Dissolved gas exsolution to enhance gas production and transport during bench-scale electrical resistance heating

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A B S T R A C T

Condensation of volatile organic compounds in colder zones can be detrimental to the performance of an in situ thermal treatment application for the remediation of chlorinated solvent source zones. A novel method to increase gas production and limit convective heat loss in more permeable, potentially colder, zones involves the injection and liberation of dissolved gas from solution during heating. Bench-scale electrical resistance heating experiments were performed with a dissolved carbon dioxide and sodium chloride solution to investigate exsolved gas saturations and transport regimes at elevated, but sub-boiling, temperatures. At sub-boiling temperatures, maximum exsolved gas saturations of $S_g = 0.12$ were attained, and could be sustained when the carbon dioxide solution was injected during heating rather than emplaced prior to heating. This gas saturation was estimated to decrease groundwater relative permeability to $k_{rw} = 0.64$. Discontinuous gas transport was observed above saturations of $S_g = 0.07$, demonstrating the potential of exsolved CO_2 to bridge vertical gas transport through colder zones.

1. Introduction

In situ thermal treatment (ISTT) is being increasingly used to treat chlorinated solvent dense non-aqueous phase liquid (DNAPL) source zones. Common ISTT technologies include electrical resistance heating (ERH), where heating results from the resistance of the subsurface to the flow of electrical current between a network of electrodes; thermal conductive heating (TCH), where the subsurface is heated by subsurface heating elements; and steam-enhanced extraction (SEE), where the subsurface is heated by the injection of pressurized steam. Recent ISTT applications have shown improved reductions in dissolved concentration and mass flux, and shortened remediation time frames at heterogeneous sites, where the advective delivery of amendments to lower permeability zones using injection-based technologies can be inhibited e.g., [1–3]. In ERH or TCH applications, the dominant mechanism of mass removal is vaporization and subsequent gas capture by soil vapor or multiphase extraction e.g., [4–8]. As such, the effective performance of ISTT requires the establishment of continuous gas channels or discontinuous gas pathways to enable

the transport of vaporized volatile organic compounds (VOCs) to subsurface extraction points [7–9].

ERH and TCH applications typically aim to increase subsurface temperatures up to the groundwater boiling temperature, to nucleate and establish steam channels throughout the subsurface [7,8]. This temperature is higher than the co-boiling (i.e., steam distillation) temperature of volatile organic compound (VOC) and groundwater, where gas nucleation occurs only at DNAPL–water interfaces. Lower DNAPL–water co-boiling temperatures are not preferred because gas bubbles that nucleate and grow from DNAPL–water interfaces can lead to slower discontinuous transport e.g., [10] and gas accumulation or lateral migration below heterogeneous lenses [9]. Despite the intent to reach groundwater boiling temperatures, convective heat loss due to rapid groundwater fluxes through more permeable zones can prevent target temperatures from being achieved [3,8]. This has been observed at ERH field sites where maximum representative heated zone temperatures can be limited to below 90 °C [2]. Non-uniform power distributions can also cause subsurface temperatures to be lower in the areas furthest from electrode or heater locations at earlier times e.g., [11,12]. These colder zones are detrimental to ISTT performance because heating may not be sufficient to produce a gas phase in these zones. Also, if gas is produced elsewhere and transported to these zones, the condensation of steam can inhibit gas channel formation and, if below co-boiling temperatures, the condensation of VOCs can create DNAPL [8,10]. Furthermore,

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dissolution of condensed VOCs following buoyant transport into colder zones can spread the overall extent of contamination into areas that were clean before treatment [8,13,14]. As such, ISTT applications require potential cold zones to be identified and incorporated into the design of the heating and extraction systems. The optimization of existing remediation technologies to address site-specific limitations such as this was recently recognized as a key research priority [3].

Design features to mitigate convective heat loss include the installation of physical or hydraulic barriers (e.g., sheet piles or extraction wells) to decrease groundwater flux, additional electrodes or heaters to increase power density and dissolved ion solution injection schemes to increase electrical conductivity. This study introduces a novel method that has the potential to decrease convective heat loss and increase gas production in colder zones: dissolved gas exsolution. In this method, a dissolved gas, such as carbon dioxide (CO_2), is liberated from solution as the groundwater is heated but at a lower temperature than the groundwater boiling point e.g., [15]. The exsolution of dissolved gas could improve treatment in colder zones by both the production of gas at a temperature lower than either the co-boiling or water boiling temperature, to allow the gas-phase transport of vaporized VOC, and a decrease in groundwater relative permeability, to limit the flow of colder water into the treatment zone. Dissolved gas could be delivered upgradient of the target heated zone by diffusive emitters e.g., [16] or injected as a saturated solution prepared above ground. Unlike the pressure-activated exsolution of gas-supersaturated water [17,18], heat-activated exsolution can use saturated solutions or solutions with high dissolved gas concentrations that are slightly below saturation. These solutions can be injected in colder regions upgradient, and gas production from these solutions can then be initiated within a heated treatment volume that may not be in close proximity to the injection location.

