aérosol AY	AAY	Sodium diamyl sulfosuccinate	Cytec	Pennel et al. (1994)
Genapol ZRO	ZRO	Alkyl ether sulfonate sodium salt	Clariant	
Genapol LRO	LRO	Alcoxy-diglycolsulfate sodium	Clariant	Martel et al. (1993)
Hostapur OS	OS	Alpha-olefinesulfonate-sodium salt	Clariant	
Steol CS-330	Steol	Sodium laureth sulfate	Stepan	Peters et al. (1997)
Hostapur SAS 60	SAS	Secondary alkanesulfonate	Clariant	Martel et al. (1993, 1996, 1998a,b,c)
Dowfax 3B2-D	3B2	Decyl benzenesulfonic	Dow Chemicals	
Dowfax 8390-D	8390	Hexadecyl diphenyl oxide disulfonate	Dow Chemicals	Sabatini et al. (1997)
Hostapal BV	BV	Alkylaryle sulfate polyglycolique	Clariant	
Nansa HS85	HS85	Linear dodecylbenzene sulfonate	Albright & Wilson	
Nonionic surfactants				
Hoes 4004	Hoes	Fettalcoholpolyglycolether	Clariant	
Witconol 2722	W2722	Polysorbate 80	Witco	Pennel et al. (1994)
Arkopal N-090	Arko-90	Ethoxylate nonylphenol	Clariant	
Surfonic PE-2597	Surfonic	Phosphated polyglycol ether	Huntsman	Fountain et al., (1996) , Herrin et al.
Cationic surfactants				
Genaminox LA	LA	Lauryl dimethylamine oxyde	Clariant	
Genaminox MYX	MYX	Alkyl dimethylamine oxyde	Clariant	

2.4.3 Tie lines and plait point determination

Once the miscibility curve is drawn, the recovery mechanism of some solutions was predicted from the slopes of tie lines on the phase diagram. Below the miscibility curve, the aqueous and NAPL phase compositions at equilibrium are determined by the tie lines. The tie line endpoints lie on the miscibility curve and its slope defines the equilibrium partitioning of the washing solution between the aqueous (left side) and NAPL (right side) phases. Contrary to the miscibility curve, tie lines can only be determined from laboratory analysis of TCE and alcohol with a gas chromatograph. The determination of tie lines for i-BuOH/SAS and W2722/SAS solutions requires, in addition, laboratory analysis of the water content and SAS concentration (only for W2722/SAS). The water content was determined by titration with a Karl Fisher apparatus and the concentration of surfactant was obtained by a titration method with NaOH (Zhen Cao, 1978). The mixing of pure water with TCE and different quantities of active matter in proportions falling under the miscibility curve generates two liquid phases after equilibration. The analysis of components which have partitioned between these two phases allows the construction of tie lines. Data used to draw tie lines are presented in Appendix C.

Tie lines in Figure 2.2 have a negative slope (Winsor Type II-) which indicates that the active matter (surfactant or alcohol) in the washing solution preferentially partitions into the aqueous rather than the NAPL phase. Such a solution preferentially dissolves TCE (Lake, 1989). On the contrary, a positive slope (Winsor Type II+) implies that active matter within a washing solution preferentially partitions into the NAPL phase thus leading to swelling and displacement of TCE (Winsor, 1954). Each tie line also represents a line of constant interfacial tension (IFT) which decreases continuously from the TCE/water axis to the plait point. At the plait point, the two phases become miscible and merge into a single phase and the IFT reaches zero.

The TCE recovery mechanisms in soil columns are influenced by the injection concentration of active matter in the washing solutions. The tie line slopes can predict only the recovery mechanism when the solution injection concentration is below the critical tie line extension (Falta, 1998). If a solution is injected in soil with a concentration above the critical tie line extension, it will generally mobilize TCE independently of the orientation of tie line slopes.

The position of the critical tie line and the plait point can be determined by a graphical method described by Novosad and Sayegh (1983). The variation in solution composition is plotted against the slope of the tie line. This graph allows the extrapolation of the critical tie line slope. A line with this slope is then drawn and adjusted to be tangent to the miscibility curve to find the location of the plait point. The critical tie line and plait point were determined for three solutions (Appendix B).

2.5 Results and discussion

2.5.1 Selection of washing solutions

Through the literature review and laboratory experiments, washing solutions that dissolve or mobilize TCE with a good efficiency were found. The position of the miscibility curves of 6 selected alcohols were determined in a ternary phase diagram (Figure 2.4). The solutions with the lower miscibility curves in the water rich zone (EtOH and n-PrOH) were chosen for further tests. The alcohol with the lowest miscibility curve (i-PrOH) was not chosen because other researchers have already often studied it. The alcohol i-BuOH was selected to compare the behavior of a solution having a miscibility curve located higher in the phase diagram. The selected alcohol was combined with surfactants to increase the efficiency of the washing solutions.

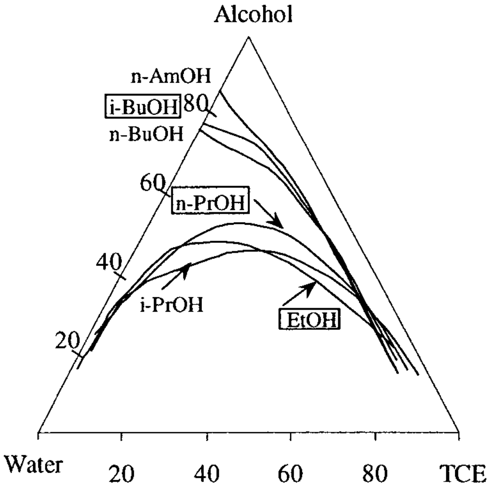

Figure 2.4 - Phase diagram with miscibility curves for alcohols. Selected alcohols are framed.

As mentioned, the washing solutions selection method developed by Martel et al. (1993) and Desnoyers et al. (1983) was used. According to the hypothesis that : 1) the lower the miscibility curve is in the phase diagram, the better is the solution to dissolve TCE and 2) variables such as alcohol types, surfactant types and alcohol/surfactant ratio are independent; approximately 50 phase diagrams were drawn to test 11 alcohols, 11 anionic, 5 nonionic and 2 cationic surfactants. At first, a n-BuOH/SAS solutions with different ratios were used in phase diagrams to select the best alcohol/surfactant ratio (Figure 2.5a). The ratios 2 and 2.5 were selected because they lead to miscibility curves located lower in the diagram. Second, at a fixed ratio of 2.5 the alcohol n-BuOH and i-BuOH were selected (Figures 2.5b and 2.5c) among other alcohols based on the position of their miscibility curve in the diagrams. Third, surfactant types were evaluated with i-BuOH at a fixed ratio of 2.5. The initial SAS selection was correct because this solution is clearly more efficient in phase diagram (Figures 2.6a and 2.6b). Other tests were made with a ratio of 2 and the alcohol/surfactant solution i-BuOH/SAS=2 was chosen. The EtOH/SAS=2 solution was also selected to compare the efficiency of a miscibility curve located higher in the phase diagram (Figure 2.6c).

Finally, SAS was combined with a ratio of 2 with nonionic surfactants. The lowest curve from these combinations was W2722/SAS=2 (Figure 2.6d). Cationic surfactants (LA and

MYX) were used in combination with an alcohol (i-BuOH) but their miscibility curves were too high compared to other selected solutions. Moreover, these surfactants created a gel zone which makes them unusable for soil washing technology. This type of surfactant was studied because it is potentially suited for soil washing with positively charged minerals such as carbonates (Martel et al., 1993). Data used to plot the miscibility curves in phase diagrams are presented in Appendix A.

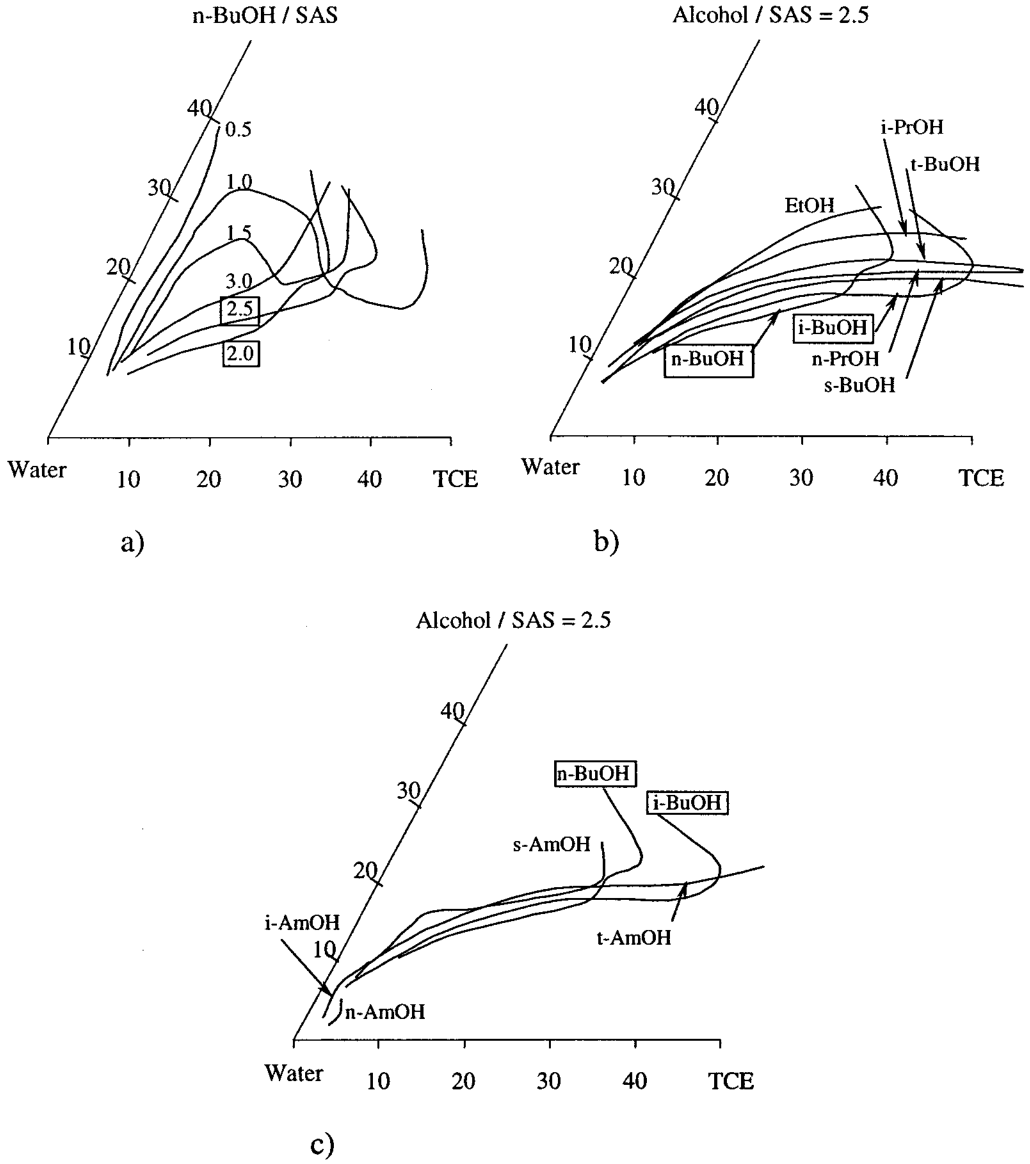

Figure 2.5 - Phase diagrams with miscibility curves for different a) alcohol/surfactant ratios b) and c) alcohol types. Selected ratios and alcohols are framed.

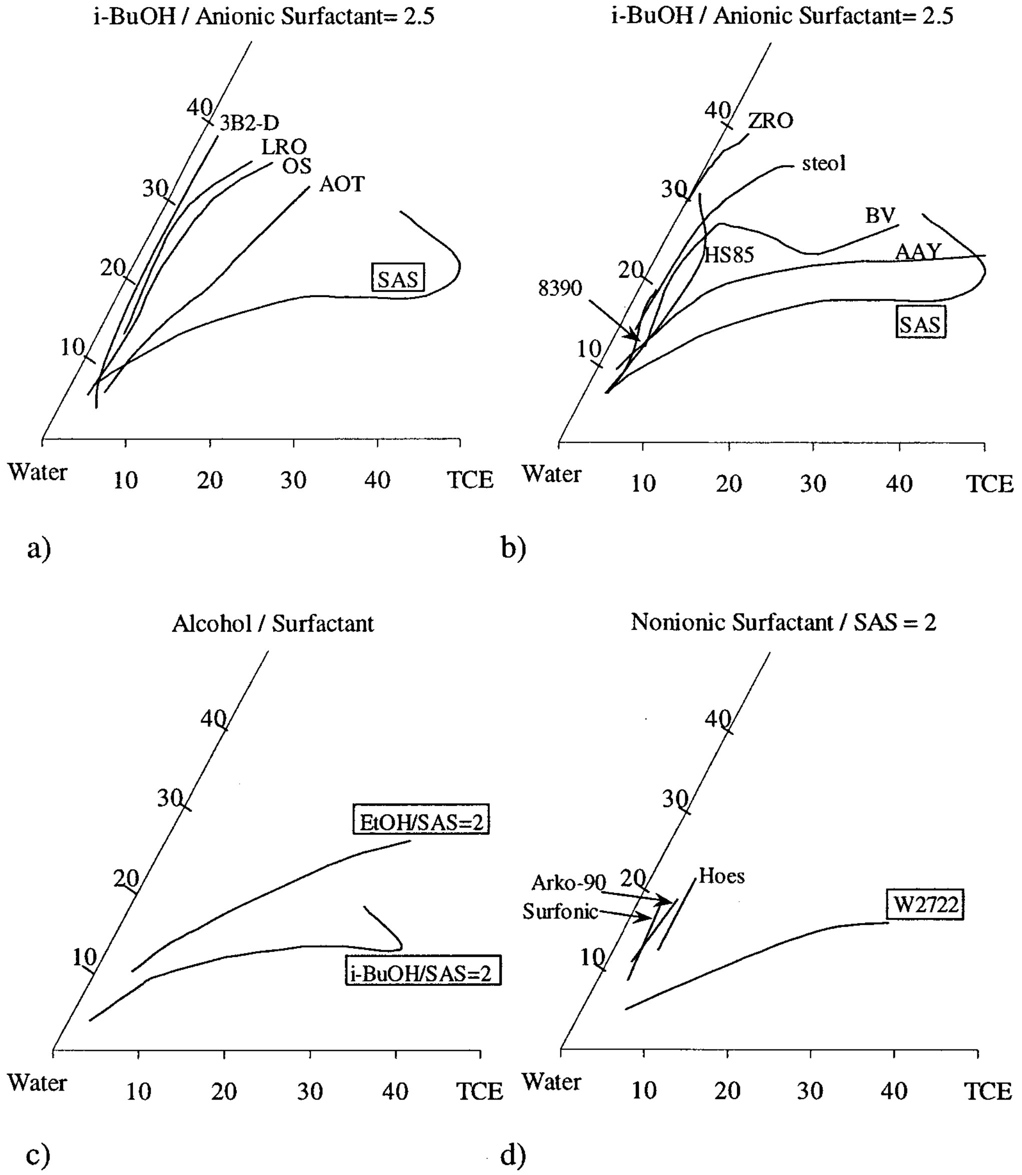

Figure 2.6 - Phase diagrams with miscibility curves for different a) and b) anionic surfactant types c) a fixed ratio of 2 and d) nonionic surfactant types. Selected surfactants are framed.

2.5.2 Prediction of the dominant recovery mechanism through tie lines

The recovery mechanisms of the chosen micellar and alcohol solutions (EtOH, n-PrOH, i-BuOH, EtOH/SAS, i-BuOH/SAS and W2722/SAS) were predicted based on their tie lines. Tie lines determined by chemical analysis for alcohols are shown in Figures 2.7 and 2.8. The dotted line in these phase diagrams represents the miscibility curve determined with the titration method using the cloud point. The plain line represents the miscibility curve from chemical analysis. The implication of the miscibility zone (F.C.M., M.C.M. and I) is explained in Chapter 3. Figures 2.7 and 2.8 show that the miscibility curve obtained with the rapid titration method is consistent with the miscibility curve obtained with laboratory analysis. The slope of tie lines reflects the equilibrium partition of active matter between the aqueous and organic phases. Based on its negative slope, ethanol would dissolve TCE whereas n-PrOH and i-BuOH with a positive slope would tend to mobilize TCE. These results were foreseeable because alcohols with a low molecular weight (EtOH) are soluble in water and tend to dissolve TCE. However, alcohols with a high molecular weight (n-PrOH and i-BuOH) are less soluble in water and tend to transfer into TCE.

Bottles shown in Figure 2.7 a) and b) present that process. Each numbered bottle corresponds to its tie line and each end-point corresponds to its phase in the bottles (aqueous and organic phases). It can be observed in Figure 2.7 a) that, for negative tie line where the alcohol tends to transfer in the aqueous phase, this latest phase volume in the bottles is increased. In Figure 2.7 b), the opposite phenomenon is observed and the organic phase volume is increased.

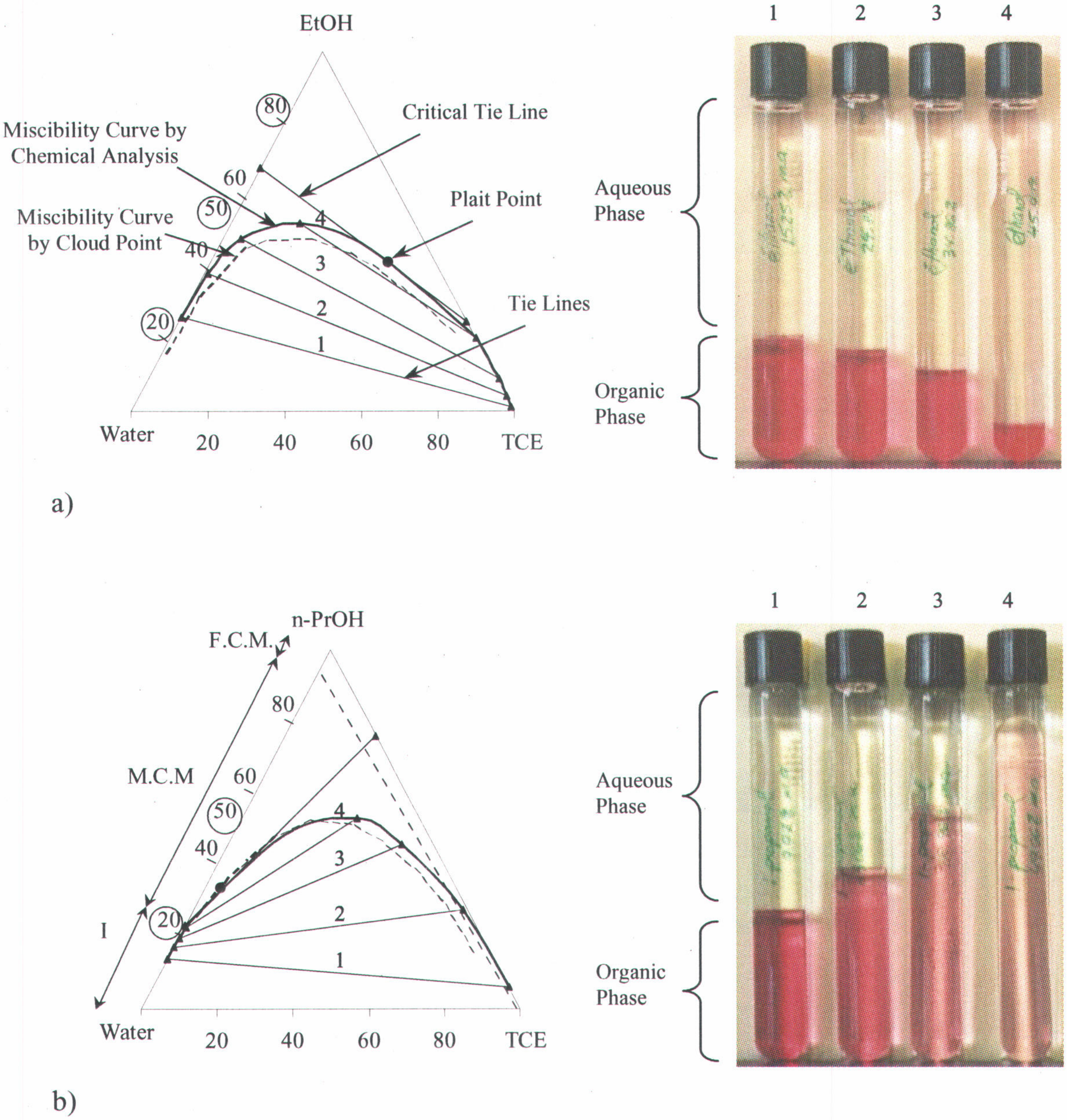

Figure 2.7 - Miscibility curves and tie lines for a) EtOH, b) n-PrOH solutions. The dotted curves were obtained from the cloud point technique whereas the plain line is based on chemical analysis. The abbreviations F.C.M, M.C.M and I mean respectively: First Contact Miscibility zone, Multiple Contact Miscibility zone and Immiscible zone. Circled numbers are the concentrations of solutions injected in sand column experiments (Chapter 3).

