# Dehalogenation of trichloroethylene vapors by partially saturated zero-valent iron

Daniela Zingaretti, Iason Verginelli, Renato Baciocchi *

*Laboratory of Environmental Engineering, Department of Civil Engineering and Computer Science Engineering, University of Rome "Tor Vergata", Via del Politecnico, 1, 00133 Rome, Italy*

## HIGHLIGHTS

- We examined the reduction of TCE vapors by granular zero-valent iron.
- The particle size of the granular material plays a key role in the iron reactivity.
- The manufacturing process of iron was found to not affect the TCE removal.
- Using an acid washed iron a 99% reduction of TCE was observed after 6 weeks.

## GRAPHICAL ABSTRACT
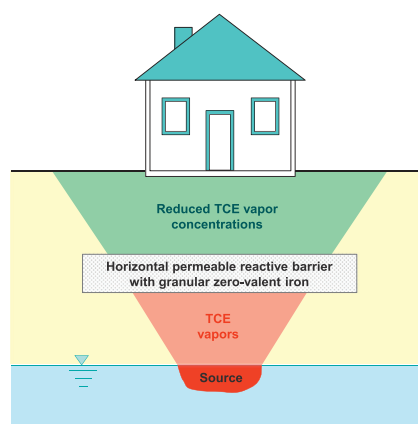


## ARTICLE INFO

## ABSTRACT

The reduction of trichloroethylene (TCE) in gas phase by different types of granular zero-valent iron (Fe$^0$) was examined in anaerobic batch vapor systems performed at room temperature. Concentrations of TCE and byproducts were determined at discrete time intervals by analysis of the headspace vapors. Depending on the type of iron used, reductions of TCE gas concentration from 35% up to 99% were observed for treatments of 6 weeks. In line with other experimental studies performed with aqueous solutions, the particle size was found to play a key role in the reactivity of the iron. Namely an increase of the TCE removal up to almost 3 times was observed using iron powders with particle size lower than 425 μm compared to iron powders with particle size lower than 850 μm. The manufacturing process of the iron powder was instead found to play only a limited role. Namely, no significant differences were observed in the TCE reduction by Fe$^0$ obtained using an iron powder attained by water atomization and sieving compared to the removal achieved using an iron powder subjected to a further annealing processes to reduce the content of oxides. Conversely, the pretreatment of the iron powder with HCl was found to enhance the reactivity of the iron. In particular, by washing the iron powder of 425 μm with HCl acid 0.1 M the reduction of TCE after 6 weeks of treatment increase from approximately 80% for the as received material to >99% for the pretreated iron powder. We also performed tests at different humidity of the iron observing that not statistical differences were obtained using a water content of 10% or 50% by weight. In all the experiments, the only detectable byproducts of the reactions were C4–C6 alkenes and alkanes that can be attributed to a hydrogenation of the C—Cl bond.

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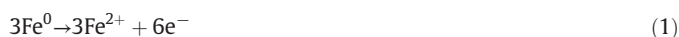
* Corresponding author.
*E-mail address:* baciocchi@ing.uniroma2.it (R. Baciocchi).

## 1. Introduction

The intrusion of vapors from the subsurface to overlying buildings is one of the major concerns for human health of residents at sites contaminated by chlorinated solvents (Eklund et al., 2012). Due to their massive use in industry, chlorinated compounds such as Tetrachloroethylene (PCE) or Trichloroethylene (TCE) are widely present in urban settings (Rivett et al., 2011). Besides, because of the low biodegradability of these compounds that makes natural attenuation in most cases not significant, even relatively low contamination by chlorinated solvents in the subsurface can pose potential long-term risks for human health (Bekele et al., 2013). This latter scenario is one of the most challenging to be faced. Traditional clean up strategies (e.g. soil vapor extraction or in situ chemical oxidation) are in this case not effective from both an economical and technical point of view (CityChlor, 2013). For diffuse contamination (i.e. large areas contaminated at a relatively low level), the adoption of traditional clean up techniques implies the use of significant quantities of reagents and/or energy that makes the traditional clean up strategies not sustainable. Risk management strategies aimed at interrupt the migration pathway of vapors into the building are more indicated for this contamination scenario. To mitigate the intrusion of vapors into the buildings from the subsurface different strategies were designed. For instance, the intrusion of vapors can be controlled by the depressurization of the sub-slab using fans or blowers installed below the building foundation, the over-pressurization of non-residential buildings by adjusting the heating, ventilating and air conditioning (HVAC) system, the enhancement of building ventilation using fans or natural ventilation and the installation of passive barriers below the building to physically block vapors access (ITRC, 2007; U.S. EPA, 2015).

