

Reduction of trichloroethylene in a reactive permeable wall containing iron and catalyst

Shian-chee Wu, Sen-tong Yung, Shu-fen Cheng
Graduate Institute of Environmental Engineering, National Taiwan University
Taipei, Taiwan 106, Republic of China

INTRODUCTION

Soil and groundwater pollution in Taiwan

The mass outbreaks of series of events of soil and groundwater pollution in Taiwan started back in early 1970s. The earliest renowned case resulted from the continuous discharging of industrial wastewater containing cadmium and lead into irrigation ditches in Taoyuan county in northern Taiwan. From 1977 till the water pollution control authority found that the rice fields, rice grains and the sediments in the irrigation channel contained high concentrations of these heavy metals in 1983, there were 83 hectares of rice fields having been contaminated. Many cases of soil contaminated by heavy metals were identified afterwards. Total area of soils known contaminated or suspected being contaminated with heavy metals is more than 790 hectares. It is believed that many sites have not been identified yet. Efforts have been paid for the remediation of these contaminated rice fields. Mixing the topsoil with clean lower layer of soil has been used to treat contaminated soils with relatively low metal concentration. There is no solution for cleaning up the soils containing high concentration of metals so far.

Groundwater provides about one quarter of the source of water supply in Taiwan. However, many supply wells had to be abandoned due to serious water quality deterioration resulted from contamination of the groundwater aquifers by leakage of storage tanks or illegal discharge of wastewater and dumping of industrial wastes. A famous case happened with the RCA electronic manufacturing factory. Since early 1970s, the workers in the plant dumped un-treated waste solvents in the company's backyard. Dense solvent liquid containing chlorinated hydrocarbons, e.g. trichloroethylene (TCE) and perchloroethylene (PCE), leached into the groundwater aquifer. The operation of the production was stopped in about 1992. The plant was sold to GE and Thomson. Soon, the site was bought by a local development company. In 1994 several groundwater wells were found contaminated by a variety of chlorinated organic compounds. Investigation revealed that 2000 m² of soils were contaminated, the contaminant plume in groundwater aquifer extended to 800 meters and the existence of dense non-aqueous phase liquid (DNAPL) was likely. GE and Thomson were asked to investigate the site and clean it up.

Contaminated soil was removed and piled on an aeration system consisting of a series of perforated pipes. Volatile pollutants were extracted by drawing air through the pile. Successful removal of contaminants was achieved in five months. The contaminated soils underneath the buildings were also cleaned by soil vapor extracting wells. However, pump-and-treat system failed to reduce the concentrations of pollutants in the monitoring wells after pumping for nine months. "Technology Impracticability" or "Natural Attenuation" has been proposed by GE and Thomson as possible alternatives but was not accepted by the Environmental Protection Administration, ROC.

between very low to 441 g/L. Further studies are necessary to understand the mechanisms controlling the reduction of TCE and to find the better recipe of the composite reactive material.

Evaluation of the feasibility of application on the RCA site

If funnel-and-gate remediation method were applied to the RCA site mentioned before and iron-Pd catalyst were used as the reactive reductive agent, the gate will be 30 m long and 10 m high. The required thickness of the permeable reactive wall is 0.5 cm for the effective reduction of the concentration of TCE, 10 mg/L initially, under groundwater flow velocity at 0.5 m/d and a safety factor of 4 to the clean-up standard, 0.1 mg/L. The cost of the permeable reactive material including iron, quartz sands and Pd-catalyst is totally 1.56 million NT dollars (about 45 thousand US dollars). If only iron were used in the permeable wall, the cost would be about ten times of that of iron-Pd catalyst system due to very large amount of iron powder used.