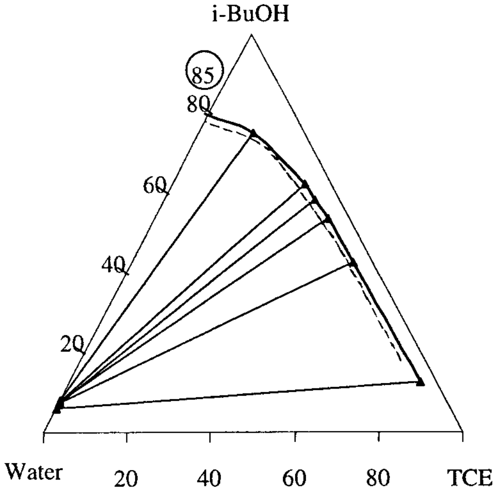

Figure 2.8 - Miscibility curves and tie lines for i-BuOH solutions. The dotted curves were obtained from the cloud point technique whereas the plain line is based on chemical analysis. Circled numbers are the concentrations of solutions injected in sand column experiments (Chapter 3).

The drawing of tie lines for solutions which are a combination of two components (EtOH/SAS, i-BuOH/SAS and W2722/SAS) needs some modifications of the phase diagrams because only one component can be represented on each end-point. Some experiments done in the laboratory have shown that SAS transfers preferentially in the aqueous phase and not in the NAPL phase. This surfactant is thus combined with water at its end-point in the phase diagram.

Tie lines for solutions EtOH/SAS and i-BuOH/SAS are negative, which mean that these solutions would dissolve TCE if concentrations selected are below the critical tie line (Figure 2.9). The tie lines of the solution W2722/SAS were not presented because an analytical method for the W2722 was not available. However, it is possible to determine approximately the tie lines position using the water, SAS and TCE concentrations in aqueous and organic phases. Using this technique, a negative slope can be observed. The solutions i-BuOH/SAS and W2722/SAS were selected for their low miscibility curve position in phase diagram and their potential to dissolve TCE.

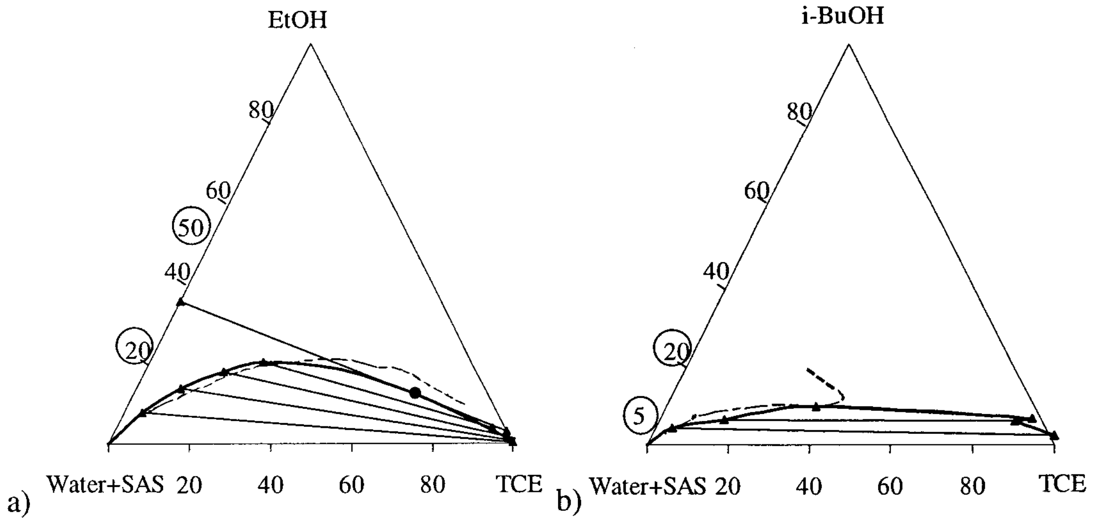

Figure 2.9 - Miscibility curve and tie lines for a) EtOH/SAS and b) i-BuOH/SAS solutions. The dotted curves were obtained from the cloud point technique whereas the plain line is based on chemical analysis. Circled numbers are the concentrations of solutions injected in sand column experiments (Chapter 3).

Solutions selected for soil column experiments are presented in Table 2.4. The concentrations of solutions injected in soil columns, the position of the concentrations relative to the critical tie line and the recovery mechanisms predicted for these experiments are also presented in this Table. The results of sand column washing tests with these solutions are presented in Chapter 3.

Table 2.4 – Selected solutions and their injection concentrations for sand column tests.

Selected solution	Slope of tie lines	Selected concentration for soil column (% active matter)	Position relative to critical tie line	Anticipated recovery mechanism
EtOH	-	20	Below	Dissolution
		50	Below	Dissolution
		80	Above	Mobilization
n-PrOH	+/-	20	Below	Mobilization
		50	Above	Mobilization
i-BuOH	+	85	-	Mobilization
EtOH/SAS=2	-	20	Below	Dissolution
		50	Above	Mobilization
i-BuOH/SAS=2	-	5	Below	Dissolution
		20	Above	Mobilization
W2722/SAS=2	-	20	Below	Dissolution

2.6 Conclusion

This research shows that solutions can be selected rapidly by a titration method using the cloud point technique which defines the miscibility curve in the water-rich zone. This method does not require laboratory analysis. The solutions were selected based on the high or low position of the miscibility curve in the phase diagrams. The lowest positions in the diagram correspond to the best solutions. However, to predict the behavior of these solutions in phase diagrams, tie lines must be drawn with the help of chemical analysis. Also, the critical tie line is necessary to predict the TCE recovery mechanism according to the solution injection concentration selected compared to the position of this tie line.

More than 50 phase diagrams were drawn to select the most promising alcohol and micellar solutions to dissolve or mobilize TCE. Based on position of the miscibility curve, the best solutions for TCE recovery by dissolution or mobilization at same injection concentration located below the critical tie line are i-BuOH/SAS=2 > W2722/SAS=2 > EtOH/SAS=2 > n-PrOH > EtOH > i-BuOH. However, for solutions mobilizing TCE located above the critical tie line, it is not possible to rank them without sand column tests.

The main recovery mechanism of these solutions was analyzed based on their tie line slopes. Negative tie line slopes for EtOH, EtOH/SAS, i-BuOH/SAS and W2722/SAS solutions show a preferential partition into the aqueous phase and a tendency to dissolve TCE. Positive tie line slopes for n-PrOH and i-BuOH show preferential partition of alcohol solution in the organic phase and a tendency to mobilize TCE. Sand column experiments (Chapter 3) are necessary to evaluate the recovery efficiency of solutions and to confirm the recovery mechanisms predicted from tie line slopes. Solutions are thus selected for sand column tests and their injection concentrations are located above and below the critical tie line to study the recovery mechanisms associated to these positions.

2.7 Acknowledgments

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CHAPITRE 3

TCE RECOVERY MECHANISMS USING MICELLAR AND ALCOHOL SOLUTIONS: 2-EVALUATION OF RECOVERY EFFICIENCY WITH SAND COLUMN EXPERIMENTS

3.1 Abstract

Sand column experiments were conducted to evaluate the efficiency of three types of washing solutions, to identify the recovery mechanisms involved and to classify the solutions according to their efficiency to recover TCE at residual saturation. This study demonstrates that: (1) an alcohol and a surfactant combination is more efficient than an alcohol used alone in water; (2) the prediction of the dominant recovery mechanism from the tie line slopes in phase diagram is accurate and can be reproduced in sand column experiments; (3) TCE recovery in sand column experiments is generally well represented by the position of the miscibility curve in phase diagrams. However, the miscibility curve cannot be used to predict exactly the TCE recovery. Thus, the use of miscibility curves and tie lines in phase diagrams are useful to select washing solutions and predict the dominant recovery mechanism associated to their injection concentration in sand columns.

The sand column experiments identify the recovery efficiency of each solution and their recovery mechanisms. The solutions i-BuOH/SAS=2 (20% a.m.), W2722/SAS=2 (20% a.m.), EtOH (50% a.m.) and EtOH/SAS=2 (50% a.m.) have a field application potential

and have a low relative cost. The solutions W2722/SAS=2 (20% a.m.) and EtOH/SAS=2 (50% a.m.) with a total TCE recovery of 95.8% and 99.8% respectively after the injection of 4 pore volumes of solution could be combined with an *in situ* bioremediation technique to potentially reach the drinking water standard of TCE in an aquifer. However, other factors such as sweep efficiency or density contrast must be controlled to reach this goal. Contrary to W2722/SAS=2 (20% a.m.) solution, EtOH/SAS=2 (50% a.m.) solution requires an underlying aquitard because it partly mobilizes TCE. Solutions i-BuOH/SAS=2 (20% a.m.), n-PrOH (50% a.m.), EtOH (80% a.m.) and i-BuOH (85% a.m.) are mobilizing solutions that create a mobilized TCE bank. These solutions can be followed by a dissolution solution to extract the TCE in soil after the mobilized bank has been recovered. However, the i-BuOH/SAS=2 (20% a.m.) solution is the best choice for mobilization because this solution is efficient, not too expensive, nor too concentrated. The EtOH (50% a.m.) solution can have a field potential if more pore volumes are injected. However, this solution can partly mobilize TCE.

3.2 Introduction

Many *in situ* aquifer remediation methods cannot be applied to DNAPL contaminated sites. Traditional pump and treat methods are not efficient when faced with DNAPL contamination. Also, excavation of contaminated soils is not suitable in cases where contaminants extend to great depths or are located under buildings. Several approaches originally developed in the petroleum industry such as enhanced oil recovery methods are currently being adapted for the remediation of NAPL-contaminated sites. These techniques include alcohol flooding, surfactant flooding, alcohol/surfactant flooding and polymer flooding.

The previous chapter allowed the selection of alcohol and micellar solutions from the position of the miscibility curve in phase diagram. Based on the position of the miscibility curve, many combinations of alcohol and surfactant were prepared to finally choose the washing solutions which dissolve TCE efficiently. Finally, the dominant recovery mechanism of selected solutions was predicted from the slope of tie lines in phase diagrams.

The objective of our experiments was to evaluate the efficiency of three types of washing solutions injected through sand columns contaminated by residual TCE: alcohol, alcohol/ anionic surfactant and nonionic surfactant/anionic surfactant. The liquid effluents recovered from these column experiments allow the identification of the TCE recovery mechanisms involved and the classification of the solutions according to their recovery potential. These results allow the validation of the recovery mechanisms predicted from the tie line slopes and the injection concentration used in relation to the critical tie line of the phase diagrams (Chapter 2). Other sand column experiments have been carried to evaluate the washing solutions efficiency with NAPL mixtures (Martel et al., 1996; Martel et al., 1998a; Martel et al., 1998b). However, only a few experiments were carried out on a single DNAPL component to understand its behavior when recovered in sand column with different types of washing solutions. TCE was an ideal component to study because it is ubiquitous in contaminated sites and more research is required to efficiently apply soil washing technologies to recover it from contaminated aquifers.

3.3 Methods

3.3.1 Selected solutions

Chapter 2 documented the miscibility curves in phase diagrams which were drawn to select the most efficient alcohol and micellar solutions for the recovery of residual TCE in soils. The miscibility curves of the selected washing solutions are reproduced in Fig. 3.1. Iso-butanol also is among the alcohols selected previously but its miscibility curve does not appear in this diagram because it is out of scale.

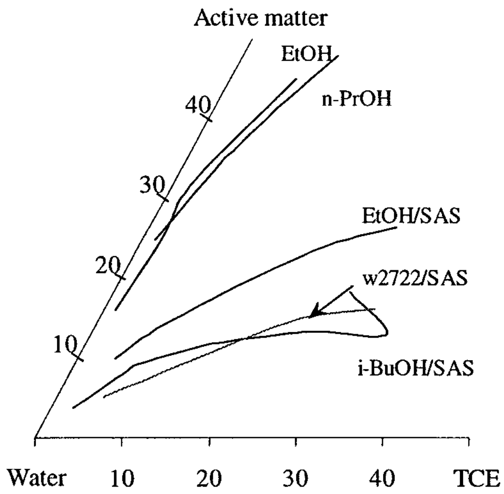


Figure 3.1 - Miscibility curves of selected solutions.

The TCE recovery mechanisms, either dissolution or mobilization, of these solutions were also predicted based on their tie lines (Chapter 2) in accordance with the principles presented by Falta (1998). The endpoints of a tie line lie on the miscibility curve and its slope defines the equilibrium partition of a washing solution between the aqueous and TCE-rich phases. The endpoints are the chemical composition of these phase equilibriums.

3.3.2 Sand column experiment procedure

Figure 3.2 shows the type of sand column used in the experiments. The columns were filled with Ottawa sand (C-109) which is mainly composed of quartz with no clay, silt or organic particles. The size of the grains varies from 0.1 to 1.0 mm and the mean grain diameter (d_{50}) is 0.33 mm. The grains size curve is presented in Appendix D. The columns are capped at both ends using a perforated Teflon® cap. A Viton® O-Ring provides a seal between the glass cylinder and the Teflon® cap. A stainless steel screen covering each cap prevents the loss of fines. Inside each cap, a small reservoir is built to allow the uniformly distribution of injected liquids. The columns were filled progressively in steps of approximately 5 mm (10 g) sand layers. Each layer was placed uniformly by hitting the side of the column 25 times and subsequently compacted by dropping 12 times a weight of 180 g from a height of 7 cm. The layer surfaces were scarified between each step to allow a better connection between subsequent sand layers. The procedures are detailed in Martel and Gélinas (1996).

The columns were saturated with water from the base to prevent air trapping with approximately 10 pore volumes of degassed distilled water. Before saturation with water, interstitial air was eliminated from the soil by circulating carbon dioxide. A peristaltic pump was used to flush the column with TCE. The TCE was previously colored with Oil red O to follow the distribution of the contaminant visually. The low TCE injection velocity produced a stable mobilization front between TCE and water in the column. Residual TCE saturation was finally obtained in the column by flushing mobile TCE out of the column with 300-400 ml of water at high velocity (Table 3.1). Conditionally stable mobilization conditions prevailed during this flushing but the high water injection velocity used reduces the mobilization instability (Lake, 1989). An average total of 20 g of residual TCE remains trapped in the column, which corresponds to a residual TCE saturation (S_{or}) near 26% (Table 3.1). The presence of residual TCE in sand columns decreases the average effective hydraulic conductivity from 1.70×10^{-4} m/s to 0.93×10^{-4} m/s. The procedure used to prepare the sand columns leads to very consistent initial conditions from one experiment to the next. The characteristics of each sand column experiment are presented in Appendix D.

Table 3.1 - Characteristics of sand column experiments.

Column length (cm)	Column diameter (cm)	Sand dry density (kg/m³)	Porosity	Total pore volume (cm³)	K_w [a] (10^{-4} m/s)	K_{we} [b] (10^{-4} m/s)	S_{or} [c] (%)
14.99	3.68	1814	0.33	52.77	1.70	0.93	25.7
± 0.04		± 10	± 0.004	± 0.74	± 0.10	± 0.08	± 0.9

[a] Hydraulic conductivity
[b] Effective hydraulic conductivity at S_{or}
[c] Residual TCE saturation

The injection direction, velocity and rate during the experiment are presented in Table 3.2. The column was oriented vertically. The washing solutions were injected from the top of the sand columns as shown in Figure 3.2. The vertical injection direction is better suited to evaluate the recovery mechanisms. Downward washing was selected because the mobilization front is stable when a lighter and more viscous washing solution is displacing water (Lake, 1989; Martel et al., 1998b). However, this injection direction increases TCE mobilization. Approximately 4 pore volumes of washing solution were circulated through the sand at a temperature of 8 °C (mean ground water temperature in Quebec) similar to the conditions used for the phase diagrams. The effluent solutions were stored in small test tubes of 8 ml and 11 ml at 8 °C.

Table 3.2 - Sand column injection conditions

Experimental steps	Injection direction	Injection velocity (m/day)	Injection rate (L/day)
1) Water saturation	Upward	-	-
2) TCE saturation	Upward	14.68 ± 0.56	3.30 ± 0.10
3) Water injection to obtain S_{or}	Downward	3630 ± 620	935 ± 160
4) Washing experiment	Downward	1.77 ± 0.11	0.62 ± 0.04

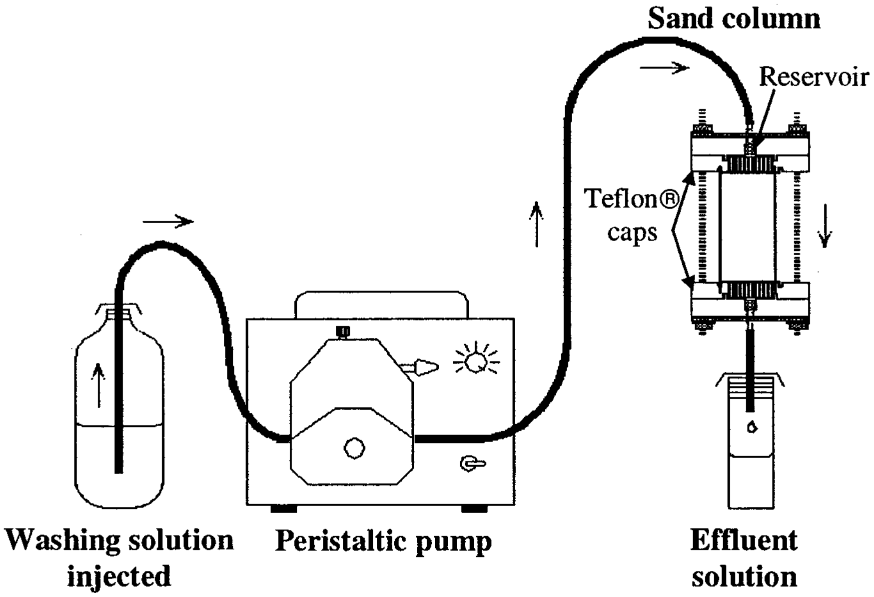


Figure 3.2 - Sand column washing setup (adapted from Martel et al., 1998a).

Washing solutions containing 5% to 85% by weight of active matter dissolved in water were injected in sand columns. To verify the reproducibility of the results, 15% of the experiments were repeated. The percentage of active matter for the washing solutions used as well as their density, viscosity and cost are presented in Table 3.3. Density measurements were made with a pycnometer and viscosity with a Cannon-Fenske viscometer. The approximate cost of the solutions is given in US$ dollar per m³ of washing solution. All selected solutions have a higher viscosity than water and TCE. All solutions except one (F) are lighter than water.

Table 3.3 - Characteristics of the washing solutions selected for sand column experiments.