The overall goal of this study was to investigate the exsolution of CO_2 gas during heating by ERH. The specific objectives were to (i) determine whether the resulting gas flow occurred as bubble flow or continuous gas flow, and (ii) measure the gas saturation at the onset of transport and the maximum gas saturation attained during exsolution. Measurements of gas saturation are important to connect observations of gas transport to other studies of gas processes in porous media, and to establish detailed data for the validation of numerical models of ISTT. Bench-scale ERH experiments were performed where room-temperature solutions of water (H_2O), sodium chloride (NaCl) and dissolved CO_2 were emplaced or injected into a translucent silica sand pack, and light transmission methods were used to quantify gas production and transport over time.

2. Background

2.1. Electrical resistance heating

Field applications of ERH use 60 Hz three- or six-phase electrical power to conduct alternating current (AC) between phase-shifted electrodes within a target treatment volume. Electric current flows by electrolytic conduction through the pore water, and can be approximated using Ohm's law. The resistance of the subsurface to the movement of ions in the pore water results in the transformation of kinetic energy to heat [4,11,19,20]. The ERH power density increases with the effective subsurface electrical conductivity, which depends on temperature, fluid saturation, dissolved ion concentration and other properties of the media e.g., [21]. The modified Archie [22] equation can be used to approximate the saturation and temperature dependence of the effective subsurface electrical conductivity in nonconductive media:

$$\sigma = \sigma_w \frac{\phi^m}{a} S_w^n f(T, T_0) \tag{1}$$

where σ is the effective subsurface electrical conductivity (S/m), σ_w is the pore water electrical conductivity (S/m), ϕ is the porosity, S_w is the water saturation, m is the cementation exponent, a is the tortuosity factor, n is the saturation exponent and $f(T, T_0)$ is a temperature dependence term that describes increased electrical conductivity at a higher temperature (T) above an initial temperature (T_0) (°C) e.g., [19]. Empirical correlations for the temperature dependence term have been presented by Arps [23] and McNeill [21] for NaCl solutions; generally, an approximate threefold increase in conductivity can be expected for a 100 °C temperature increase [19]. Subsurface temperature distributions are governed by thermal conduction, convection, resistive heat dissipation, and phase change, which can be approximated with energy balances [11,13,19,20]. Heat losses in more permeable layers, as a result of cold groundwater transport into or hot groundwater transport out of the target heated zone, can prevent vaporization or cause condensation and thus inhibit gas extraction.

2.2. Dissolved gas exsolution

The solubility of a dissolved gas is described by Henry's law:

$$P_i = x_i k_{Hx,i} \tag{2}$$

where P_i is the partial pressure of dissolved compound i (Pa), x_i is the aqueous phase mole fraction, and $k_{Hx,i}$ is the temperature dependent Henry's law constant in units of pressure and mole fraction (e.g., Pa mol/mol). In the absence of NAPL, the liberation of a dissolved gas from solution (i.e., exsolution) in porous media will occur at elevated temperatures or reduced liquid pressures when the sum of the dissolved gas partial pressures and water vapor pressure exceeds the surrounding water pressure and is equal to the sum of the water pressure and capillary pressure:

$$\sum P_i + P_{v,w} = P_w + P_c \tag{3}$$

where $P_{v,w}$ is the vapor pressure of water (Pa), P_w is the water pressure (Pa) and P_c is the capillary pressure (Pa). Previous studies of gas exsolution by liquid depressurization [24,25] and liquid vaporization by boiling [26] have observed heterogeneous gas bubble nucleation at hydrophobic crevice sites followed by detachment and growth in pore bodies. Heterogeneous bubble nucleation models approximate the capillary pressure term in Eq. (3) with the Young–Laplace equation for the local crevice radius [18,27–29]. After nucleation, growth is driven by mass transfer of dissolved gases and volatilized water across the gas–liquid interface e.g., [18,28] and occurs as a series of pressurization and drainage steps through neighboring pore throats and bodies [24]. Growth, and the coalescence of adjacent gas clusters, continues until sufficient cluster sizes allow buoyant mobilization.

Eq. (3) shows that gas can be produced at temperatures lower than the boiling point of water due to exsolution of dissolved gases. If volatile NAPL is present, it can also contribute to gas production at lower temperatures in a process referred to as co-boiling [30,31], but NAPL–water co-boiling is not the focus of this study. The relatively lower Henry's law constant for CO_2 (Eq. (2)), compared to other common gases, allows a greater mass of the gas to be dissolved in water at a given temperature. CO_2 was selected for this ISTT enhancement because this mass is available for exsolution at higher temperatures, and promotes the production of higher gas volumes.