Summary

Platinum-coated catalysts showed excellent catalytic capability either with Al₂O₃-carrier or activated-carbon carrier. The half life of TCE was 5-10 hours or less than 1 hour, respectively. Columns packed with iron powder, catalytic metals and quartz sands were used to mimic the permeable reactive wall. The reductive-dechlorination rate coefficients are 7.79 hr⁻¹ and 15.7 hr⁻¹ for the columns with the platinum-coated catalyst content of 14.7g/L and 29.4 g/L, respectively. The permeable reactive barrier method could be an effective remediation approach on the RCA site in Taiwan if iron-Pd catalyst system would be applied.

References

- Appleton, E. L., 1996, A nickel-iron wall against contaminated groundwater, *Environ. Sci. Technol.*, 30, 536A-539A.
- Cheng, S. F. Wu, S. C., 2001, "Feasibility of using metals to remediate water containing TCE", *Chemosphere*, 43, 1023-1028.
- CH2M Hill Taiwan Branch, Aeration Completion Report, Taoyuan Site, prepared by CH2M Hill Taiwan Branch for General Electric Company and Thomson Consumer Electronics, April 1998.
- Day, S. R., O'Hannesin, S. F., and Marsden, L., 1999, Geotechniques for the construction of reactive barriers, *Journal of Hazardous Materials*, B67, 285-297.
- Environmental Impact Assessment Report, RCA Taoyuan Site for New Use, Hong-I Development Inc. Co., 2000.
- Grittini, C., Malcomson, M., Fernando, Q., Korte, N., 1995, Rapid dechlorination of polychlorinated biphenyls on the surface of a Pd/Fe bimetallic system, *Environ. Sci. Technol.*, 29(11), 2898-2900.
- Matheson, L. J., Tratnyek, P.G., 1994, Reductive dehalogenation of chlorinated methanes by iron metal, *Environ. Sci. Technol.*, 28, 2045-2053.
- Muftikian, R., Fernando, Q., Kote, N., 1995, A method for the rapid dechlorination of low molecular weight chlorinated hydrocarbons in water, *Water Res.*, 29, 2434-2441.
- O'Hannesin, S. F. and Gillham, R. W., 1998, Long-term performance of an in situ iron wall for remediation of VOCs, *Ground Water*, 36(1), 164-170.

RESULTS AND DISCUSSIONS

Batch tests of the reduction of TCE by Fe/Ni bimetallic system

Technical grade and analytical grade of both iron powder and nickel powder were tested. The results of the reduction of TCE at a concentration of 10mg/L by four different combinations of metals are shown in Fig. 2. Fe(B)/Ni(B) system shows the highest reductive potential where both metals are analytical grade. Technical grade iron, Fe(A), can substitute Fe(B) with about half of the reductive potential. Since the technical grade iron is much cheaper than the analytical grade iron, it is feasible to use technical grade iron in the field and achieve reasonable cost effectiveness.

Technical grade nickel, Ni(A), has no enhancing effect possibly because the nickel powders contain 0.05% of sulfur according to the element analysis report of the manufacturer. Sulfur is known to be toxic to the noble metal catalysts.

Batch tests of the reduction of TCE by iron and catalysts

Both Pd-Al₂O₃ and Pd-activated carbon have significant enhancing effect on the reduction of TCE (Fig. 3). With iron as a reductant and Pd on the surface of the porous supporting material as a solid catalyst, the TCE was effectively transformed in one hour. Pd(A), Pd-Al₂O₃, acts as a catalyst, therefore, has no reducing power by itself neither capability of removing TCE. Pd(B), Pd coated on activated carbon, exhibits some treatment capability possibly due to its adsorbing nature of the supporting material made of activated carbon. Some TCE may adsorbed on the supporting material instead of being degraded.

Reduction of TCE in the permeable reactive column

Iron with Pd- Al₂O₃ catalyst and quartz sands effectively removed TCE with an inflowing concentration at 10 mg/L and the linear flow rate ranging from 4.7 to 8.5 m/d. The dropping down of the TCE concentration depends on the residence time (i.e. the contact time with the reactive matrix) and looks like a first-order decay process (Fig. 4). Flow velocity has insignificant effect on the contact-time-dependent decay rate (data not shown). It seems that the time scale of the mass transfer of TCE across the boundary layer on the particle surface or through the intra-particle pores are all shorter than the time of contact or the reaction time.