Solution identification	Solution type	Active matter (%weight)	Density (kg/m³)	Absolute viscosity (mPa·s)	Cost ($ US/m³)
A	i-BuOH/SAS=2	5	997	1.80	103
B	EtOH	20	958	3.60	115
C	n-PrOH	20	960	3.84	432
D	EtOH/SAS=2	20	989	3.95	197
E	i-BuOH/SAS=2	20	988	4.83	410
F	W2722/SAS=2	20	1025	11.30	649
G	EtOH	50	894	4.69	268
H	n-PrOH	50	903	4.87	1015
I	EtOH/SAS=2	50	960	11.26	477
J	EtOH	80	831	2.71	398
K	i-BuOH	85	835	5.03	1576
-	Water	0	998	1.0	-
-	TCE	100	1464	0.57	-

Note: For solution containing two components, the number after the equal sign is the mass ratio of components

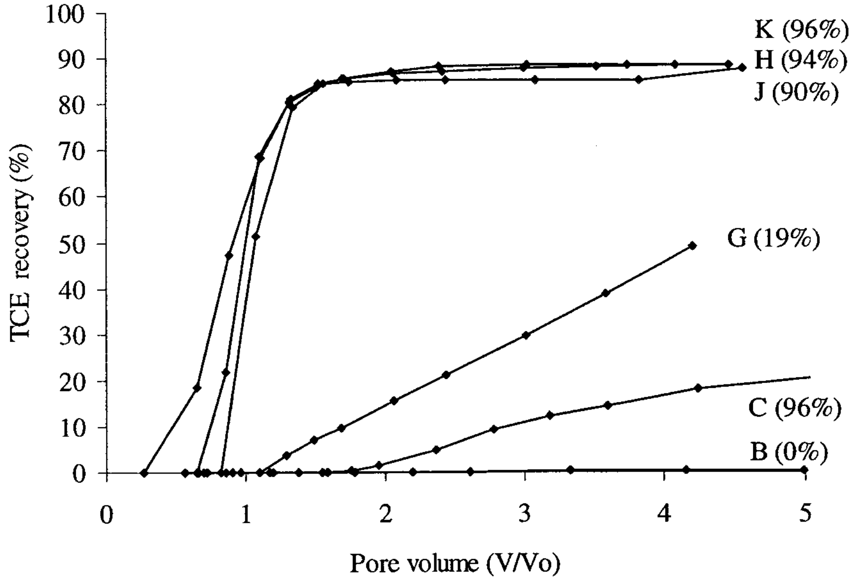
The liquid effluents exiting the columns could be made up of one or two separate phases. When two phases were produced simultaneously, the phases were separated, with a syringe after letting the solution stand still for few days at 8 °C. The mass of each phase was determined. The separation of the phases was facilitated by the TCE coloration with

Oil Red O that gave a pink color to the organic phase. The TCE concentration in each phase was obtained by analysis with a gas chromatograph (Variant CP3800/FID detector /column DB Petro100). The TCE dissolved in the aqueous phase is considered recovered by dissolution whereas the TCE found in the organic phase is considered mobilized. The effluent concentrations and the proportions of the TCE recovered by dissolution and mobilization were thus obtained for each column test.

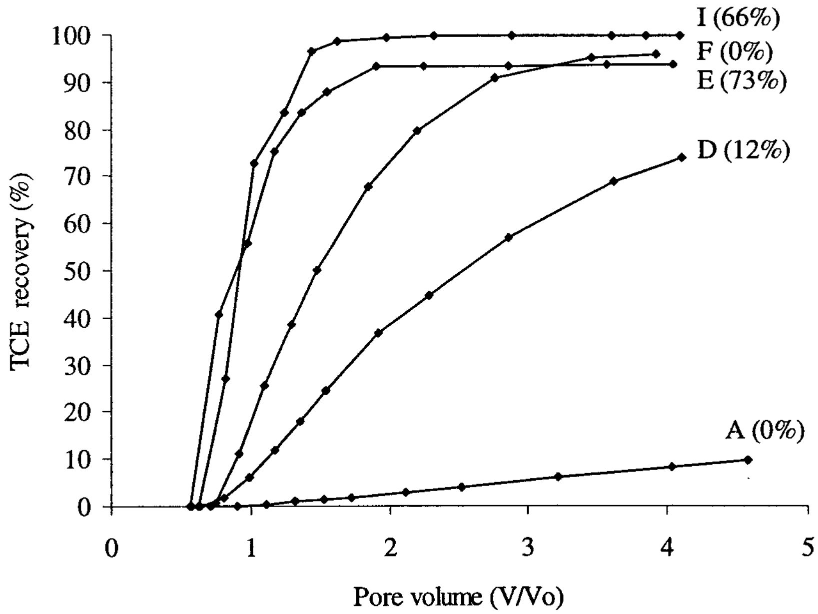
After washing experiments, the soil recovered from the columns was also analyzed to determine the residual TCE still present in the sand. Mass balances were done for each column based on the TCE initially present in the column, the TCE recovered in the liquid effluents and the residual TCE remaining in the sand after the experiment. The mass of TCE in the soil added to the mass recovered in the test tubes from the liquid effluent must coincide with the TCE quantity injected initially in the soil to create the residual saturation. Corrections were done on TCE concentrations when surfactant was present in the solutions. The presence of surfactant in solutions containing TCE decreases the TCE concentration in gas chromatograph analysis. After some analyses done with different solutions, a TCE correction factor of 1.07, 1.17, 1.05 and 1.23 were observed and applied to the liquid effluent of solutions such as EtOH/SAS (20%a.m.), EtOH/SAS (50%a.m.), i-BuOH/SAS (20%a.m.) and W2722/SAS (20%a.m.) respectively.

3.4 Results and discussion

More than 20 sand column experiments were carried. TCE recovery curves from alcohol, combination of alcohol/anionic surfactant and nonionic surfactant/anionic surfactant solutions are shown in Figures 3.3 a) and b). During TCE recovery, the mobile aqueous fluid volume in the column increases because of the removal of residual TCE. There is no constant reference pore volume during the washing experiment. Thus, the reference volume V_o used to calculate the pore volume injected V/V_o correspond to the mobile aqueous phase saturated pore volume at the end of the test (Martel et al., 1998b).



a)

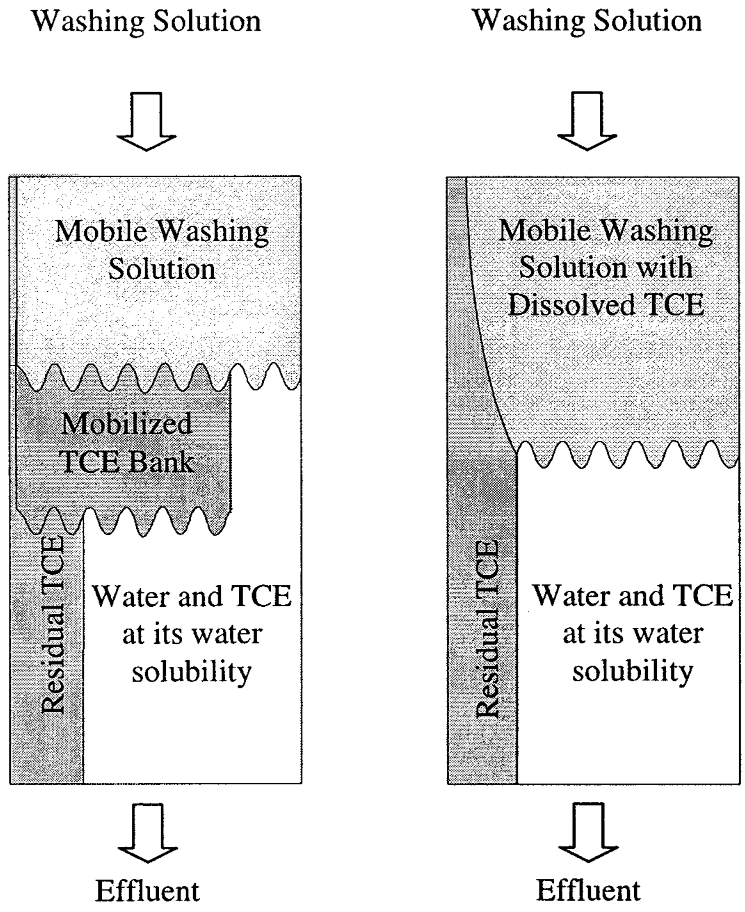


b)

Figure 3.3 - TCE recovery in sand columns with a) alcohol and b) micellar solutions. The letters correspond to the solution identification in Table 3.3 and the percentages refer to the TCE recovery by mobilization in these experiments.

TCE was recovered in two different ways, as a separate TCE phase in the DNAPL bank ahead of the washing solution (mobilization) or dissolved in the washing solution. The most efficient solutions (E, F, H, I, J and K) recovered between 88 and 100 % of TCE mainly by mobilization except for the solution F. However, solutions H and K are much more expensive (1015 and 1576 $US/m^3) than solutions E, I and J (398 to 477 $US/m^3). The TCE recovery by mobilization is very efficient and rapid because the TCE bank is formed ahead the washing solution (Figure 3.4a). The majority of TCE is recovered after the injection of only 2 pore volumes of the washing solution. The TCE bank is the lower phase in bottles 2 to 5 presented in Figure 3.5. Although efficient in terms of TCE recovery, the formation of a DNAPL bank is not recommended for most field conditions. This recovery mechanism must be used only when a very low permeability and non fractured layer of geological materiel is present under the contaminated zone. Otherwise, the TCE bank will migrate downward due to its high density (1464 kg/m^3) and thus increase the volume of contaminated soil.

Contrary to mobilization, dissolution is a gradual process which occurs after the first pore volume (Figure 3.4b). Solutions such as A, B, D, F and G are more appropriate for most field conditions because they dissolve TCE. These solutions are less expensive (103 to 268 $US/m^3) than mobilizing solutions. However, these solutions achieved only a recovery of 1 to 74 % of TCE after the injection of 4 pore volumes. Solutions A and B dissolved TCE but removed only 10% and 1% of its residual phase. Also, solutions D and G may not be suitable because they can partially mobilize TCE. For solution F, which is more expensive (649 $US/m^3), the residual TCE recovery is 96%. However, the dissolution front containing high concentration of TCE may have a density higher than water and could present the same drawback as the mobilizing solutions (especially the solution F that is denser than water without having any TCE). The bottles in Figure 3.6 show the tailing effect related to dissolution.



a) TCE Recovery by Mobilization

b) TCE Recovery by Dissolution

Figure 3.4 - Schematic liquid distribution in sand column according to the dominant recovery mechanism a) mobilization and b) dissolution.

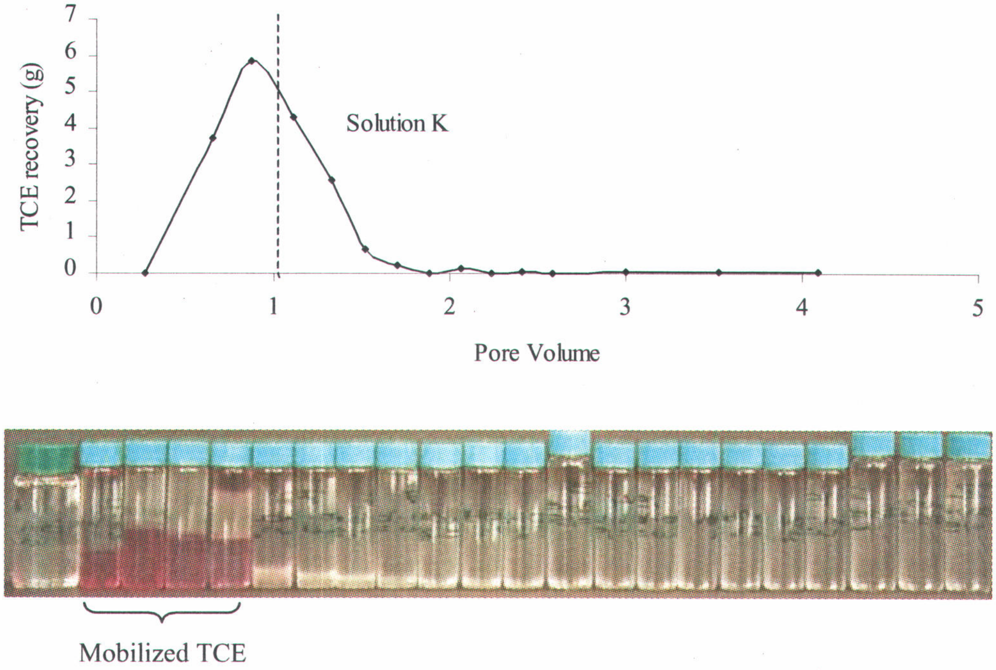


Figure 3.5 - Formation of a TCE bank in liquid effluents.

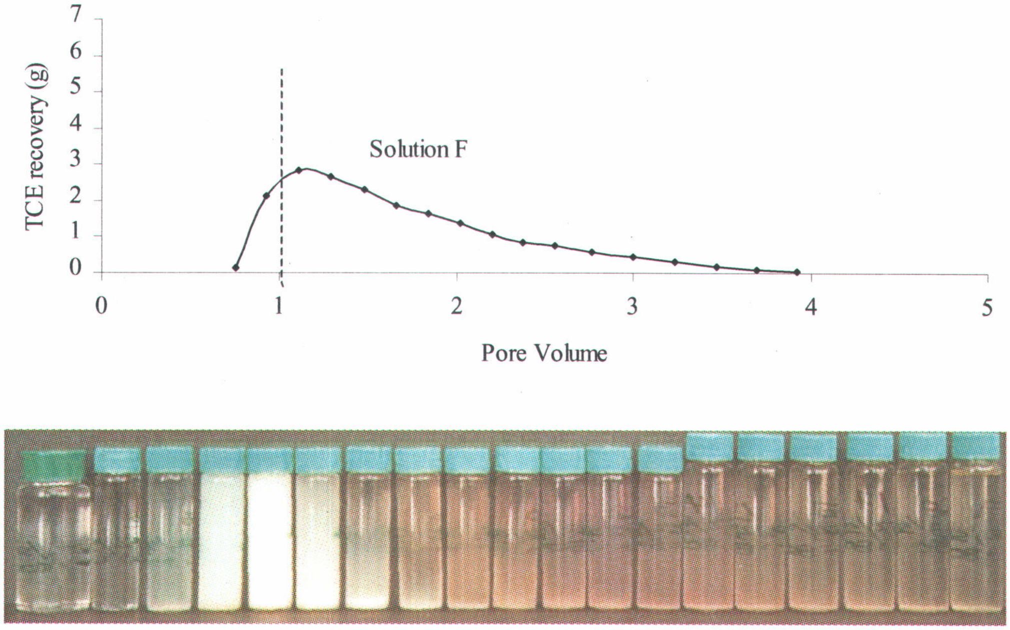


Figure 3.6 - Formation of a dissolution front in liquid effluents.

Washing solutions were injected at concentrations below and above the critical tie line extension to study the TCE recovery efficiency and mechanisms predicted from the tie line slopes (Chapter 2). The recovery mechanisms predicted from the tie line slopes and observed in column experiments, the number of pore volumes of solution injected, the percentage of TCE recovered and the TCE mass balance for each sand column experiment are presented in Table 3.4. Two experiments were done at 8 pore volumes and their results are presented farther in this chapter.

Table 3.4 - Summary of sand column experiment results.

Solution	Concentration relative to critical tie line	Dominant recovery mechanism anticipated	Dissolution vs mobilization observed (%)	Total PV* injected	Total TCE recovered (%)	Relative cost ($US/kg TCE recovered)	TCE mass balance (%)
A	Below	Dissolution	100 / 0	4.7	9.8	9.0	67.5
B	Below	Dissolution	100 / 0	5.7	0.6	166.5	45.1
C	Below	Mobilization	4 / 96	5.5	22.6	16.5	69.9
D	Below	Dissolution	88 / 12	4.2	73.8	2.8	83.4
E	Above	Mobilization	27 / 73	4.2	93.2	2.3 +	93.9
F	Below	Dissolution	100 / 0	4.0	95.8	7.2	96.2
G	Below	Dissolution	81 / 19	4.6	52.0	5.1	78.9
H	Above	Mobilization	6 / 94	4.8	87.2	6.4 +	88.6
I	Above	Mobilization	34 / 66	4.2	99.5	2.4 +	109.3
J	Above	Mobilization	10 / 90	4.7	85.1	2.3 +	87.8
K	-	Mobilization	4 / 96	4.7	86.6	9.3 +	89.3

Note : Solution K does not have a critical tie line
* PV (pore volume)
\+ calculated at 2.0 PV because no TCE is recovered after this.

As seen in Table 3.4, the prediction of the dominant recovery mechanism (dissolution or mobilization) from the tie line slopes was accurate in all cases studied. The recovery mechanism predicted for each solution was observed to be the main recovery mechanism in sand column tests. The experiments performed with solution concentrations above the critical tie line resulted in much higher TCE recovery than solutions with concentrations below the critical tie line. Contrary to injection concentrations below the critical tie line for which the recovery mechanism depends on the slope of the tie line, the injection of solutions with concentrations above the critical tie line is always associated with mobilization.

For solutions with positive tie lines (n-PrOH and i-BuOH), we must verify that injection concentrations are located in the appropriate miscibility zone of the phase diagram. There are three different miscibility zones in the phase diagram; first contact miscibility (F.C.M.), multiple contact miscibility (M.C.M.) and immiscible zones (I.) (Novosad and Sayegh, 1983; Lake, 1989). In the first two zones, near miscibility is achieved between the washing solution and displaced contaminant either by direct or multiple contact between the fluids. The interfacial tension between the washing solution and TCE is then low enough to mobilize TCE. Washing solutions injected at concentrations falling in these two miscibility zones lead to quite similar results. However, in the immiscible zone, the interfacial tension between the fluids is not low enough to significantly mobilize TCE. High residual TCE saturations remain when the washing solution concentrations used fall in the immiscible zone. The 20% a.m. n-PrOH solution is located in the immiscible zone which means that only a small proportion of TCE should be recovered. The 50% a.m. n-PrOH and 85% a.m. i-BuOH solutions are located in the multiple contact miscibility zone. These solutions should thus efficiently mobilize TCE. For field applications, it is more economical to select mobilizing washing solutions with concentrations in the multiple contact miscibility zone. This way, the minimal amount of active matter is used to achieve efficient TCE recovery. These three zones are represented in the phase diagram in Figure 2.7 b) of Chapter 2.

TCE mass balances were done to evaluate the mass loss or analytical problems and to verify the accuracy of the experiments. The TCE mass balances of these experiments vary from 45 to 109%. Some of the mass balances are low. One of the reasons associated with the low mass balances is that TCE is a volatile compound and in each experimental step there is a possibility to loose some TCE. However, the most interesting solutions worthy of further investigations and having potential field applications have an acceptable mass balance between 79 to 109 %.

As found by Martel and Gélinas (1996), these column experiments confirm that a solution made of alcohol and surfactant is more efficient than an alcohol used alone in water. EtOH/SAS solutions with 50% (solution I) and 20% (solution D) of active matter recovered more TCE than EtOH alone with respectively 50% (solution G) and 20% (solution B) of active matter as shown in Figure 3.7.