Over recent years, Mahmoodlu et al. (2014, 2015) proposed an alternative vapor intrusion mitigation system that involves the use of solid potassium permanganate to create a horizontal permeable reactive barrier (HPRB) aimed at treating upward volatile organic compounds (VOCs). Later, Verginelli et al. (2017) showed that theoretically HPRBs of potassium permanganate with a thickness of <1 m are able to attenuate chlorinated solvent vapors of orders of magnitude for several years. One of the possible drawbacks related to the use of soluble oxidants such potassium permanganate, is the progressive dissolution and leaching of the reactive material by infiltrating water that can lead to a depletion of the barrier and consequently to possible subsidence issues (Verginelli et al., 2017). This issue can be overcome using a less soluble reactive material. For instance, the use of zero-valent iron as a filler material of HPRBs can represent an attractive alternative from both the leaching behavior and reactivity point of view. Indeed, zero-valent iron is a strong reducing agent that proved to be effective in treating PCE, TCE and other chlorinated solvents (Gavaskar, 1999). Over the past 30 years, zero-valent iron has been used successfully to remediate groundwater by construction of permeable reactive barrier (PRB) of zero-valent iron to intercept and dechlorinate chlorinated hydrocarbons such as TCE in groundwater plumes (Cook, 2009; Obiri-Nyarko et al., 2014; Fu et al., 2014). PRBs treat chlorinated solvents in groundwater due to dehalogenation by both abiotic or biotic processes. The abiotic process oxidizes the zero-valent iron and reduces the dissolved chlorinated solvents (ITRC, 2011). The process induces highly reducing conditions that promote substitution of a chloride atom with a hydrogen atom in the chlorinated solvent molecule (Arnold and Roberts, 2000).

Iron reacts with the chlorinated organic compounds through electron transfer, in which ethane and chloride are the primary products, as shown below for the degradation of TCE (ITRC, 2011):

$$3Fe^0 \rightarrow 3Fe^{2+} + 6e^- \tag{1}$$

$$C_2HCl_3 + 3H^+ + 6e^- \rightarrow C_2H_4 + 3Cl^- \tag{2}$$

$$3Fe^0 + C_2HCl_3 + 3H^+ \rightarrow 3Fe^{2+} + C_2H_4 + 3Cl^- \tag{3}$$

The two mechanisms generally considered for the dechlorination of chlorinated ethenes with zero-valent iron are the β-elimination and hydrogenolysis pathway (Roberts et al., 1996; Arnold and Roberts, 2000). The β-elimination pathway produces chloroacetylene intermediates, which are unstable and rapidly reduced to ethene (Campbell et al., 1997). The hydrogenolysis pathway is a slower reaction during which less-chlorinated intermediates are produced and subsequently degraded (Arnold and Roberts, 2000). β-elimination is the main pathway for dechlorination of TCE by zero-valent iron (Roberts et al., 1996). This conclusion is based on the fact that most of the products resulting from TCE reacting with iron are ethene, ethane and C1–C6 hydrocarbons which is consistent with the β-elimination pathway (Orth and Gillham, 1996). Usually, <10% by mole of TCE dechlorination byproducts are a DCE isomer or vinyl chloride, which are the expected products of the hydrogenolysis pathway (Gillham et al., 2010).

While the applicability of zero-valent iron for the treatment of TCE in aqueous solutions has been investigated from the early 1990s by several authors at both lab and field-scale (Obiri-Nyarko et al., 2014; Fu et al., 2014), to our knowledge, only a couple of studies are available in the literature focusing on the treatment of TCE in the gas phase (Uludag-Demirer and Bowers, 2001, 2003). In this paper, we report the results of some experimental tests aimed at assessing the feasibility of using granular iron to treat TCE vapors as filling material of HPRB. In particular, the reduction of TCE in gas phase by different types of zero-valent iron was examined in anaerobic batch systems performed at room temperature. Concentrations of TCE and byproducts were determined at discrete time intervals by analysis of the headspace vapors.

## 2. Materials and methods

### 2.1. Materials

Table 1 reports the main characteristics of the tested iron powders that were provided by Pometon S.p.A. (Maerne, Italy). Specifically, three types of iron powder called Ferblast MT, Ferelet MT and Ferelet RI, obtained with different manufacturing processes, were used. The iron Ferblast MT and Ferelet MT were attained by water atomization and sieving and is characterized by a controlled content of oxides, S and C. The iron Ferelet RI is similar to Ferelet MT but with added processing of annealing ($H_2$ furnace) to reduce the content of oxides. For the iron powders MT, two different particle size were used: iron powder with particle size lower than 850 μm (Ferblast MT 850) and lower than 425 μm (Ferelet MT 425). For the Ferelet RI, an iron powder with particle size lower than 425 μm (Ferelet RI 425) was used. Fig. 1 shows the particle-size distribution of the tested iron powders.

To obtain an oxide-free $Fe^0$ surface, in one set of experiments the Ferelet MT 425 was preliminarily washed with HCl 0.1 M for 30 min, then rinsed with $N_2$-purged water and dried in a $N_2$ atmosphere.

TCE (99 + %) used in the experiments was purchased from Sigma-Aldrich.

**Table 1**
Characteristics of the iron powders used in this work provided by Pometon S.p.A.

| Parameter | Unit | Ferblast 850 MT | Ferelet 425 MT | Ferelet 425 RI |
|---|---|---|---|---|
| Particle size – D90 | μm | 889 | 381 | 330 |
| Particle size – D50 | μm | 644 | 229 | 215 |
| Apparent density | g/cm³ | 3.7 | 3.69 | 3.68 |
| Oxides ($O_t$) | % | 0.49 | 0.87 | 0.15 |
| Carbon (C) | % | 0.038 | 0.039 | 0.001 |
| Sulphur (S) | % | 0.012 | 0.012 | 0.009 |