Increasing the fraction of Pd-catalyst in the matrix raises the transformation rate proportionally (Fig. 4). By fitting the data with a time-dependent first-order decay model, we could quantify the reduction efficiency with the best-fit first-order rate constant. For the system with 14.7 g/L of Pd-catalyst the rate constant is 7.79 hr⁻¹, for that with 29.4 g/L of Pd-catalyst the rate constant is 15.7 hr⁻¹. There is a good linear relationship between the mass of Pd-catalyst and the reactivity. A second-order reaction model may better describe the reduction reaction.

The influence of the fraction of iron

Higher fraction of iron did not increase the reactivity of the composite permeable material (Fig. 5). With 235 g/L of iron powder, the first-order rate constant is 22.1 hr⁻¹ which is higher than that with 441 g/L of iron powder, 7.79 hr⁻¹. When replace all quartz sands with iron the reactivity was totally suppressed (data not shown). It is suggested that hydrogen molecules are produced on the iron surface and then attach and are activated on the Pd surface. However, excess hydrogen molecules may block all the active sites on the catalyst and inhibit the access of TCE to the catalyst. Optimum fraction of iron seem

Iron A	30-150	98.5%	Hoganas	W40.37 technical
Iron B	<200	99%	Riedel-deHean,	12310 analytical
Nickel A	200-500	99.8%	Westaim	SF200x500 technical
Nickel B	<100	99.99%	Acros	20390-4 analytical
Pd catalyst A	<325	1%Pd + 99%Al ₂ O ₃	Aldrich	20570-2 analytical
Pd catalyst B	<325	1%Pd + 99%activated carbon	Acros	19523-5 analytical
Quartz sands	300µm-850µm			

Batch tests

Different combination of metals and catalysts were added in a 15ml serum bottle. The serum bottle was then filled with water containing TCE and capped with Teflon lined septum and an aluminum crimp without any headspace. The mixture was shaken in a water bath at 35°C. After a certain period of time, the TCE concentration was analyzed with a headspace method with a gas chromatograph (HP5890II Hewlett Packard) equipped with an electron capture detector and a 30m x 0.53mm(ID) x 3.0µm (thickness) DB624 analytical column (J&W).

Column experiments

The apparatus for column experiment shown in Figure 1 was made of a glass column with an inner diameter of 5 cm, a total length of 60 cm and nine sampling ports on the side. The column was firstly filled with 3 cm of quartz sands from the bottom fritted glass plate then with 20 cm of the mixture of iron powder, Pd catalyst and quartz sands. The TCE aqueous solution was stored in a Teflon sampling bag and pumped into the column with a vermicular metering pump. During the experiment, a 10 ml syringe was used to periodically withdraw 5ml of liquid sample from the sampling port and the sample was immediately injected into a 15 ml brown serum vial, and sealed with an aluminum crimp cap with a Teflon faced septum. The vials were placed in a thermostat at 25°C for over 1 hour to let the compounds reach the equilibrium between the headspace and the aqueous phase. Five µl of the headspace gas was taken by using a glass gas-tight syringe, and then analyzed with a gas chromatograph. Design for the column experiments is shown in Table 2.

Table 2. The design of column experiments

Exp. No.	Content of quartz sand (g/L)	Content of iron powder (g/L)	Content of Pd catalyst (g/L)	Porosity	Linear flow rate (m/d)
1	1470	441	14.7	0.36	4.7
2	1470	441	14.7	0.36	6.3
3	1470	441	14.7	0.36	8.5
4	1470	441	29.4	0.36	6.3
5	0	4680	14.7	0.41	6.3
6	1470	235	14.7	0.39	6.3

Similar DNAPL contamination cases occurred in several locations, including Scientific Industrial Park in Hsin-Chu County, a VCM factory in Miaow-li County and Philip Electronics in Hsin-Chu County.