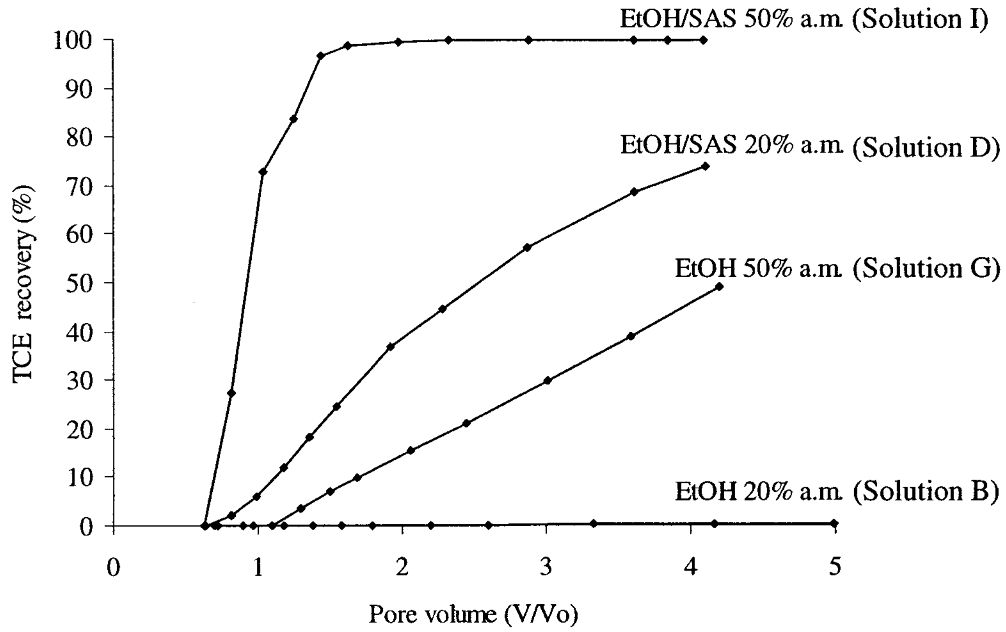


Figure 3.7 - TCE recovery using alcohol/surfactant (ratio of 2) flooding compared to alcohol flooding. The percentage of active matter (a.m.) is indicated for each solution.

A relationship can be established between the position of the miscibility curve in phase diagrams and TCE recovery (Figure 3.8). The lower the miscibility curve in the phase diagram, the higher is TCE recovery for a solution with 20% of active matter injected at a concentration below the critical tie line. The position of the miscibility curve confirms that the selection procedure used in Chapter 2 is valid. However, it is not possible to predict the TCE recovery efficiency of solutions injected at concentrations located above the critical tie line according to the position of their miscibility curve. The right graph in Figure 3.8 shows the correlation between the position of the miscibility curve in phase diagram (theoretical TCE dissolve) and the TCE recovery in sand column experiments for solutions injected at concentrations below the critical tie line. It seems that the TCE recovery predicted from the miscibility curves underestimates the recovery from sand column experiments after the injection of two pore volumes of washing solution (or one pore volume of washing solution recovered). It means that selection of washing solutions based on the position of the miscibility curves is good to predict the relative efficiency of solutions but cannot predict exactly the recovery for injection concentrations below the critical tie line.

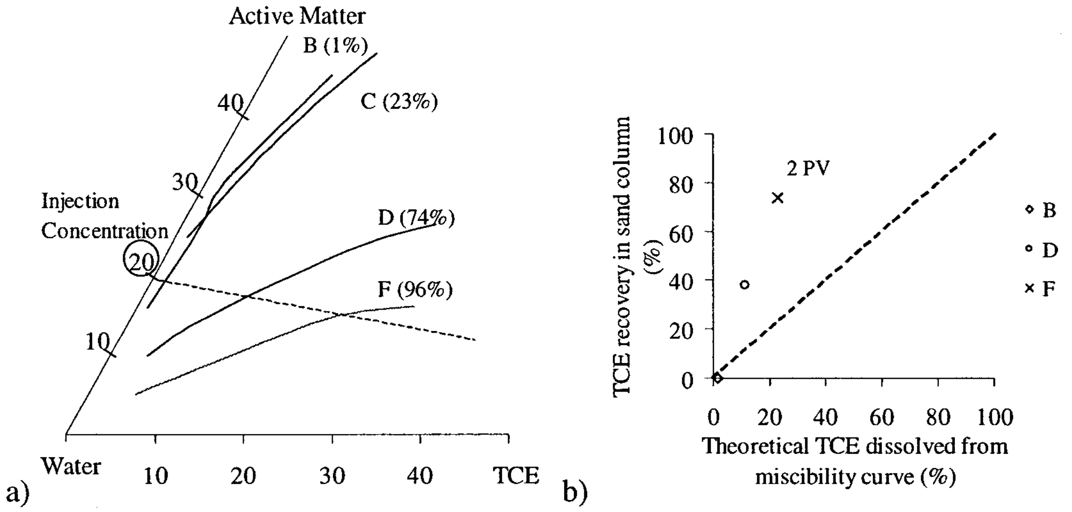


Figure 3.8 - Miscibility curves and recovery rate for 20% active matter solutions. a) the position of the miscibility curve in phase diagram associated to the total TCE recovery b) the correlation between the miscibility curve position in the phase diagram and the TCE recovery in sand column. The letter corresponds to the solution identification in Table 3.3 and the percentage in the phase diagram refers to the TCE recovery in this experiment.

To meet the constraint of the maximum TCE concentration limit in drinking water (5µg/L), a remediation technique must extract from soils nearly 100% of the TCE contamination. The solutions used in sand column were generally not sufficiently efficient to meet such an objective after the injection of four pore volumes of washing solution. Other experiments were thus performed to improve TCE recovery in sand columns. The most efficient solutions, whose recovery mechanism is dissolution (D, F), were injected with higher pore volumes. In this case, 8 pore volumes of the solution were injected in the sand columns instead of 4 pore volumes. Experimental results are presented in Table 3.5 and in Figure 3.9. TCE recovery with solution D increases from

79.7% to 87.3% with the injection of 4 additional pore volumes. Even if additional solution is added, the recovery is not increased in the last 3 pore volumes. For solution F, the maximum recovery was reached after 4 pore volumes and the injection of 4 additional pore volumes did not increase TCE recovery.

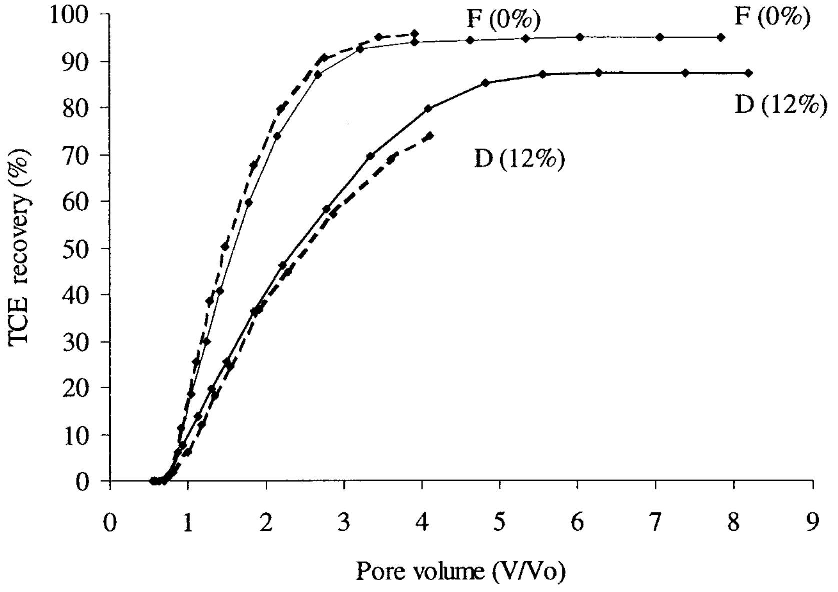


Figure 3.9 - TCE recovery in sand columns after the injection of 8 pore volumes of solution. The letter corresponds to the solution identification in Table 3.3 and the percentage refers to the TCE recovery by mobilization in this experiment. The dotted line is the TCE recovery after 4 pore volumes in a previous sand column test (Figure 3.3b).

Table 3.5 - Summary of supplementary sand column experiment results.

Solution	Concentration relative to critical tie line	Dominant recovery mechanism anticipated	Dissolution vs mobilization observed (%)	Total PV* injected	Total TCE recovered (%)	Relative cost ($US/kg TCE recovered)	TCE mass balance (%)
D	Below	Dissolution	88 / 12	8.2	87.3	4.9	87.6
F	Below	Dissolution	100 / 0	7.9	94.9	14.9	96.2

* PV (pore volume)

Another way to increase the efficiency of this remediation technique is to use other injection strategies. To investigate this option, we could use washing solutions whose main TCE recovery mechanism is mobilization ahead of another washing solution operating by dissolution. A solution such as E (i-BuOH/SAS=2, 20%a.m.) or I (EtOH/SAS=2, 50%a.m.) can be injected for 2 pore volumes followed by another solution such as F (W2722/SAS=2, 20% a.m.). Only a few pore volumes of this last solution could be injected to achieve a recovery of nearly 100% because the majority of TCE would be recovered by the first solution. However this option must consider a favorable field condition before the application of the technology.

Combination of remediation techniques can also be an option to meet the constraint of the drinking water standard for TCE. The soil washing can be followed by *in situ* bioremediation if the residual TCE in soil is low. However, other factors such as sweep efficiency or density contrast must be controlled to reach this goal.

3.5 Conclusion

Sand column experiments were conducted to classify solutions according to their extraction efficiency and to identify the recovery mechanisms involved. This study demonstrates that: (1) an alcohol and a surfactant combination is more efficient than an alcohol used alone in water; (2) the prediction of the dominant recovery mechanism from the tie line slopes in phase diagram is accurate and can be reproduced in sand column experiments; (3) TCE recovery in sand column experiments is generally well represented by the position of the miscibility curve in phase diagrams. However, the miscibility curve cannot be used to predict exactly the TCE recovery.

Miscibility curves and tie lines from phase diagrams are thus useful to select the most effective washing solutions for TCE recovery but also to predict the dominant TCE recovery mechanism with these solutions.

The sand column experiments identify the recovery efficiency of each solution and their recovery mechanisms. The solutions i-BuOH/SAS=2 (20% a.m.), W2722/SAS=2 (20% a.m.), EtOH (50% a.m.) and EtOH/SAS=2 (50% a.m.) have a field application potential and have a low relative cost. The solutions W2722/SAS=2 (20% a.m.) and EtOH/SAS=2

(50% a.m.) with a total TCE recovery of 95.8% and 99.8% respectively after the injection of 4 pore volumes of solution could be combined with an *in situ* bioremediation technique to potentially reach the drinking water standard of TCE in the aquifer. However, other factors such as sweep efficiency or density contrast must be controlled to reach this goal. Contrary to W2722/SAS=2 (20% a.m.) solution, EtOH/SAS=2 (50% a.m.) solution requires an underlying aquitard because it partly mobilizes TCE. Solutions i-BuOH/SAS=2 (20% a.m.), n-PrOH (50% a.m.), EtOH (80% a.m.) and i-BuOH (85% a.m.) are mobilizing solutions that create a mobilized TCE bank. These solutions can be followed by a dissolution solution to extract the TCE in soil after the mobilized bank has been recovered. However, the i-BuOH/SAS=2 (20% a.m.) solution is the best choice for mobilization because n-PrOH (50% a.m.) and i-BuOH (85% a.m.) solutions are too expensive and EtOH (80% a.m.) solution is very concentrated and can override the contaminated zone with a density of 831 kg/m^3. The EtOH (50% a.m.) solution can have a field potential if more pore volumes are injected. However, this solution can partly mobilize TCE.

3.6 Acknowledgments

This project was funded by the NSERC program (Natural Sciences and Engineering Research Council of Canada). We would like to thank M. Jalal Hawari from BRI (Biotechnology Research Institute) and Stéphane Deschamps for their assistance for the laboratory analysis. Special thanks go to Thomas Robert, a graduated student at INRS-Géoressources, who helped in the laboratory manipulation.

CHAPITRE 4

CONCLUSION GÉNÉRALE

Ce travail de recherche visait principalement à développer des solutions de lavage capables de récupérer efficacement du TCE à saturation résiduelle dans les aquifères contaminés et d'étudier les mécanismes responsables de cette récupération. Des solutions tensioactives et des solutions composées d'alcool capables de solubiliser et de mobiliser le TCE ont été développées. Ces solutions ont été sélectionnées à l'aide des diagrammes de phases et leur efficacité de récupération a été évaluée à l'aide d'essais en colonnes de sable. Le principal mécanisme de récupération du TCE a été prédit pour chaque solution à l'aide des courbes de distribution dans les diagrammes de phases. Cette prédiction a ensuite été vérifiée par l'analyse des effluents liquides résultant de l'injection des solutions en colonnes de sable. Ces différentes étapes sont donc essentielles au bon choix d'une solution de lavage.

Ainsi, cette recherche a permis d'appliquer une procédure de sélection des solutions nettoyantes pour la restauration des aquifères contaminés par des liquides immiscibles. La procédure est la suivante : (1) détermination de la position de la courbe de miscibilité de plusieurs solutions à l'aide de la méthode du point trouble; (2) sélection des courbes de miscibilité les plus basses qui sont les meilleures solutions nettoyantes; (3) détermination des courbes de distribution et de la courbe de distribution critique pour prévoir le principal mécanisme de récupération de ces solutions; (4) sélection de solutions selon le mécanisme de récupération approprié aux conditions de terrain; (5) réalisation des essais en colonnes de sable; (6) choix d’une ou plusieurs solutions selon leur efficacité de récupération, leur coût et leur potentiel de réutilisation et recyclage.

RECOMMANDATIONS

Cette technique de décontamination requiert des connaissances supplémentaires avant d'être utilisée de façon efficace sur le terrain. Premièrement, certains travaux de laboratoire sont encore nécessaires pour mettre au point les solutions. La densité et la viscosité des solutions sont des facteurs à considérer. La tension interfaciale entre le TCE et les alcools ou les tensioactifs injectés dans le sol est un élément qu'il faut connaître pour mieux caractériser le comportement des solutions. Il faut également mieux caractériser les phases aqueuses et organiques qui résultent du lavage de sol, c'est-à-dire mieux connaître la densité et la viscosité de chacune d'elles ainsi que la tension interfaciale entres elles. Il serait très intéressant de développer des solutions de lavage qui permettent de changer la densité du contaminant (s'il s'agit d'un LID) avant d'extraire par mobilisation celui-ci du sol pour ne pas qu'il se propage en profondeur. Il faut également s'assurer de développer des solutions solubilisante dont le front de solubilisation crée ne sera pas plus dense que l'eau afin d'éviter également des problèmes de migration verticale du TCE lors de sa récupération. L'utilisation d'un procédé de traitement des effluents dans le but de recycler les ingrédients pour diminuer les coûts d'utilisation de cette technologie serait à prévoir.

Dans un second temps, les solutions doivent être étudiées dans un contexte qui se rapproche de l'application de terrain. L'injection des solutions de lavage à plus grande échelle en bacs de sable serait utile pour mieux simuler ces conditions.

Finalement, l'utilisation d'un modèle numérique permettrait d'interpréter les essais réalisés en laboratoire et de mieux comprendre les processus de récupération des LID. Cet outil permettrait également de développer des stratégies d'injection/pompage en fonction des conditions de terrain et des solutions utilisées.

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ANNEXE A

COORDONNÉES DES DIFFÉRENTES COURBES DE MISCIBILITÉ

Alcool utilisé sans combinaison

éthanol

# point	% m.a.	% w	% tce
1	21.44	5.03	73.53
2	29.24	8.57	62.19
3	39.41	15.82	44.76
4	44.00	20.51	35.49
5	47.87	58.56	23.57
6	47.48	40.82	11.70
7	45.85	46.99	7.15
8	31.50	66.47	2.03
9	26.00	71.87	2.13
10	15.94	82.75	1.30

1-propanol

# point	% m.a.	% w	% tce
1	15.66	4.43	79.92
2	29.9	5.56	64.54
3	37.54	7.94	54.52
4	47.03	12.95	40.02
5	51.65	18.35	30
6	52.65	28.75	18.59
7	47.81	41.1	11.09
8	41.19	51.5	7.31
9	36.29	58.61	5.11
10	34.92	60.73	4.35
11	24.76	73.85	1.39

2-propanol

# point	% m.a.	% w	% tce
1	14.42	2.36	83.21
2	26.18	4.28	69.54
3	36.66	8.97	54.37
4	44.80	18.84	36.36
5	45.81	29.98	24.21
7	43.00	40.09	16.90
8	39.10	52.61	8.29
9	35.11	60.51	4.38
10	33.08	63.97	2.95
11	20.54	77.06	2.40

n-butanol

# point	% m.a.	% w	% tce
1	16.02	7.03	76.95
2	46.17	6.34	47.50
3	55.02	8.25	36.73
4	65.06	10.89	24.05
5	68.52	17.11	14.38
6	71.96	18.70	9.34
7	73.94	20.94	5.12
8	76.79	23.21	0.00

iso-butanol

# point	% m.a.	% w	% tce
1	18.10	5.79	76.11
2	46.31	6.10	47.59
3	53.69	7.20	39.10
4	63.55	8.73	27.71
5	73.11	11.92	14.96
6	78.31	21.69	0.00

n-amyl

# point	% m.a.	% w	% tce
1	14.80	7.00	78.20
2	52.82	6.71	40.47
3	64.01	7.39	28.60
4	71.25	9.40	19.35
5	76.88	13.88	9.24
6	86.37	13.63	0.00

Ratio n-butanol/SAS

Ratio 0.5

#point	% m.a.	% w	% tce
1	39.15	59.19	1.65
2	34.35	62.89	2.76
4	26.24	70.38	3.38
5	16.00	81.74	2.26
6	7.82	88.79	3.39

Ratio 1

#point	% m.a.	% w	% tce
1	26.01	40.61	33.38
2	19.94	43.19	36.86
2a	16.30	47.52	36.18
3	17.55	53.04	29.41
4	18.55	54.36	27.09
4a	18.98	55.34	25.67
5	21.13	55.58	23.29
6	27.96	54.06	17.98
7	31.26	60.44	8.30
8	27.36	67.00	5.64
9	24.22	70.62	5.16
10	18.49	76.97	4.54
11	8.37	87.73	3.90

Ratio 1.5

#point	% m.a.	% w	% tce
1	31.23	47.07	21.69
2	26.45	49.65	23.90
3	21.71	53.05	25.24
4	19.25	60.79	19.97
5	19.92	61.63	18.45
6	22.06	62.01	15.92
7	22.61	62.19	15.20
8	25.07	63.69	11.24
9	21.63	71.66	6.71
10	17.40	76.75	5.85
11	10.49	84.52	4.99

Ratio 2

#point	% m.a.	% w	% tce
1	33.55	50.65	15.80
2	29.17	52.15	18.68
3	21.44	54.52	24.04
4	18.77	59.51	21.72
5	14.19	66.15	19.67
6	12.09	72.07	15.85
7	10.63	78.07	11.30
8	7.92	86.23	5.86

Ratio 2.25

#point	% m.a.	% w	% tce
1	32.97	49.87	17.17
2	24.69	48.13	27.17
3	20.85	52.24	26.91
4	16.18	59.17	24.65
5	13.36	71.15	15.49
6	11.46	78.05	10.48

Ratio 2.5

#point	% m.a.	% w	% tce
1	31.66	47.74	20.60
2	23.25	47.59	29.16
3	20.61	52.86	26.54
4	17.65	56.90	25.45
5	15.26	66.27	18.47
6	13.21	75.26	11.53
7	10.44	82.47	7.10

Ratio 3

#point	% m.a.	% w	% tce
1	32.18	48.92	18.90
2	27.06	54.05	18.88
3	20.52	61.69	17.79
4	17.17	70.17	12.66
5	14.51	77.13	8.36
6	9.49	86.18	4.33

Alcool/SAS=2.5

éthanol

#point	% m.a.	% w	% tce
1	28.87	46.22	24.91
2	28.39	49.20	22.41
3	26.25	56.52	17.23
4	22.26	65.17	12.56
5	17.52	73.93	8.55
6	12.57	82.22	5.21
7	8.76	88.64	2.60

1-propanol

#point	% m.a.	% w	% tce
1	20.69	32.52	46.79
2	20.65	43.00	36.35
3	20.77	47.23	32.00
4	20.42	52.98	26.59
5	19.94	59.27	20.78
6	17.94	68.80	13.25
7	11.63	83.37	5.00

2-propanol

#point	% m.a.	% w	% tce
1	25.00	38.28	36.72
2	25.15	39.94	34.91
3	25.56	44.13	30.31
4	25.26	50.61	24.13
5	23.99	58.16	17.85
6	21.21	65.83	12.96
7	17.55	74.51	7.94
8	11.39	83.73	4.88

n-butanol

#point	% m.a.	% w	% tce
1	31.66	47.74	20.60
2	23.25	47.59	29.16
3	20.61	52.86	26.54
4	17.65	56.90	25.45
5	15.26	66.27	18.47
6	13.21	75.26	11.53
7	10.44	82.47	7.10

iso-butanol

#point	% m.a.	% w	% tce
1	28.54	42.95	28.51
1a	22.00	39.00	39.00
1b	18.00	45.00	37.00
2	17.87	54.25	27.88
3	17.76	60.14	22.10
4	16.08	67.80	16.13
5	13.66	75.82	10.52
6	8.97	86.30	4.73
7	6.76	90.44	2.81

sec-butanol

#point	% m.a.	% w	% tce
1	18.31	29.9	51.79
2	19.65	40.44	39.91
3	19.76	46.42	33.81
4	19.71	53.33	26.96
5	18.86	60.86	20.28
6	15.68	73.09	11.24
7	13.04	79.88	7.08
8	11.96	82.16	5.88
9	6.65	90.41	2.94

tert-butanol

#point	% m.a.	% w	% tce
1	20.75	31.65	47.60
2	21.44	37.49	41.08
3	22.10	45.70	32.20
4	22.00	52.48	25.52
5	20.70	61.16	18.14
6	18.08	70.47	11.45
7	15.28	77.36	7.35
8	11.61	84.16	4.23

n-amyl

#point	% m.a.	% w	% tce
1	5.10	91.83	3.08
2	3.36	92.90	3.74
3	1.90	94.84	3.25

iso-amyl

#point	% m.a.	% w	% tce
1	9.90	86.18	3.92
2	6.96	91.17	1.87
3	2.95	94.98	2.07

Alcool/SAS=2.5 (suite)

sec-amyl

#point	% m.a.	% w	% tce
1	31.26	47.39	21.35
2	24.97	51.36	23.67
3	19.82	54.48	25.70
4	17.58	65.11	17.30
5	16.51	71.52	11.97
6	15.86	76.75	7.39
7	10.63	84.73	4.64

tert-amyl

#point	% m.a.	% w	% tce
1	22.04	33.90	44.06
2	19.85	44.05	36.10
3	19.60	52.87	27.53
4	18.84	62.11	19.05
5	14.85	75.15	10.00
6	11.09	83.81	5.10
7	8.01	88.72	3.27

iso-butanol/tensioactif anionique=2.5

LRO

# point	% m.a.	% w	% tce
1	34.99	53.12	11.89
2	34.73	54.26	11.01
3	34.9	57.49	7.61
4	31.12	65.04	3.84
5	28.82	68.43	2.75
6	25.46	72.42	2.12
7	13.29	83.55	3.15

ZRO

# point	% m.a.	% w	% tce
1	38.59	58.40	3.00
2	37.48	60.15	2.37
3	36.89	61.52	1.59
4	36.50	62.29	1.20
5	34.87	64.36	0.77
6	34.01	65.53	0.46
7	32.19	67.62	0.19
8	30.13	69.87	0.00

Stéol

# point	% m.a.	% w	% tce
1	34.56	55.01	10.43
2	34.03	58.08	7.89
3	28.7	67.76	3.54
4	21.12	76.45	2.43
5	14.08	83.83	2.09

Dowfax 8390

# point	% m.a.	% w	% tce
1	19.11	78.93	1.95
2	16.55	81.58	1.87
3	10.17	86.60	3.23
4	6.11	91.42	2.47

Aérosol AY

# point	% m.a.	% w	% tce
1	23.64	36.54	39.82
2	22.85	46.40	30.75
3	22.62	54.89	22.49
4	21.34	63.81	14.86
5	18.87	72.82	8.31
6	12.94	82.88	4.19
7	9.22	88.63	2.15

Aérosol OT

# point	% m.a.	% w	% tce
1	31.75	52.24	16.00
2	22.87	65.23	11.90
3	19.23	70.30	10.47
4	15.38	76.83	7.79
5	11.21	82.94	5.85
6	5.82	89.54	4.63

Dowfax 3B2-D

# point	% m.a.	% w	% tce
1	38.03	59.95	2.02
2	26.81	71.67	1.52
3	17.03	81.05	1.91
4	7.83	89.14	3.03
5	3.99	91.50	4.50

HS85

# point	% m.a.	% w	% tce
1	31.11	67.8	1.09
2	21.98	72.59	5.43
3	6.16	91.03	2.81

Hostapur-OS

# point	% m.a.	% w	% tce
1	35.18	53.66	11.16
2	34.76	55.11	10.13
3	32.09	61.01	6.9
4	29.19	65.86	4.95
5	21.67	74.93	3.41
6	13.98	82.28	3.74
7	5.64	91.65	2.71

Hostapal-BV

# point	% m.a.	% w	% tce
1	27.23	46.47	26.31
2	23.96	56.38	19.66
3	23.82	59.59	16.59
4	25.92	62.28	11.80
5	27.11	66.16	6.73
6	27.02	68.05	4.92
7	20.97	76.00	3.03
8	12.07	83.76	4.17

iso-butanol/tensioactif anionique=2.5 (suite)

SAS

# point	% m.a.	% w	% tce
1	28.54	42.95	28.51
1a	22.00	39.00	39.00
1b	18.00	45.00	37.00
2	17.87	54.25	27.88
3	17.76	60.14	22.10
4	16.08	67.80	16.13
5	13.66	75.82	10.52
6	8.97	86.30	4.73
7	6.76	90.44	2.81

tensioactif nonionique/SAS=2

Hoes

#point	% m.a.	% w	% tce
1	21.56	73.03	5.41
2	12.56	82	5.45

Witconol 2722

#point	% m.a.	% w	% tce
1	5.06	89.62	5.32
2	9.18	78.62	12.2
3	13.92	65.16	20.92
4	15.5	58.06	25.61
5	16.03	52.74	31.23

Arkopal 90

#point	% m.a.	% w	% tce
1	18.91	76.48	4.61
2	11.04	85.86	3.1

Surfonic

#point	% m.a.	% w	% tce
1	18.61	78.56	2.84
2	8.78	87.5	3.72

tensioactif cationique/SAS=2

Genapol MYX

#point	% m.a.	% w	% tce
1	20.16	78.39	1.45
2	13.08	82.89	4.04
3	4.5	91.79	3.71

Genapol LA

#point	% m.a.	% w	% tce
1	17.75	81.27	0.98
2	12.79	86.15	1.06

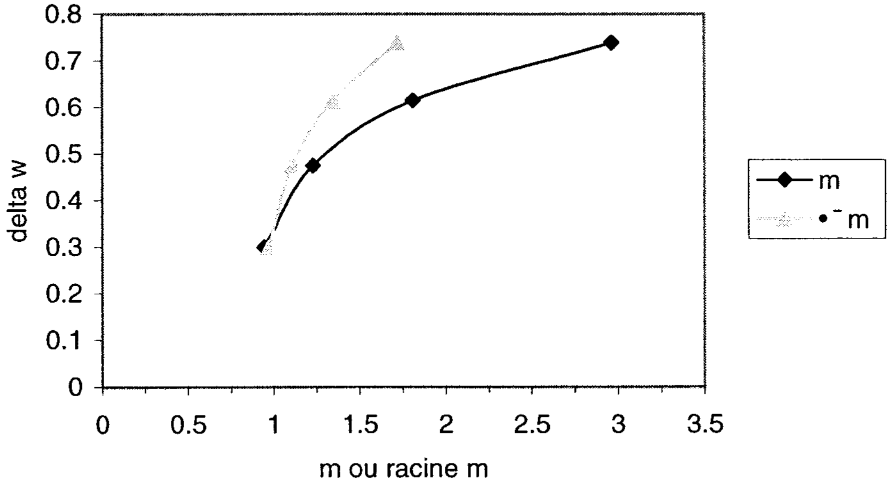
ANNEXE B

CALCUL DU PLAIT POINT ET DÉTERMINATION DE LA POSITION DES COURBES DE DISTRIBUTION CRITIQUE

Calcul du plait point

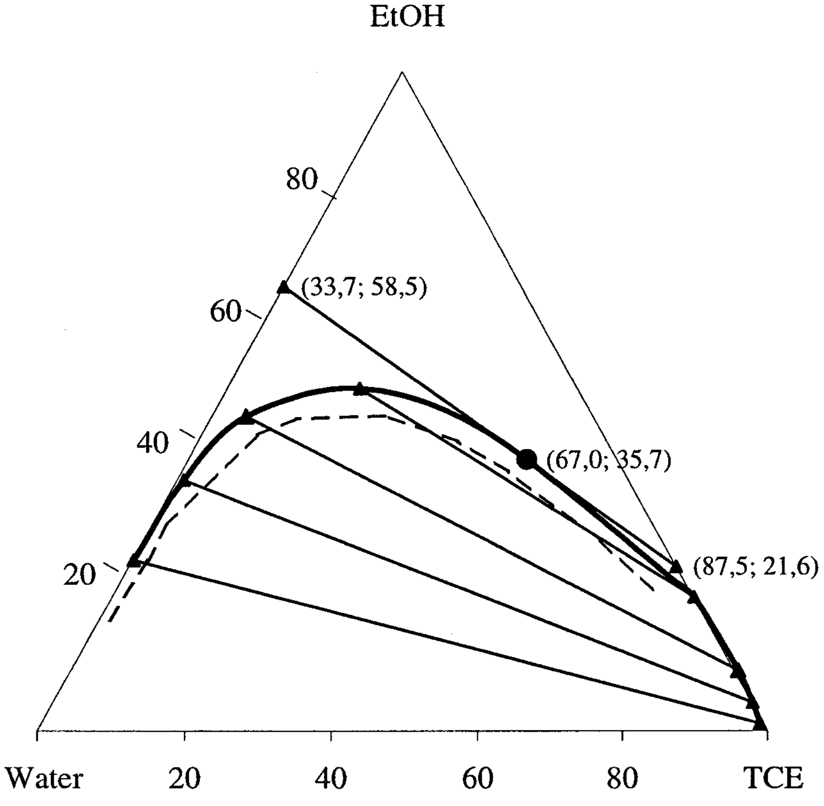
ÉTHANOL

delta w	m	racine m
0.738	2.964	1.722
0.614	1.811	1.346
0.475	1.231	1.109
0.299	0.946	0.973



Solution	% TCE	% alcool	w%	tce mod. (x)	cos/s mod. (y)	m	m
éthanol org.	75.0	25.0	0.0	87.50	21.65	0.765	0.764705882
éthanol aq.	0.0	67.5	32.5	33.75	58.46		
plait point	**46.4**	**41.21**	**12.4**	67.01	35.69		

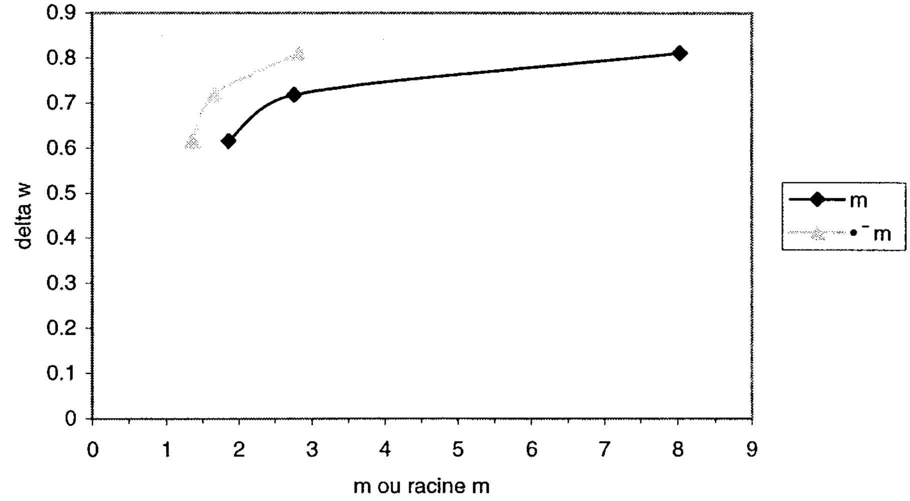
y =	35.6864	y tri=	41.20710529
x =	67	x tri =	46.39644735



Calcul du plait point

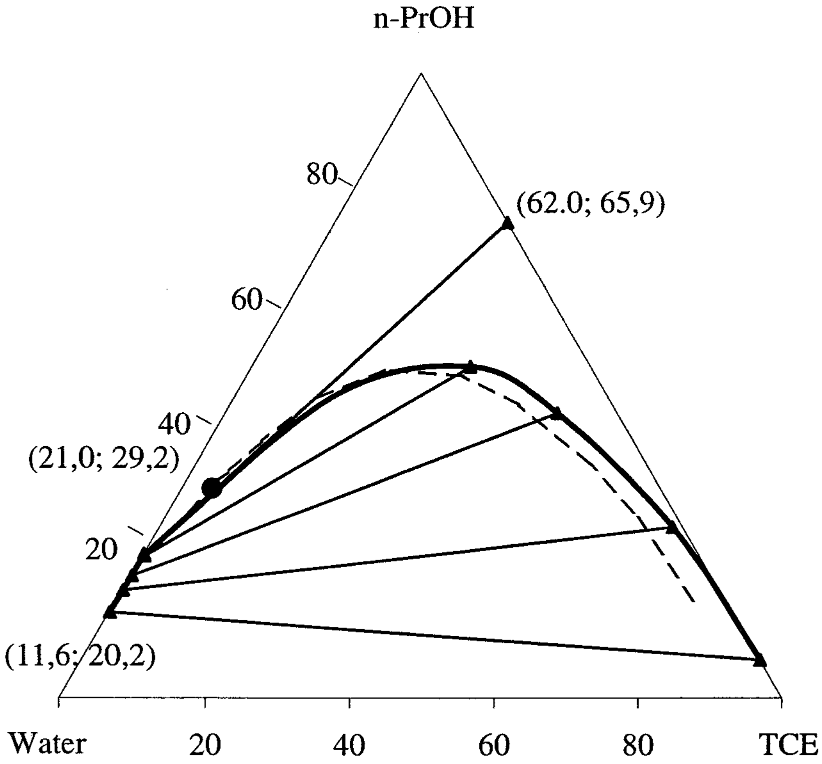
N-PROPANOL

delta w	m	racine m
0.861	11.182	3.344
changement de pente		
0.811	8.03	2.834
0.718	2.761	1.662
0.616	1.861	1.364



Solution	% TCE	% alcool	w%	tce mod. (x)	cos/s mod. (y)	m	m
-propanol org.	24.0	76.1	0.0	61.98	65.86	-1.45	-1.454028436
ı-propanol aq.	0.0	23.3	76.7	11.65	20.18		
plait point	**4.2**	**33.7**	**62.2**	21.00	29.16		

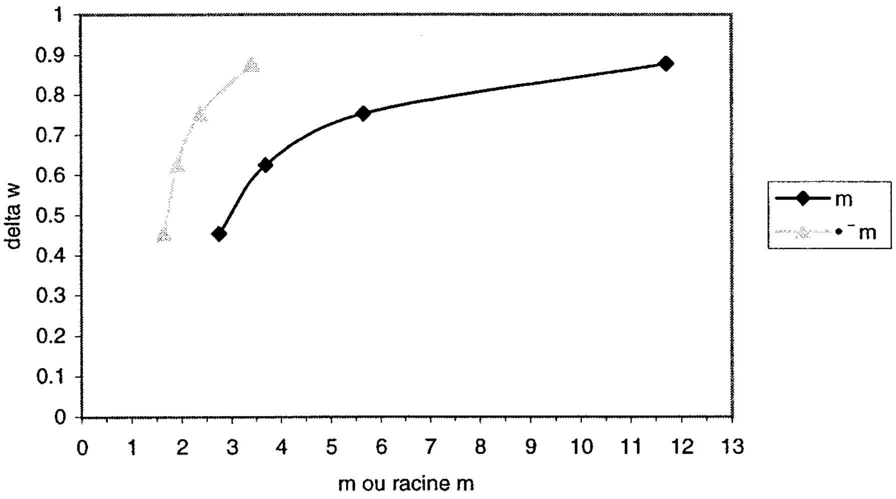
y = 29.1551 y tri= 33.66540967
x = 21 x tri = 4.167295167



Calcul du plait point

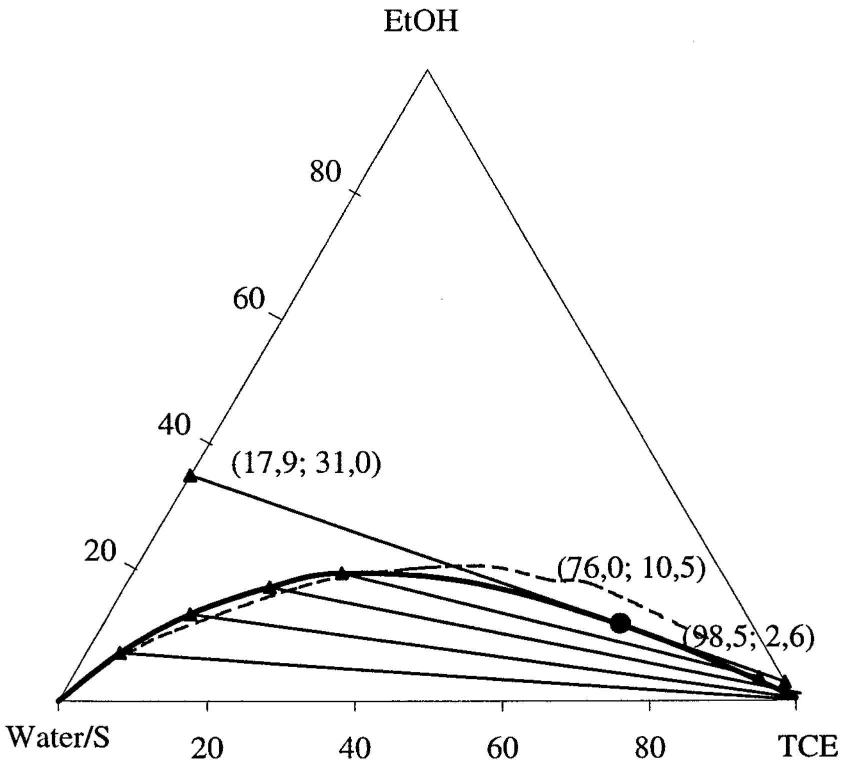
ÉTHANOL/SAS

delta w	m	racine m
0.878	11.707	3.421
0.753	5.662	2.379
0.625	3.698	1.923
0.454	2.752	1.659



Solution	% TCE	% alcool	w%	tce mod. (x)	cos/s mod. (y)	m	m
thanol/sas org.	97.0	3.0	0.0	98.50	2.60	1.95	1.957317073
thanol/sas aq.	0.0	35.8	64.2	17.90	31.00		
plait point	**69.9**	**12.2**	**17.9**	76.00	10.53		

y =	10.5296	y tri=	12.15853479
x =	76	x tri =	69.92073261



ANNEXE C

DÉTERMINATION DE LA POSITION DES COURBES DE DISTRIBUTION ET PARTITION DE CERTAINS ALCOOLS DANS LA PHASE ORGANIQUE ET LA PHASE AQUEUSE