Other major sources of soil and groundwater pollution are illegal hazardous waste dumping sites. Six sites were classified as “imminent hazard” out of 150 unknown dumping sites investigated in 1999. Soils and groundwater aquifers were polluted by the leachate from the wastes containing heavy metals and toxic organic compounds. Also, about 10% of the 2062 gasoline stations in addition to Kaohsiung refinery complex and several oil storage facilities have leaking and contamination problems.

Reactive permeable wall as a possible solution of DNAPL contamination of groundwater

Since active treatment methods (e.g. pump-and-treat) for halogenated hydrocarbons in groundwater has difficulties due to the high specific density, low biodegradability and low solubility of these compounds, passively treating the contaminant plume with permeable reactive barriers combined with a water-flow guiding system becomes an attractive alternative. The permeable wall is constructed in front of the plume with active reductant, oxidant or substrate for microorganisms. When the groundwater flows through the wall the pollutants will be degraded or transformed to other compounds. The advantages of the permeable reactive barriers methods are low operating cost, low energy consumption and continuous use of the land surface (Day et al., 1999).

Reduction of chlorinated hydrocarbon by iron

Zero valence iron granules have been reported to have capability to reduce dissolved chlorinated hydrocarbons and remove chlorine from the compounds (O’Hannesin and Gillham 1998). The reductive dechlorination reaction by iron has two possible path ways (Matheson and Tratnyek, 1994). In the first path way, chlorinated compounds are adsorbed on the metal surface and electrons are transferred from the iron directly to the compounds, which results in the reduction and replacement of chlorine atom with a hydrogen atom. However, there is another pathway in which hydrogen is produced from the reduction of water by metal iron, then hydrogen and chlorinated compounds react on the surface of a catalyst and produce a compound with lower number of chlorine and a free chloride ion.

Adding noble metals (e.g. nickel, palladium, and platinum) in iron have been found to have significant enhancing effect on the dechlorination reaction (Muftikian et al., 1995; Grittini et al., 1995; Appleton, 1996; Chen, 2001). Searching for better catalysts, raising the treatment efficiency and lowering the construction cost of the permeable reactive barrier are necessary for the application of this technique in the field. The purpose of this study was to investigate the effect of adding some metals or catalysts in the iron matrix and to identify possible reaction mechanisms and the optimum ratio of catalysts to iron granules.

MATERIALS AND METHODS

Materials

Analytical grade trichloroethylene was dissolved in methanol as stock solution (10000mg/L) and further diluted with Milli-Q reagent water to a desired aqueous concentration. The metals and catalysts used in the experiments are listed in Table 1.

Table 1. Reactive materials used in the experiments

Name	Particle size mesh	purity	Manufacturer	Lot No., Grade

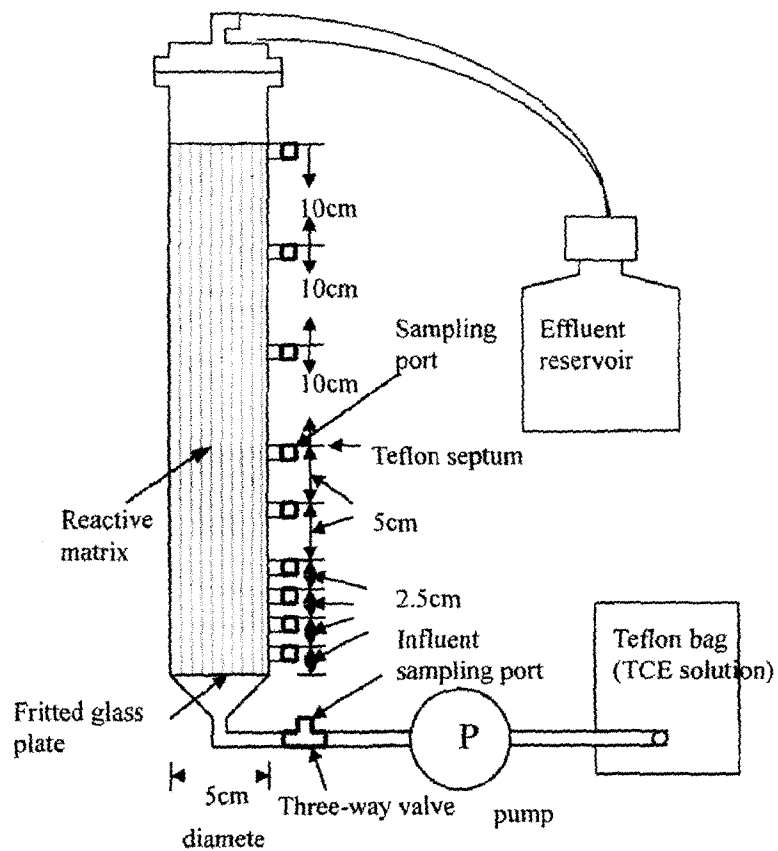


Figure 1. Apparatus of column

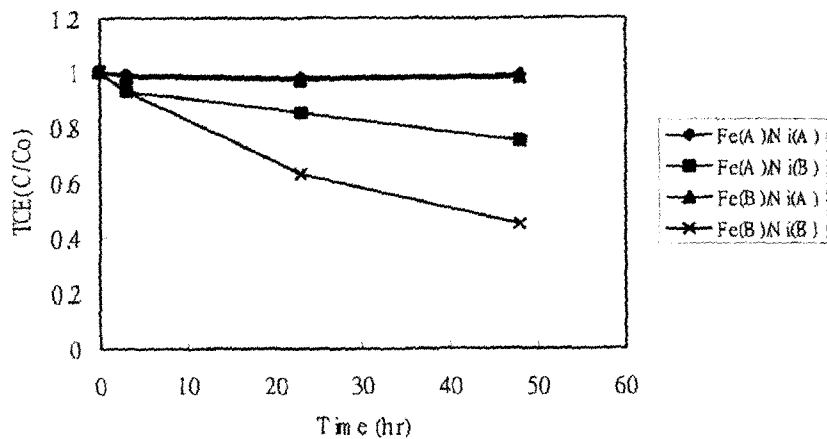


Figure 2. Reduction of TCE, at initial concentration of 10 mg/L, by different combination of 3 gm of iron and 3 gm of nickel powders. Fe(A), Fe(B), Ni(A) and Ni(B) represent technical grade iron, analytical grade iron, technical grade nickel and analytical grade nickel, respectively. The vertical coordinates is the TCE concentration normalized with the initial concentration.

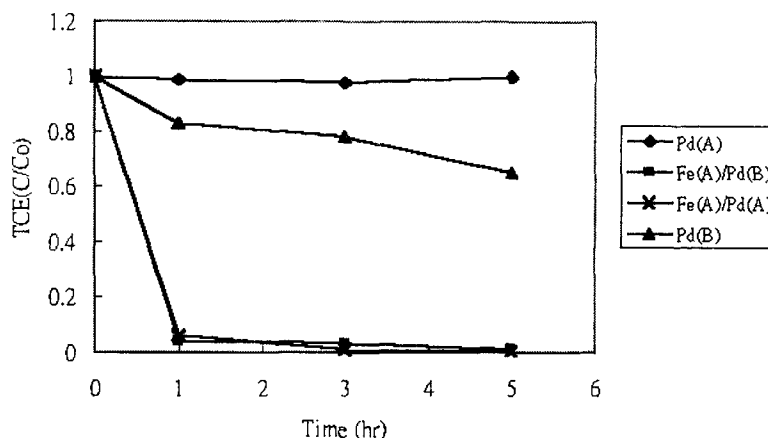


Figure 3. Reduction of TCE, at initial concentration of 10 mg/L, by different combination of 3 gm of technical grade iron with 0.05 gm of Pd catalyst. Fe(A), Pd(A) and Pd(B) represent technical grade iron, Pd catalyst based onsluminum oxide and Pd catalyst based on activated carbon, respectively. The vertical coordinates is the TCE concentration normalized with the initial concentration. Symbles of Pd(A) and Pd(B) represent blanks without iron powders.