Tie lines

Solution	% m.a.	% TCE	% alcool	% w
éthanol org.	15.25	100.0	1.1	0.0
éthanol aq.	-	0.2	26.0	73.8
éthanol org.	24.84	97.2	4.3	0.0
éthanol aq.	-	0.4	38.2	61.4
éthanol org.	34.86	92.9	9.2	0.0
éthanol aq.	-	4.7	47.8	47.5
éthanol org.	45.92	80.5	20.4	0.0
éthanol aq.	-	18.1	52.0	29.9
n-propanol org.	9.97	97.8	6.1	0.0
n-propanol aq.	-	0.1	13.8	86.1
n-propanol org.	23.06	71.2	27.5	1.4
n-propanol aq.	-	0.1	17.4	82.5
n-propanol org.	36.96	46.0	45.7	8.3
n-propanol aq.	-	0.2	19.7	80.1
n-propanol org.	49.66	28.9	56.0	15.2
n-propanol aq.	-	0.3	22.9	76.8
iso-butanol org.	9.95	86.6	12.5	0.9
iso-butanol aq.	-	0.1	6.0	93.9
iso-butanol org.	30.19	52.4	42.6	5.0
iso-butanol aq.	-	0.1	7.6	92.4
iso-butanol org.	49.00	31.5	62.3	6.2
iso-butanol aq.	-	0.1	7.4	92.6
iso-butanol org.	70.48	12.9	75.3	11.8
iso-butanol aq.	-	0.0	8.0	92.0
iso-butanol org.	40.06	42.1	53.7	4.1
iso-butanol aq.	-	0.0	7.7	92.2
iso-butanol org.	44.93	34.9	58.5	6.6
iso-butanol aq.	-	0.1	7.1	92.8
				% w + % SAS
éthanol/sas org.	27.56	90.0	3.8	6.2
éthanol/sas aq.	-	28.1	20.3	51.6
éthanol/sas org.	20.96	100.0	1.2	0.0
éthanol/sas aq.	-	19.5	18.1	62.5
éthanol/sas org.	14.43	100.0	0.5	0.0
éthanol/sas aq.	-	10.9	13.8	75.3
éthanol/sas org.	7.24	100.0	0.2	0.0
éthanol/sas aq.	-	4.5	7.7	87.8
iso-butanol/sas org.	5.26	98.0	2.4	-0.4
iso-butanol/sas aq.	-	4.2	4.2	91.6
iso-butanol/sas org.	9.97	87.6	5.9	6.5
iso-butanol/sas aq.	-	15.8	6.4	77.8
iso-butanol/sas org.	14.77	91.4	6.7	1.9
iso-butanol/sas aq.	-	37.0	9.5	53.5
iso-butanol/sas org.	19.72	41.8	12.4	45.8
iso-butanol/sas aq.	-	0.2	5.3	94.5
iso-butanol/sas org.	22.13	41.0	16.2	42.7
iso-butanol/sas aq.	-	0.1	2.8	97.1

Tie lines (suite)

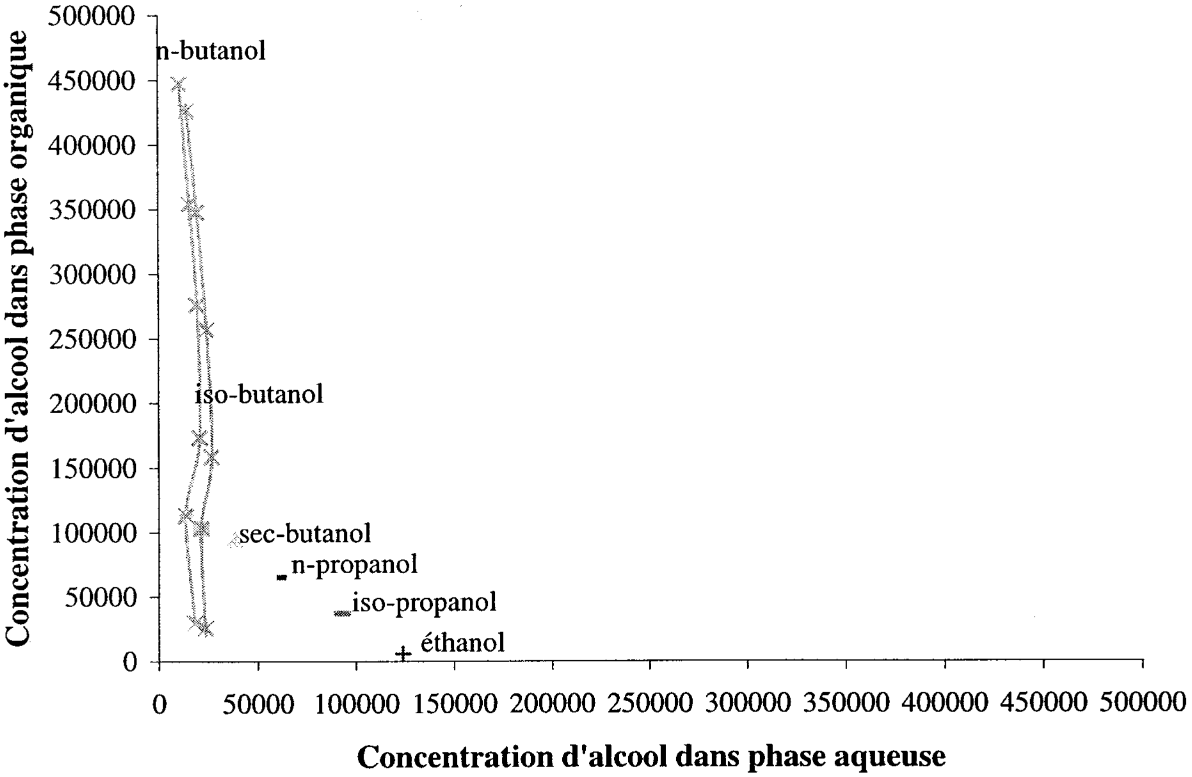
Solution	% m.a.	% TCE	% alcool	% w + % SAS
w2722/sas org.	6.40	90.4	9.6	0.00
w2722/sas aq.	-	12.5	8.8	78.66
w2722/sas org.	12.74	87.5	1.3	11.22
w2722/sas aq.	-	12.2	11.5	76.31
w2722/sas org.	19.35	97.5	-35.0	37.47
w2722/sas aq.	-	25.8	20.1	54.18
w2722/sas org.	25.98	50.7	4.4	44.91
w2722/sas aq.	-	15.0	32.5	52.50

Coefficient de partition

Solution	% m.a.	% TCE	% alcool	w%
éthanol org.	13.56	99.86	1.21	-1.08
éthanol aq.	-	0.24	26.86	72.90
n-propanol org.	13.49	89.97	11.58	-1.55
n-propanol aq.	-	0.14	15.38	84.49
iso-propanol org.	13.37	94.16	7.00	-1.16
iso-propanol aq.	-	0.16	21.85	77.99
n-butanol org.	13.43	81.93	18.38	-0.31
n-butanol aq.	-	0.08	3.98	95.94
iso-butanol org.	13.53	83.49	17.01	-0.50
iso-butanol aq.	-	0.08	6.06	93.86
sec-butanol org.	13.51	88.36	16.08	-4.44
sec-butanol aq.	-	0.07	10.42	89.50
n-butanol	5.02	93.11	6.03	0.86
n-butanol		0.11	3.74	96.15
n-butanol	20.00	70.33	30.91	-1.24
n-butanol		0.08	5.34	94.58
n-butanol	30.01	56.20	45.44	-1.64
n-butanol	-	0.03	6.06	93.91
n-butanol	40.04	39.04	53.77	7.19
n-butanol	-	0.05	6.34	93.61
n-butanol	49.94	28.49	62.70	8.81
n-butanol	-	0.06	6.03	93.91
iso-butanol org.	5.00	90.25	5.23	4.52
iso-butanol aq.	-	0.09	4.76	95.15
iso-butanol org.	20.00	66.22	28.65	5.14
iso-butanol aq.	-	0.08	6.80	93.12
iso-butanol org.	30.19	52.42	42.61	4.97
iso-butanol aq.	-	0.06	7.57	92.36
iso-butanol org.	40.06	42.13	53.72	4.15
iso-butanol aq.	-	0.04	7.74	92.22
iso-butanol org.	49.00	31.47	62.28	6.25
iso-butanol aq.	-	0.06	7.39	92.55

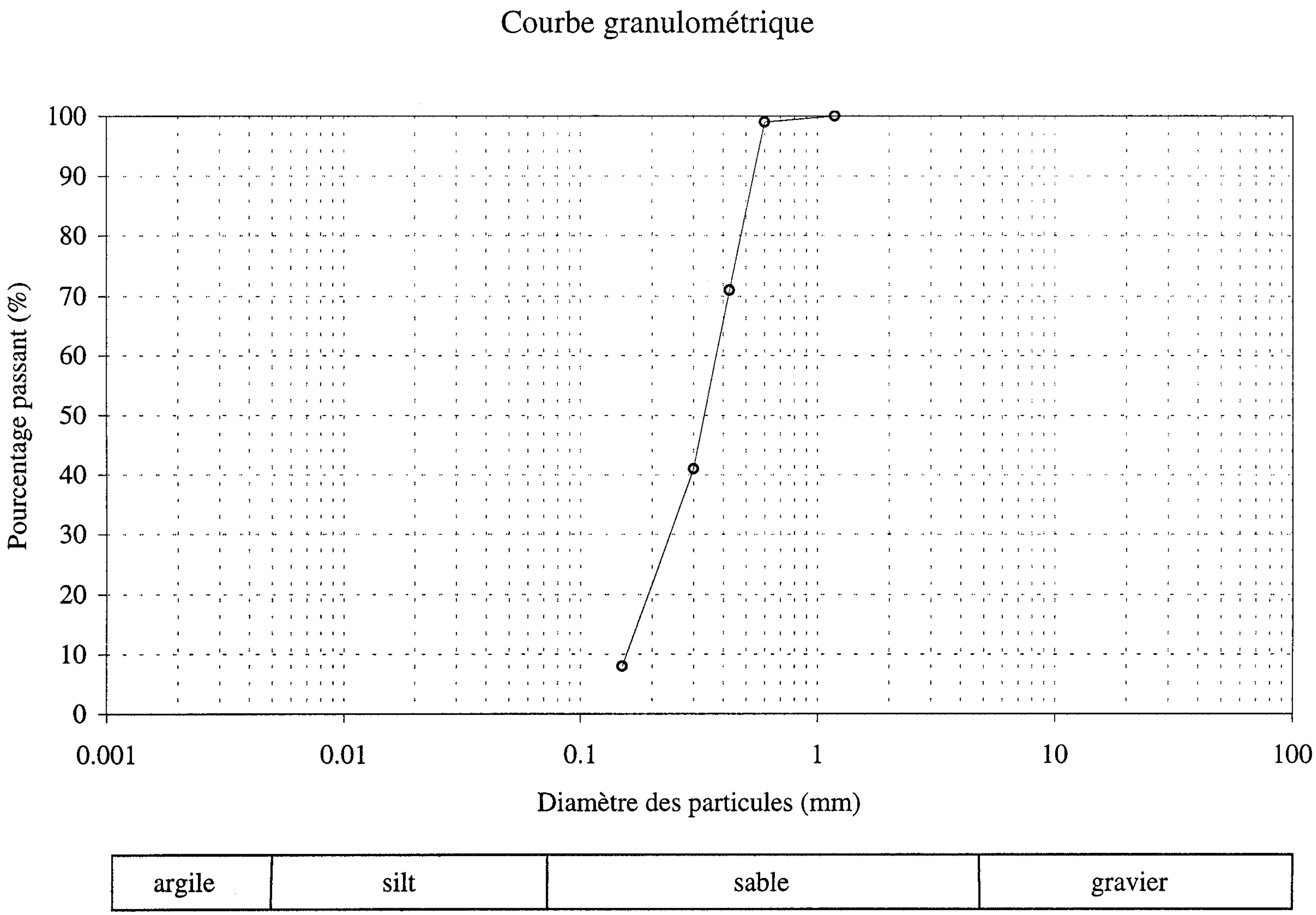
voir graphique du Kd

Détermination du Kd



ANNEXE D

COURBE GRANULOMÉTRIQUE DU SABLE UTILISÉ ET RÉSULTATS DES ESSAIS EN COLONNE DE SABLE


Courbe granulométrique
100
90
80
70
60
50
40
30
20
10
0
Pourcentage passant (%)
0.001
0.01
0.1
1
10
100
Diamètre des particules (mm)
argile
silt
sable
gravier

Caractéristiques des essais en colonne de sable

Solutions	% a.m.	Diamètre colonne (cm)	Longueur colonne (cm)	Masse sable (g)	Masse eau bouchon excl. (g)	Densité sable sec (g/cm3)	Densité sable saturé (g/cm3)	Porosité	K (cm/s)	densité globale * (g/cm3)	densité globale sèche * (g/cm3)	cond. hyd. eff. sat. rés, (cm/s)	Saturation résiduelle TCE (%)
éthanol	20	3.68	14.96	289.56	53.52	1.82	2.16	0.34	0.016	2.06	1.72	0.0101	26.63
w2722/sas=2	20	3.68	15.04	287.01	53.35	1.79	2.13	0.33	0.018	2.07	1.73	0.0096	24.63
n-propanol	20	3.68	15.00	286.48	52.61	1.80	2.13	0.33	0.017	2.07	1.74	0.0090	26.84
iso-butanol	85	3.68	14.93	288.42	52.11	1.82	2.14	0.33	0.016	2.07	1.74	0.0092	25.89
éthanol	50	3.68	15.04	288.56	53.45	1.80	2.14	0.34	0.017	2.06	1.73	0.0089	25.71
éthanol/sas=2	20	3.68	15.03	289.05	51.91	1.81	2.13	0.33	0.018	2.08	1.75	0.0085	24.6
éthanol/sas=2	50	3.68	15.04	289.81	52.89	1.81	2.14	0.33	0.018	2.07	1.74	0.0091	24.89
w2722/sas=2 (D)	20	3.68	15.00	290.92	52.92	1.82	2.16	0.33	0.018	2.07	1.74	0.0082	25.31
n-propanol	50	3.68	14.96	289.64	51.91	1.82	2.15	0.33	0.018	2.08	1.75	0.0111	25.12
éthanol (D)	50	3.68	14.98	289.41	53.59	1.82	2.15	0.34	0.017	2.06	1.72	0.0108	26.34
iso-buOH/sas=2	5	3.68	15.06	290.68	52.70	1.81	2.14	0.33	0.017	2.07	1.74	0.0093	26.37
éthanol	80	3.68	14.99	290.70	51.67	1.82	2.15	0.32	0.016	2.08	1.76	0.0089	27.6
iso-butanol/sas=2	20	3.68	14.92	289.44	51.79	1.82	2.15	0.33	0.017	2.08	1.75	0.0095	26.48
éthanol/sas=2 (8VP)	20	3.68	14.98	288.21	51.47	1.81	2.13	0.32	0.015	2.08	1.76	0.0081	25.23
w2722/sas=2 (8VP)	20	3.68	15.01	291.32	53.24	1.82	2.16	0.33	0.016	2.07	1.73	0.0089	24.5
	moyenne	3.68	14.99	289.28	52.61	1.814	2.14	0.33	0.0169	2.07	1.74	0.00928	25.74
	écart-type	0	0.04	1.38	0.74	0.010	0.01	0.004	0.0009	0.01	0.01	0.0008	0.94

Résultat des essais en colonne (caractéristiques des effluents récupérés)

Conc TCE (mg/kg)	Identification solution	1/2 VP	Effluent (g)	Masse TCE (g)	TCE/vial (g)	Tce cumul. (g)	récup. (%)
0	2	0.72		0	0	0	0.0
247	3 - éthanol w=79.92	0.97	9.1327	0.0023	0.0023	0.0023	0.0
278	4 - éthanol w=79.92	1.17	8.9171	0.0025	0.0025	0.0047	0.0
976	5 - éthanol w=79.92	1.38	9.0086	0.0088	0.0088	0.0135	0.1
137	6 - éthanol w=79.92	1.58	8.6535	0.0012	0.0012	0.0147	0.1
40	7 - éthanol w=79.92	1.79	9.0441	0.0004	0.0004	0.0151	0.1
	8	1.99		0.0010	0.0010	0.0161	
282	9 - éthanol w=79.92	2.20	9.0116	0.0025	0.0025	0.0186	0.1
	10	2.40		0.0015	0.0015	0.0201	
69	11 - éthanol w=79.92	2.60	8.8351	0.0006	0.0006	0.0207	0.1
	12	2.81		0.0030	0.0030	0.0237	
	13	3.05		0.0080	0.0080	0.0317	
997	14 - éthanol w=79.92	3.33	12.2128	0.0122	0.0122	0.0439	0.2
	15	3.61		0.0120	0.0120	0.0559	
	16	3.88		0.0110	0.0110	0.0669	
949	17 - éthanol w=79.92	4.16	12.1047	0.0115	0.0115	0.0784	0.4
	18	4.44		0.0100	0.0100	0.0884	
	19	4.72		0.0100	0.0100	0.0984	
876	20 - éthanol w=79.92	4.99	11.8938	0.0104	0.0104	0.1088	0.5
	21	5.27		0.0100	0.0100	0.1188	
	22	5.54		0.0100	0.0100	0.1288	
			Total part. =	0.1288	**TCE sol =**	21.2979	
			Masse TCE sol =	9.4864			
			Total =	9.6152			
			bilan de masse % =	45.1462			
			% récupération =	0.6			
			% mobilisation =	0.0			
			% solubilisation =	100.0			

Conc TCE (mg/kg)	Identification solution	1/2 VP	Effluent (g)	Masse TCE (g)	TCE/vial (g)	TCE corrigé (g)	TCE cumul.	récup. (%)
0	2	0.51		0	0	0.0000	0	0.0
0.326	3 - w2722/sas w=80.16	0.68	0,6399/1,7876/7,5324	0.00001	0.00001	0.0000	0.0000	0.0
51300	4 - w2722/sas w=80.16	0.83	8.6871	0.4456	0.4456	0.5481	0.5482	2.8
77130	5 - w2722/sas w=80.16	0.98	0,7030/1,8295/7,8077	1.5672	1.5672	1.9277	2.4758	12.6
193611	6 - w2722/sas w=80.16	1.14	10.0211	1.9402	1.9402	2.3864	4.8623	24.7
171956	7 - w2722/sas w=80.16	1.32	9.9696	1.7143	1.7143	2.1086	6.9709	35.4
	8	1.50		1.5000	1.5000	1.8450	8.8159	
142231	9 - w2722/sas w=80.16	1.67	9.7236	1.3830	1.3830	1.7011	10.5170	53.5
	10	1.85		1.1000	1.1000	1.3530	11.8700	
92303	11 - w2722/sas w=80.16	2.03	9.7275	0.8979	0.8979	1.1044	12.9744	66.0
	12	2.20		0.7500	0.7500	0.9225	13.8969	
	13	2.41		0.6000	0.6000	0.7380	14.6349	
43110	14- w2722/sas w=80.16	2.65	12.9081	0.5565	0.5565	0.6845	15.3193	77.9
	15	2.88		0.3500	0.3500	0.4305	15.7498	
	16	3.12		0.1500	0.1500	0.1845	15.9343	
5810	17 - w2722/sas w=80.16	3.35	12.9252	0.0751	0.0751	0.0924	16.0267	81.5
2374	18 - w2722/sas w=80.16	3.59	12.9475	0.0307	0.0307	0.0378	16.0645	81.7
			Total part. =	16.0645	**TCE sol =**	19.6664		
			Masse TCE sol =	0.1759				
			Total =	16.2404				
			bilan de masse % =	82.5793				
			% récupération =	81.7				
			% mobilisation =	0.0				
			% solubilisation =	100.0				