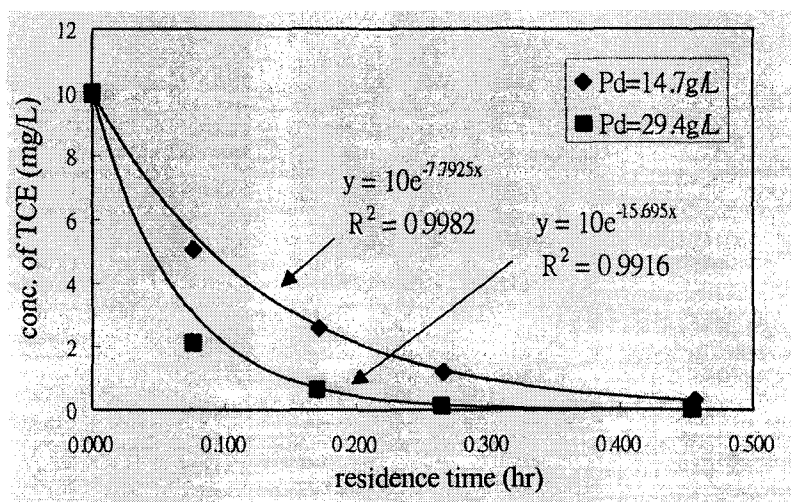


Figure 4. The effects of the dose of Pd-Al₂O₃ catalyst on the degradation of TCE with inflowing concentration at 10 mg/L in permeable reactive column. The flow rate of the TCE solution is 6.3 m/d, iron powder content is 441 g/L, quartz sands is 1470 g/L, Pd catalyst is either 14.7 g/L or 29.4g/L. The symbols represent experimental data. The solid lines are the simulation results with the first-order decay model.

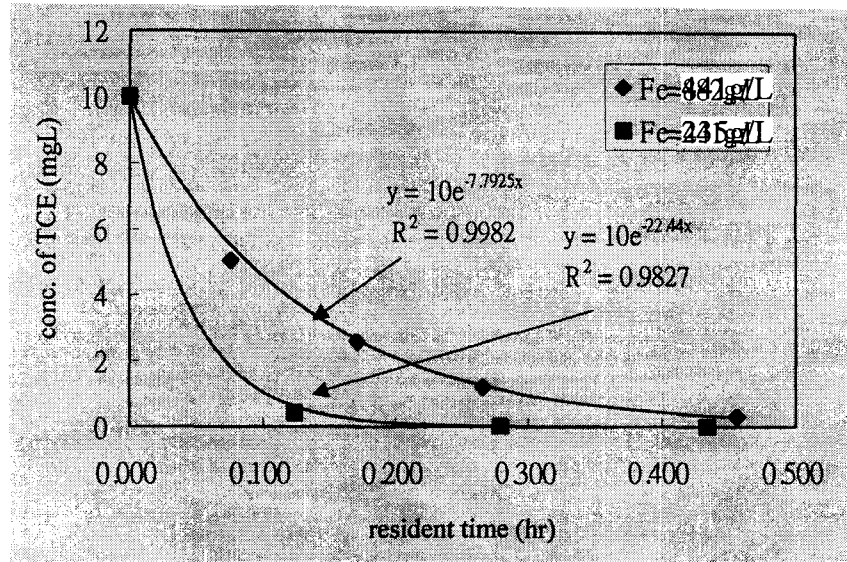


Figure 5. The effects of the dose of iron powders on the degradation of TCE with inflowing concentration at 10 mg/L in permeable reactive column. The flow rate of the TCE solution is 6.3 m/d, iron powder content is 441 g/L or 235g/L, quartz sands is 1470 g/L and Pd catalyst is 14.7g/L. The symbols represent experimental data. The solid lines are the simulation results with the first-order decay model.