Conc TCE (mg/kg)	**Identification solution**	**1/2 VP**	**Effluent (g)**	**Masse TCE (g)**	**TCE/vial (g)**	**TCE corrigé (g)**	**TCE cumul.**	**récup. (%)**
0	2	0.62		0	0	0.0000	0	0.0
1000000	3 - éthanol/sas w=49.11 org.	0.81	4.5613	4.5613		0.0000	0.0000	
1028	3 - éthanol/sas w=49.11 aq.	0.81	6.1194	0.0063	4.5676	5.3441	5.3441	27.1
1000000	4 - éthanol/sas w=49.11 org.	1.03	7.5908	7.5908		0.0000	5.3441	
18025	4 - éthanol/sas w=49.11 aq.	1.03	3.8199	0.0689	7.6597	8.9618	14.3059	72.6
382239	5 - éthanol/sas w=49.11 org.	1.24	0,7344/1,9311	0.7381		0.0000	14.3059	
128954	5 - éthanol/sas w=49.11 aq.	1.24	8.6424	1.1145	1.8526	2.1676	16.4734	83.6
223440	6 - éthanol/sas w=49.11	1.44	9.6545	2.1572	2.1572	2.5239	18.9974	96.4
40008	7 - éthanol/sas w=49.11	1.62	8.8427	0.3538	0.3538	0.4139	19.4113	98.5
	8	1.80	8.6642	0.1500	0.1500	0.1755	19.5868	
1202	9 - éthanol/sas w=49.11	1.98	8.7353	0.0105	0.0105	0.0123	19.5991	99.5
	10	2.15	8.7067	0.0080	0.0080	0.0094	19.6084	
754	11 - éthanol/sas w=49.11	2.33	8.7557	0.0066	0.0066	0.0077	19.6162	99.5
	12	2.50	8.7274	0.0063	0.0063	0.0074	19.6235	
	13	2.68	8.7159	0.0060	0.0060	0.0070	19.6306	
481	14 - éthanol/sas w=49.11	2.89	11.9100	0.0057	0.0057	0.0067	19.6373	99.7
	15	3.13	11.9253	0.0052	0.0052	0.0061	19.6433	
	16	3.37	11.9213	0.0046	0.0046	0.0054	19.6487	
342	17 - éthanol/sas w=49.11	3.61	12.0522	0.0041	0.0041	0.0048	19.6536	99.7
290	18 - éthanol/sas w=49.11	3.85	11.9637	0.0035	0.0035	0.0041	19.6576	99.8
	19	4.09	11.9114	0.0020	0.0020	0.0023	19.6600	99.8

Total part. = 19.6600 **TCE sol =** 19.7055
Masse TCE sol = 1.8831
Total = 21.5431
bilan de masse % = 109.3251
% récupération = 99.8
% mobilisation = 65.6
% solubilisation = 34.4

Conc TCE (mg/kg)	**Identification solution**	**1/2 VP**	**Effluent (g)**	**Masse TCE (g)**	**TCE/vial (g)**	**Tce cumul. (g)**	**récup. (%)**
0	2	0.56		0	0	0	0.0
827	3 - éthanol w=20	0.82	9.0835	0.0075	0.0075	0.0075	0.0
1000000	4 - éthanol w=20 org.	1.07	10.8921	10.8921		0.0075	
259	4 - éthanol w=20 aq.	1.07	1.5394	0.0004	10.8925	10.9000	51.1
992647	5 - éthanol w=20 org.	1.34	6.0645	6.0199		10.9000	
1850	5 - éthanol w=20 aq.	1.34	4.6942	0.0087	6.0286	16.9286	79.4
131013	6 - éthanol w=20	1.56	8.5122	1.1152	1.1152	18.0438	84.6
8672	7 - éthanol w=20	1.75	7.4364	0.0645	0.0645	18.1083	84.9
	8	1.92	7.3686	0.0300	0.0300	18.1383	
1534	9 - éthanol w=20	2.09	7.4240	0.0114	0.0114	18.1497	85.1
	10	2.26	7.4757	0.0090	0.0090	18.1587	
1013	11 - éthanol w=20	2.44	7.7412	0.0078	0.0078	18.1665	85.2
	12	2.62	7.9071	0.0080	0.0080	18.1745	
	13	2.84	10.5745	0.0080	0.0080	18.1825	
778	14 - éthanol w=20	3.08	10.6262	0.0083	0.0083	18.1908	85.3
	15	3.33	10.7006	0.0070	0.0070	18.1978	
	16	3.58	10.6978	0.0060	0.0060	18.2038	
490	17 - éthanol w=20	3.83	10.6407	0.0052	0.0052	18.2090	85.4
	18	4.07	10.5856	0.1000	0.1000	18.3090	
	19	4.32	10.6898	0.1000	0.1000	18.4090	
28675	20 - éthanol w=20	4.57	10.4858	0.3007	0.3007	18.7097	87.8

Total part. = 18.7097 **TCE sol =** 21.3183
Masse TCE sol = 0.0157
Total = 18.7254
bilan de masse % = 87.8372
% récupération = 87.8
% mobilisation = 90.4
% solubilisation = 9.6

Conc TCE (mg/kg)	Identification solution	1/2 VP	Effluent (g)	Masse TCE (g)	TCE/vial (g)	Tce cumul. (g)	récup. (%)
0	2	0.66		0	0	0	0.0
134	3 - n-propanol w=79.71	0.85	8.3855	0.0011	0.0011	0.0011	0.0
	4	1.05	8.6394	0.0010	0.0010	0.0021	
5	5 - n-propanol w=79.71	1.20	8.6676	0.0000	0.0000	0.0022	0.0
	6	1.35	8.8674	0.0008	0.0008	0.0030	
95	7 - n-propanol w=79.71	1.55	8.8214	0.0008	0.0008	0.0038	0.0
54243	8 - n-propanol w=79.71 org.	1.75	0,0946/1,6093	0.0873		0.0038	
813	8 - n-propanol w=79.71 aq.	1.75	8.6301	0.0070	0.0943	0.0981	0.5
108881	9 - n-propanol w=79.71 org.	1.96	0,1941/1,6364	0.1782		0.0981	
955	9 - n-propanol w=79.71 aq.	1.96	8.602	0.0082	0.1864	0.2845	1.3
	10	2.16	8.7859	0.3400		0.2845	
	10	2.16		0.0090	0.3490	0.6335	
199657	11 - n-propanol w=79.71 org.	2.36	0,3603/1,7043	0.3403		0.6335	
1001	11 - n-propanol w=79.71 aq.	2.36	8.48	0.0085	0.3488	0.9823	4.7
	12	2.57	9.0963	0.5000		0.9823	
	12	2.57		0.0095	0.5095	1.4918	
236801	13 - n-propanol w=79.71 org.	2.78	0,4985/1,7648	0.4179		1.4918	
1152	13 - n-propanol w=79.71 aq.	2.78	8.2541	0.0095	0.4274	1.9192	9.1
	14	2.98	8.9485	0.4200		1.9192	
	14	2.98		0.0095	0.4295	2.3487	
141456	15 - n-propanol w=79.71 org.	3.18	0,2756/1,6412	0.2322		2.3487	
1150	15 - n-propanol w=79.71 aq.	3.18	8.4196	0.0097	0.2418	2.5905	12.3
	16	3.39	9.1232	0.2300		2.5905	
	16	3.39		0.0095	0.2395	2.8300	
119656	17 - n-propanol w=79.71 org.	3.59	0,2664/1,6668	0.1994		2.8300	
1360	17 - n-propanol w=79.71 aq.	3.59	8.5837	0.0117	0.2111	3.0411	14.4
	18	3.80	8.8826	0.2000		3.0411	
	18	3.80		0.0100	0.2100	3.2511	
	19	4.00	8.9619	0.2500		3.2511	
	19	4.00		0.0160	0.2660	3.5171	
144374	20 - n-propanol w=79.71 org.	4.24	0,3227/1,7206	0.2484		3.5171	
1389	20 - n-propanol w=79.71 aq.	4.24	11.5612	0.0161	0.2645	3.7816	17.9
	21	4.52	12.162	0.2500		3.7816	
	21	4.52		0.0160	0.2660	4.0476	
	22	4.80	12.2593	0.2300		4.0476	
	22	4.80		0.0100	0.2400	4.2876	
	23	5.07	12.1717	0.2300		4.2876	
	23	5.07		0.0100	0.2400	4.5276	
	24	5.35	12.123	0.2300		4.5276	21.5
	24	5.35		0.0100	0.2400	4.7676	
			Total part. =	4.7676	**TCE sol =**	21.1057	
			Masse TCE sol =	9.9811			
			Total =	14.7487			
			bilan de masse % =	69.8802			
			% récupération =	22.6			
			% mobilisation =	96.1			
			% solubilisation =	3.9			

Conc TCE (mg/kg)	Identification solution	1/2 VP	Effluent (g)	Masse TCE (g)	TCE/vial (g)	Tce cumul. (g)	récup. (%)
0	1	0.27		0	0	0	0.0
1000000	2 - iso-butanol w=15.01 org.	0.65	3.6963	3.6963		0.0000	
631	2 - iso-butanol w=15.01aq.	0.65	5.5725	0.0035	3.6998	3.6998	18.3
952987	3 - iso-butanol w=15.01 org.	0.88	6.1114	5.8241		3.6998	
707	3 - iso-butanol w=15.01 aq.	0.88	4.3298	0.0031	5.8271	9.5270	47.2
916093	4 - iso-butanol w=15.01 org.	1.11	4.6704	4.2785		9.5270	
807	4 - iso-butanol w=15.01 aq.	1.11	5.1531	0.0042	4.2827	13.8096	68.4
428739	5 - iso-butanol w=15.01 org.	1.32	6.0191	2.5806		13.8096	
611	5 - iso-butanol w=15.01 aq.	1.32	3.0079	0.0018	2.5825	16.3921	81.2
94208	6 - iso-butanol w=15.01 org.	1.52	7.074	0.6664		16.3921	
433	6 - iso-butanol w=15.01 aq.	1.52	0,8255/1,7576	0.0008	0.6672	17.0593	84.5
31339	7 - iso-butanol w=15.01 org.	1.70	7.2684	0.2278		17.0593	
115	7 - iso-butanol w=15.01 aq.	1.70	0,5136/1,6739	0.0002	0.2280	17.2873	85.6
	8	1.88	7.7794	0.0630	0.0000	17.3503	
16288	9 - iso-butanol w=15.01	2.06	7.6914	0.1253	0.1253	17.4755	86.6
	10	2.24	7.6199	0.0800	0.0000	17.5555	
6937	11 - iso-butanol w=15.01	2.41	7.5441	0.0523	0.0523	17.6079	87.2
	12	2.58	7.6114	0.0400	0.0000	17.6479	
	13	2.79	10.5017	0.0300		17.6779	
4509	14 - iso-butanol w=15.01	3.00	7.6134	0.0343	0.0343	17.7122	87.7
	15	3.17	7.6898	0.0300		17.7422	
	16	3.35	7.6330	0.0300		17.7722	
4611	17 - iso-butanol w=15.01	3.53	7.6745	0.0354	0.0354	17.8076	88.2
	18	3.70	7.6247	0.0300		17.8376	
	19	3.88	7.6508	0.0200		17.8576	
2249	20 - iso-butanol w=15.01	4.09	10.5793	0.0238	0.0238	17.8814	88.6
	21	4.33	10.3757	0.0200		17.9014	
	22	4.56	10.3199	0.0200		17.9214	
			Total part. =	17.9214	**TCE sol =**	20.1899	
			Masse TCE sol =	0.1175			
			Total =	18.0389			
			bilan de masse % =	89.3461			
			% récupération =	88.8			
			% mobilisation =	96.4			
			% solubilisation =	3.6			

Conc TCE (mg/kg)	Identification solution	1/2 VP	Effluent (g)	Masse TCE (g)	TCE/vial (g)	Tce cumul. (g)	récup. (%)
0	2	0.70		0	0	0	0.0
213	3 - éthanol w=50.21	0.90	8.9511	0.0019	0.0019	0.0019	0.0
2076	4 - éthanol w=50.21	1.10	8.8587	0.0184	0.0184	0.0203	0.1
238241	5 - éthanol w=50.21 org.	1.30	0,4567/1,7680	0.4212		0.0203	
36988	5 - éthanol w=50.21 aq.	1.30	7.936	0.2935	0.7147	0.7350	3.6
150539	6 - éthanol w=50.21 org.	1.49	0,2932/1,6616	0.2501		0.7350	
56350	6 - éthanol w=50.21 aq.	1.49	8.0502	0.4536	0.7038	1.4388	7.1
32079	7 - éthanol w=50.21 org.	1.68	0,0616/1,6095	0.0516		1.4388	
56284	7 - éthanol w=50.21 aq.	1.68	8.3720	0.4712	0.5228	1.9617	9.7
	8	1.87		0.1000		1.9617	
	8	1.87	8.5149	0.4750	0.5750	2.5367	
	9	2.06		0.1000		2.5367	
57302	9 - éthanol w=50.21	2.06	8.4940	0.4867	0.5867	3.1234	15.5
	10	2.25		0.1000		3.1234	
	10	2.25	8.4553	0.4700	0.5700	3.6934	
	11	2.44		0.1000		3.6934	
54603	11 - éthanol w=50.21	2.44	8.5286	0.4657	0.5657	4.2591	21.1
	12	2.63		0.1000		4.2591	
	12	2.63	8.5714	0.4700	0.5700	4.8291	
	13	2.83		0.1000		4.8291	
	13	2.83	8.5572	0.4700	0.5700	5.3991	
	14	3.02		0.1000		5.3991	
57234	14 - éthanol w=50.21	3.02	8.5075	0.4869	0.5869	5.9860	29.7
	15	3.21		0.1000		5.9860	
	15	3.21	8.4861	0.4900	0.5900	6.5760	
	16	3.40		0.1000		6.5760	
	16	3.40	8.5631	0.5000	0.6000	7.1760	
	17	3.59		0.1000		7.1760	
59675	17 - éthanol w=50.21	3.59	8.6343	0.5153	0.6153	7.7912	38.6
	18	3.78		0.1000		7.7912	
	18	3.78	8.5542	0.5500	0.6500	8.4412	
	19	3.98		0.1000		8.4412	
	19	3.98	8.5274	0.5800	0.6800	9.1212	
	20	4.20		0.1000		9.1212	
54465	20 - éthanol w=50.21	4.20	11.6866	0.6365	0.7365	9.8577	48.9
	21	4.46	11.5629	0.6300	0.6300	10.4877	
			Total part. =	10.4877	**TCE sol =**	20.1612	
			Masse TCE sol =	5.4102			
			Total =	15.8979			
			bilan de masse % =	78.8542			
			% récupération =	52.0			
			% mobilisation =	19.3			
			% solubilisation =	80.7			

Conc TCE (mg/kg)	Identification solution	1/2 VP	Effluent (g)	Masse TCE (g)	TCE/vial (g)	Tce cumul. (g)	récup. (%)
0	2	0.71		0	0	0	0.0
1122	3 - iso-buoh/sas w=95	0.91	9.2502	0.0104	0.0104	0.0104	0.0
9584	4 - iso-buoh/sas w=95	1.11	9.1010	0.0872	0.0872	0.0976	0.5
11240	5 - iso-buoh/sas w=95	1.32	9.1295	0.1026	0.1026	0.2002	1.0
11688	6 - iso-buoh/sas w=95	1.52	9.1558	0.1070	0.1070	0.3072	1.5
12202	7 - iso-buoh/sas w=95	1.72	8.4095	0.1026	0.1026	0.4098	2.0
	8	1.91	8.7403	0.1000	0.1000	0.5098	
12732	9 - iso-buoh/sas w=95	2.11	9.1671	0.1167	0.1167	0.6266	3.0
	10	2.32	8.9993	0.1100	0.1100	0.7366	
12689	11 - iso-buoh/sas w=95	2.52	8.8218	0.1119	0.1119	0.8485	4.1
	12	2.71	8.7463	0.1200	0.1200	0.9685	
	13	2.95	11.9647	0.1400	0.1400	1.1085	
12646	14 - iso-buoh/sas w=95	3.22	12.1061	0.1531	0.1531	1.2616	6.1
	15	3.49	12.1645	0.1500	0.1500	1.4116	
	16	3.76	12.0457	0.1560	0.1560	1.5676	
13191	17 - iso-buoh/sas w=95	4.03	12.0603	0.1591	0.1591	1.7267	8.3
	18	4.30	12.0559	0.1500	0.1500	1.8767	
12846	19 - iso-buoh/sas w=95	4.58	12.2099	0.1568	0.1568	2.0335	9.8

Total part. = 2.0335 **TCE sol =** 20.7845
Masse TCE sol = 12.0031
Total = 14.0366
bilan de masse % = 67.5341
% récupération = 9.8
% mobilisation = 0.0
% solubilisation = 100.0

Conc TCE (mg/kg)	Identification solution	1/2 VP	Effluent (g)	Masse TCE (g)	TCE/vial (g)	TCE corrigé (g)	TCE cumul.	récup. (%)
0	2	0.58		0	0	0.0000	0	0.0
13534	3 - w2722/sas w=80.11	0.75	9.1383	0.1237	0.1237	0.1521	0.1521	0.8
175850	4 - w2722/sas w=80.11	0.92	9.7851	1.7207	1.7207	2.1165	2.2686	11.3
228016	5 - w2722/sas w=80.11	1.10	10.0524	2.2921	2.2921	2.8193	5.0879	25.4
213993	6 - w2722/sas w=80.11	1.29	10.1020	2.1618	2.1618	2.6590	7.7468	38.6
186707	7 - w2722/sas w=80.11	1.48	10.0612	1.8785	1.8785	2.3105	10.0574	50.2
	8	1.66	9.8456	1.5000	1.5000	1.8450	11.9024	
136357	9 - w2722/sas w=80.11	1.84	9.8810	1.3473	1.3473	1.6572	13.5596	67.6
	10	2.02	9.8316	1.1000	1.1000	1.3530	14.9126	
88558	11 - w2722/sas w=80.11	2.20	9.6189	0.8518	0.8518	1.0477	15.9604	79.6
	12	2.38	9.5531	0.7000	0.7000	0.8610	16.8214	
	13	2.55	9.5567	0.6000	0.6000	0.7380	17.5594	
37198	14 - w2722/sas w=80.11	2.76	12.8175	0.4768	0.4768	0.5864	18.1458	90.5
	15	3.00	12.8754	0.3500	0.3500	0.4305	18.5763	
	16	3.23	12.7173	0.2500	0.2500	0.3075	18.8838	
10971	17 - w2722/sas w=80.11	3.47	12.7135	0.1395	0.1395	0.1716	19.0554	95.1
	18	3.70	12.7699	0.0800	0.0800	0.0984	19.1538	
3591	19 - w2722/sas w=80.11	3.92	11.4615	0.0412	0.0412	0.0506	19.2044	95.8

Total part. = 19.2044 **TCE sol =** 20.0448
Masse TCE sol = 0.0768
Total = 19.2812
bilan de masse % = 96.1906
% récupération = 95.8
% mobilisation = 0.0
% solubilisation = 100.0

Conc TCE (mg/kg)	Identification solution	1/2 VP	Effluent (g)	Masse TCE (g)	TCE/vial (g)	TCE corrigé (g)	TCE cumul.	récup. (%)
0	2	0.63		0	0	0.0000	0	0.0
	3			0.2500				
10588	3 - éthanol/sas w=79.64	0.81	8.9438	0.0947	0.3447	0.3688	0.3688	1.9
	4			0.2500				
53306	4 - éthanol/sas w=79.64	0.99	9.2103	0.4910	0.7410	0.7928	1.1617	6.1
	5			0.2500				
86010	5 - éthanol/sas w=79.64	1.17	9.2761	0.7978	1.0478	1.1212	2.2828	11.9
	6			0.2500				
91882	6 - éthanol/sas w=79.64	1.36	9.1785	0.8433	1.0933	1.1699	3.4527	18.0
	7			0.2500				
93211	7 - éthanol/sas w=79.64	1.54	9.3828	0.8746	1.1246	1.2033	4.6560	24.3
	8			0.2500				
	8	1.73	9.3984	0.8600	1.1100	1.1877	5.8437	
	9			0.2500				
91560	9 - éthanol/sas w=79.64	1.92	9.3554	0.8566	1.1066	1.1840	7.0278	36.7
	10	2.10	9.2368	0.7500	0.7500	0.8025	7.8303	
71349	11 - éthanol/sas w=79.64	2.28	9.1262	0.6511	0.6511	0.6967	8.5270	44.6
	12	2.47	9.1709	0.6800	0.6800	0.7276	9.2546	
	13	2.65	9.1586	0.7500	0.7500	0.8025	10.0571	
62591	14 - éthanol/sas w=79.64	2.87	12.5616	0.7862	0.7862	0.8413	10.8984	57.0
	15	3.12	12.5245	0.7400	0.7400	0.7918	11.6902	
	16	3.36	12.5351	0.7000	0.7000	0.7490	12.4392	
51640	17 - éthanol/sas w=79.64	3.61	12.5668	0.6490	0.6490	0.6944	13.1335	68.7
	18	3.86	12.2537	0.5000	0.5000	0.5350	13.6685	
35083	19 - éthanol/sas w=79.64	4.10	11.9416	0.4190	0.4190	0.4483	14.1168	73.8

Total part. =	14.1168	**TCE sol =**	19.1307
Masse TCE sol =	1.8397		
Total =	15.9565		
bilan de masse % =	83.4079		
% récupération =	73.8		
% mobilisation =	12.4		
% solubilisation =	87.6		

Conc TCE (mg/kg)	**Identification solution**	**1/2 VP**	**Effluent (g)**	**Masse TCE (g)**	**TCE/vial (g)**	**Tce cumul. (g)**	**récup. (%)**
0	2	0.64		0	0	0	0.0
1000000	3 - n-propanol w=49,98	0.85	4.2099	4.2099		0.0000	
1063	3 - n-propanol w=49,98	0.85	6.0618	0.0064	4.2163	4.2163	21.6
1000000	4 - n-propanol w=49,98	1.09	9.1581	9.1581		4.2163	
1062	4 - n-propanol w=49,98	1.09	2.6116	0.0028	9.1609	13.3772	68.5
631273	5 - n-propanol w=49,98	1.32	3.6450	2.3010		13.3772	
1695	5 - n-propanol w=49,98	1.32	5.2598	0.0089	2.3099	15.6871	80.3
137434	6 - n-propanol w=49,98	1.51	4.5127	0.6202		15.6871	
15482	6 - n-propanol w=49,98	1.51	3.9344	0.0609	0.6811	16.3682	83.8
39155	7 - n-propanol w=49,98	1.69	8.4675	0.3315	0.3315	16.6998	85.5
	8	1.87	8.1022	0.2000	0.2000	16.8998	
16095	9 - n-propanol w=49,98	2.05	8.3387	0.1342	0.1342	17.0340	87.2
	10	2.22	8.0852	0.0900	0.0900	17.1240	
7212	11 - n-propanol w=49,98	2.40	8.3850	0.0605	0.0605	17.1845	88.0
	12	2.57	8.1316	0.0500	0.0500	17.2345	
	13	2.78	11.3168	0.0300	0.0300	17.2645	
722	14 - n-propanol w=49,98	3.02	11.3743	0.0082	0.0082	17.2727	88.5
	15	3.26	11.3106	0.0060	0.0060	17.2787	
	16	3.50	11.1404	0.0040	0.0040	17.2827	
185	17 - n-propanol w=49,98	3.74	11.4629	0.0021	0.0021	17.2848	88.5
	18	3.98	11.2724	0.0018	0.0018	17.2866	
	19	4.22	11.2697	0.0016	0.0016	17.2882	
124	20 - n-propanol w=49,98	4.46	11.3671	0.0014	0.0014	17.2896	88.5
	21	4.70	11.1772	0.0013	0.0013	17.2909	

Total part. = 17.2909 **TCE sol =** 19.5253

Masse TCE sol = 0.0060

Total = 17.2969

bilan de masse % = 88.5871

% récupération = 88.6

% mobilisation = 94.2

% solubilisation = 5.8

Conc TCE (mg/kg)	Identification solution	1/2 VP	Effluent (g)	Masse TCE (g)	TCE/vial (g)	Tce cumul. (g)	récup. (%)
0	2	0.71		0	0	0	0.0
95	3 - éthanol w=49,98	0.90	8.6885	0.0008	0.0008	0.0008	0.0
2095	4 - éthanol w=49,98	1.09	8.6062	0.0180	0.0180	0.0188	0.1
127477	5 - éthanol w=49,98	1.29	0,2271/1,669	0.2128		0.0188	
37510	5 - éthanol w=49,98	1.29	7.9069	0.2966	0.5093	0.5282	2.5
29503	6 - éthanol w=49,98	1.47	0,0518/1,5995	0.0472		0.5282	
57374	6 - éthanol w=49,98	1.47	8.0626	0.4626	0.5098	1.0380	4.9
57573	7 - éthanol w=49,98	1.66	8.5377	0.4915	0.4915	1.5295	7.2
	8	1.85		0.0400		1.5295	
	8	1.85	8.3246	0.5000	0.5400	2.0695	
	9	2.04		0.0400		2.0695	
59575	9 - éthanol w=49,98	2.04	8.6501	0.5153	0.5553	2.6248	12.4
	10	2.23		0.0400		2.6248	
	10	2.23	8.5692	0.5100	0.5500	3.1748	
	11	2.42		0.0400		3.1748	
59294	11 - éthanol w=49,98	2.42	8.6401	0.5123	0.5523	3.7271	17.7
	12	2.62		0.0400		3.7271	
	12	2.62	8.5705	0.5800	0.6200	4.3471	
	13	2.84		0.0400		4.3471	
	13	2.84	11.6759	0.6500	0.6900	5.0371	
	14	3.11		0.0400		5.0371	
57101	14 - éthanol w=49,98	3.11	11.8934	0.6791	0.7191	5.7563	27.3
	15	3.37		0.0400		5.7563	
	15	3.37	11.8448	0.6800	0.7200	6.4763	
	16	3.63		0.0400		6.4763	
	16	3.63	11.6326	0.6800	0.7200	7.1963	
	17	3.89		0.0400		7.1963	
58777	17 - éthanol w=49,98	3.89	11.7059	0.6880	0.7280	7.9243	37.6
	18	4.16		0.0400		7.9243	
	18	4.16	11.7610	0.6500	0.6900	8.6143	
	19	4.42		0.0400		8.6143	
	19	4.42	11.6882	0.6500	0.6900	9.3043	
54760	20 - éthanol w=49,98	4.68	11.6564	0.6383	0.6383	9.9426	47.1
	21	4.94	11.6026	0.6300	0.6300	10.5726	

Total part. =	10.5726	**TCE sol =**	21.1002	
Masse TCE sol =	5.4102			la bouteille a cassée, 1,27 est
Total =	15.9828			remplacé par 3,73
bilan de masse % =	75.7472			
% récupération =	50.1			
% mobilisation =	7.0			
% solubilisation =	93.0			

Conc TCE (mg/kg)	Identification solution	1/2 VP	Effluent (g)	Masse TCE (g)	TCE/vial (g)	TCE corrigé (g)	TCE cumul.	récup. (%)
0	2	0.56			0	0.0000	0	0
1000000	3 - iso-buoh/sas w=80	0.76	7.8095	7.8095		0.0000	0.0000	
1001	3 - iso-buoh/sas w=80	0.76	3.8000	0.0038	7.8133	8.2040	8.2040	40.8
1000000	4 - iso-buoh/sas w=80	0.98	2.8429	2.8429		0.0000	8.2040	
4535	4 - iso-buoh/sas w=80	0.98	6.9547	0.0315	2.8744	3.0182	11.2221	55.8
961359	5 - iso-buoh/sas w=80	1.17	3.1405	3.0191		0.0000	11.2221	
94056	5 - iso-buoh/sas w=80	1.17	7.1455	0.6721	3.6912	3.8758	15.0979	75.0
166148	6 - iso-buoh/sas w=80	1.37	9.6124	1.5971	1.5971	1.6769	16.7749	83.4
92012	7 - iso-buoh/sas w=80	1.55	9.3897	0.8640	0.8640	0.9072	17.6820	87.9
	8	1.73	8.8415	0.9000	0.9000	0.9450	18.6270	
11648	9 - iso-buoh/sas w=80	1.91	9.1921	0.1071	0.1071	0.1124	18.7394	93.1
	10	2.08	8.7084	0.0120	0.0120	0.0126	18.7520	
586	11 - iso-buoh/sas w=80	2.25	8.6185	0.0051	0.0051	0.0053	18.7573	93.2
	12	2.42	8.7659	0.0050	0.0050	0.0053	18.7626	
	13	2.62	12.152	0.0050	0.0050	0.0053	18.7678	
442	14 - iso-buoh/sas w=80	2.86	11.9186	0.0053	0.0053	0.0055	18.7734	93.3
	15	3.10	12.3627	0.0050	0.0050	0.0053	18.7786	
	16	3.34	12.2022	0.0050	0.0050	0.0053	18.7839	
365	17 - iso-buoh/sas w=80	3.58	12.2543	0.0045	0.0045	0.0047	18.7886	93.4
	18	3.81	12.0965	0.0040	0.0040	0.0042	18.7928	
353	19 - iso-buoh/sas w=80	4.05	11.8229	0.0042	0.0042	0.0044	18.7972	93.4
			Total part. =	18.7972	**TCE sol =**	20.1229		
			Masse TCE sol=	0.0888				
			Total =	18.8860				
			bilan de masse % =	93.9				
			% récupération =	93.4				
			% mobilisation =	72.7				
			% solubilisation =	27.3				

Conc TCE (mg/kg)	Identification solution	1/2 VP	Effluent (g)	Masse TCE (g)	TCE/vial (g)	TCE corrigé (g)	TCE cumul.	récup. (%)
	2	0.58		0.0000	0	0.0000	0	0
156869.7	3 - éthanol/sas w=80	0.76	0,2526/1,6734	0.2625		0.0000	0.0000	
1764.824	3 - éthanol/sas w=80	0.76	8.8111	0.0156	0.2781	0.2975	0.2975	1.6
437190.8	4 - éthanol/sas w=80	0.94	0,7699/1,9562	0.8552		0.0000	0.2975	
28948.41	4 - éthanol/sas w=80	0.94	8.55	0.2475	1.1027	1.1799	1.4775	7.8
197801	5 - éthanol/sas w=80	1.13	0,4830/1,7994	0.3559		0.0000	1.4775	
84570.35	5 - éthanol/sas w=80	1.13	8.618	0.7288	1.0848	1.1607	2.6381	13.8
92441.41	6 - éthanol/sas w=80	1.31	0,2164/1,6967	0.1568		0.0000	2.6381	
95284.42	6 - éthanol/sas w=80	1.31	8.9315	0.8510	1.0079	1.0784	3.7166	19.5
106316.8	7 - éthanol/sas w=80	1.49	0,1838/1,6811	0.1787		0.0000	3.7166	
98474	7 - éthanol/sas w=80	1.49	8.9929	0.8856	1.0643	1.1388	4.8554	25.5
	8	1.68	-	0.1000		0.0000	4.8554	
	8	1.68	-	0.9000	1.0000	1.0700	5.9254	
30455.18	9 - éthanol/sas w=80	1.86	0,0679/1,6335	0.0497		0.0000	5.9254	
99862.14	9 - éthanol/sas w=80	1.86	9.1074	0.9095	0.9592	1.0264	6.9517	36.5
	10	2.04	9.3066	0.8700	0.8700	0.9309	7.8826	
91385.28	11 - éthanol/sas w=80	2.22	9.3217	0.8519	0.8519	0.9115	8.7941	46.2
	12	2.41	9.3909	0.8000	0.8000	0.8560	9.6501	
	13	2.59	9.346	0.7000	0.7000	0.7490	10.3991	
68621.62	14 - éthanol/sas w=80	2.77	9.171	0.6293	0.6293	0.6734	11.0725	58.1
	15	2.95	9.3566	0.6500	0.6500	0.6955	11.7680	
	16	3.14	9.3239	0.6800	0.6800	0.7276	12.4956	
56530.3	17 - éthanol/sas w=80	3.35	12.5525	0.7096	0.7096	0.7593	13.2549	69.6
	18	3.60	12.566	0.6500	0.6500	0.6955	13.9504	
	19	3.84	12.442	0.6000	0.6000	0.6420	14.5924	
44126.34	20 - éthanol/sas w=80	4.09	12.7016	0.5605	0.5605	0.5997	15.1921	79.7
	21	4.34	12.5399	0.4400	0.4400	0.4708	15.6629	
	22	4.59	12.7071	0.3200	0.3200	0.3424	16.0053	
16716.59	23 - éthanol/sas w=80	4.83	12.5785	0.2103	0.2103	0.2250	16.2303	85.2
	24	5.08	12.4765	0.1600	0.1600	0.1712	16.4015	
	25	5.32	12.0128	0.1100	0.1100	0.1177	16.5192	
3847.941	26 - éthanol/sas w=80	5.56	12.3952	0.0477	0.0477	0.0510	16.5702	87.0
	27	5.80	12.3165	0.0320	0.0320	0.0342	16.6045	
	28	6.05	12.4315	0.0170	0.0170	0.0182	16.6226	
115.0964	29 - éthanol/sas w=80	6.29	12.3345	0.0014	0.0014	0.0015	16.6242	87.3
	30	6.53	12.3934	0.0011	0.0011	0.0012	16.6253	
	31	6.99	34.6706	0.0008	0.0008	0.0009	16.6262	
79.5	32 - éthanol/sas w=80	7.38	4.8848	0.0004	0.0004	0.0004	16.6266	87.3
	33	7.79	36.3783	0.0004	0.0004	0.0004	16.6270	
75	34 - éthanol/sas w=80	8.19	4.7832	0.0004	0.0004	0.0004	16.6274	87.3
			Total part. =	16.6274	**TCE sol =**	19.0534		
			Masse TCE sol=	0.0683				
			Total =	16.6957				
			bilan de masse % =	87.6				
			% récupération =	87.3				
			% mobilisation =	11.8				
			% solubilisation =	88.2				

Conc TCE (mg/kg)	Identification solution	1/2 VP	Effluent (g)	Masse TCE (g)	TCE/vial (g)	TCE corrigé (g)	TCE cumul.	récup. (%)
0	2	0.54			0.0000	0.0000	0	0
2544	3 - w2722/sas w=80	0.70	9.2115	0.0234	0.0234	0.0288	0.0288	0.2
99195	4 - w2722/sas w=80	0.87	9.5379	0.9461	0.9461	1.1637	1.1925	6.2
187640	5 - w2722/sas w=80	1.05	10.0662	1.8888	1.8888	2.3233	3.5158	18.4
179319	6 - w2722/sas w=80	1.24	10.0244	1.7976	1.7976	2.2110	5.7268	29.9
166695	7 - w2722/sas w=80	1.42	9.9461	1.6580	1.6580	2.0393	7.7661	40.6
	8	1.60	9.7908	1.5500	1.5500	1.9065	9.6726	
145807	9 - w2722/sas w=80	1.78	9.8327	1.4337	1.4337	1.7634	11.4360	59.8
	10	1.96	9.8908	1.2000	1.2000	1.4760	12.9120	
104800	11 - w2722/sas w=80	2.14	9.6127	1.0074	1.0074	1.2391	14.1511	73.9
	12	2.32	9.3113	0.8500	0.8500	1.0455	15.1966	
	13	2.49	9.6166	0.6500	0.6500	0.7995	15.9961	
52094	14 - w2722/sas w=80	2.66	9.4537	0.4925	0.4925	0.6058	16.6019	86.8
	15	2.84	9.5868	0.4000	0.4000	0.4920	17.0939	
	16	3.01	9.3437	0.3000	0.3000	0.3690	17.4629	
13928	17 - w2722/sas w=80	3.22	12.982	0.1808	0.1808	0.2224	17.6853	92.4
	18	3.45	12.7631	0.1300	0.1300	0.1599	17.8452	
	19	3.69	12.9099	0.0800	0.0800	0.0984	17.9436	
2407	20 - w2722/sas w=80	3.92	12.7519	0.0307	0.0307	0.0378	17.9813	94.0
	21	4.16	12.8531	0.0250	0.0250	0.0308	18.0121	
	22	4.39	12.9217	0.0200	0.0200	0.0246	18.0367	
1216	23 - w2722/sas w=80	4.63	12.7487	0.0155	0.0155	0.0191	18.0558	94.3
	24	4.86	12.9912	0.0150	0.0150	0.0185	18.0742	
	25	5.10	13.0359	0.0140	0.0140	0.0172	18.0914	
1040	26 - w2722/sas w=80	5.34	12.7482	0.0133	0.0133	0.0163	18.1077	94.6
	27	5.58	13.0564	0.0110	0.0110	0.0135	18.1213	
	28	5.81	12.6203	0.0090	0.0090	0.0111	18.1323	
697	29 - w2722/sas w=80	6.04	12.5736	0.0088	0.0088	0.0108	18.1431	94.8
	30	6.27	12.6358	0.0070	0.0070	0.0086	18.1517	
	31	6.71	34.8278	0.0050	0.0050	0.0062	18.1579	
621	32 - w2722/sas w=80	7.08	5.1311	0.0032	0.0032	0.0039	18.1618	94.9
	33	7.46	37.2749	0.0030	0.0030	0.0037	18.1655	
549	34 - w2722/sas w=80	7.85	4.9454	0.0027	0.0027	0.0033	18.1688	94.9
			Total part. =	18.1688	**TCE sol =**	19.137		
			Masse TCE sol=	0.2405				
			Total =	18.4093				
			bilan de masse % =	96.2				
			% récupération =	94.9				
			% mobilisation =	0.0				
			% solubilisation =	100.0				

Résultats de l'analyse des sols récupérés après l'essai

No. analyse	Conc TCE (mg/kg)	Identification solution	Effluent (g) (méthanol)	TCE (g)	TCE après correction (g)
55	44588	iso-buoh/sas w=95% (14/09/99)	213.65	9.5262	12.0031
56	20	1-propanol w=49,98% (12/05/99)	203.61	0.0041	0.0060
57	38000	1-propanol w=79,71% (30/04/99)	208.46	7.9215	9.9811
58	18260	éthanol w=50% (30/04/99)	204.34	3.7312	5.4102
59	249	w2722/sas w=80% (05/05/99)-D	212.99	0.0530	0.0768
60	36110	éthanol w=80% (08/04/99)	208.5	7.5289	9.4864
61	406	iso-buoh w=15% (30/04/99)	199.75	0.0811	0.1175
62	293	iso-buoh/sas w=80,05% (14/09/99)	209.03	0.0613	0.0888
63	565	w2722/sas w=80% (15/04/99)	214.64	0.1213	0.1759
64	6190	éthanol w=49,98% (12/05/99)-D	204.37	1.2650	1.8343
65	6299	éthanol/sas w=50% (05/05/99)	206.19	1.2987	1.8831
66	228	flomo/sas w=80% (15/04/99)	211.42	0.0481	0.0698
67	54	éthanol w=20.02% (14/09/99)	198.66	0.0108	0.0157
68	6055	éthanol/sas w=80% (05/05/99)	209.55	1.2687	1.8397
264	239	éthanol/sas w=80% (10/12/99)	197.2	0.0471	0.0683
265	777	w2722/sas w=80% (10/12/99)	213.46	0.1659	0.2405
261	61759	mesure d'erreur : C3- 19,6739g TCE	209.67	12.9490	16.3158
262	60781	mesure d'erreur : C7- 20,8913g TCE	215.69	13.1099	16.5184
263	61370	mesure d'erreur : C3- 19,5439g TCE	211.17	12.9595	16.3290
302	35156	mesure d'erreur : C2- 10,0187g TCE	216.19	7.6004	9.5765
303	33437	mesure d'erreur : C4- 10,0126g TCE	216.35	7.2341	9.1150
304	4342	mesure d'erreur : C2- 2,0120g TCE	213.34	0.9263	1.3432
305	6056	mesure d'erreur : C4- 2,0120g TCE	213.82	1.2949	1.8776