Permeable Reactive Barriers (Proceedings of the International Symposium held at Belfast, Northern Ireland, March 2004). IAHS Publ. 298, 2005.

Cost-effectiveness of *in situ* treatment of multiple contaminant mixtures in groundwater by means of sequenced units of zero valent iron and granular activated carbon

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Abstract This modelling study reveals that the sequential use of zero valent iron (ZVI) and granular activated carbon (GAC) can potentially be used for *in situ* treatment of groundwater with multiple contaminant mixtures, but crucial design rules should be followed, since the performance of the combined system depends on the interplay of both reactor units. As an example a mixture of aliphatic chlorinated hydrocarbons (PCE, TCE, and *cis*-DCE) and one aromatic chlorinated hydrocarbon (monochlorobenzene) is considered. The results show that the concentrations of less sorbing compounds such as *cis*-DCE have to be reduced in the ZVI reactor far beyond the desired maximum contaminant level in order to restrict concentration build-ups in the GAC reactor, which occur due to competitive sorption with contaminants withheld in the GAC. Results from reactor modelling studies are used to economically analyse feasible reactor designs. Cost-optimal ZVI-GAC combinations are derived by a general approach based on unit cost ratios.

Key words competitive sorption; dechlorination; economic assessment; granular activated carbon; permeable reactive barriers; pore surface diffusion model; zero-valent iron

MOTIVATION

Only in some instances are contaminant plumes characterized by the occurrence of one unique type of pollutant. In the case of a mixture of contaminants, especially if they span a broad range of physico-chemical properties, the treatment of groundwater can be a challenge. Selection of granular activated carbon (GAC), which is suited for nearly all organic compounds, might be a proper choice if a robust system applicable for complex VOC mixtures is desired. Alternatively, recent developments support combinations of a number of specified technologies such as sequential treatment technologies with zero valent iron (ZVI), bioreactors and granular activated carbon (GAC; Fiorenza *et al.*, 2000; Bell *et al.*, 2003). However, as groundwater passing through reactive media is chemically altered, treatment performance of any sequenced media may be strongly influenced by preceding treatment units. Hence, one has to be careful in addressing combined clean-up technologies as straightforward combinations of the single technologies.

The presented study discusses design considerations for the sequential use of ZVI and GAC for sanitation of groundwater contaminated by a mixture of aliphatic and aromatic chlorinated hydrocarbons. The coupling of a ZVI reactor and a GAC reactor is a promising combination for the clean-up of groundwater contaminated by organics being either suited for sorptive removal or abiotic degradation (Köber *et al.*, 2001; Kouznetsova *et al.*, 2003). Here a four-compound system consisting of monochlorobenzene (MCB), perchloroethylene (PCE), trichloroethylene (TCE), and *cis*-dichloroethylene (*cis*-DCE) is considered. MCB is assumed to be not subject to degradation within the ZVI unit and thus GAC has to be coupled to the outlet of the ZVI-reactor to completely clean up the groundwater. We use a modelling framework to simulate relevant degradation and sorption processes, as well as to glance at contaminant concentrations at the interface between both reactors. The modelling results for a hypothetical scenario serve as the basis for an exemplary economic calculation in order to reveal crucial design criterions of the combined system.

MODELLING TOOLSET

The ZVI reactor model simulates the pseudo-first order degradation mechanism which is typical for low to medium concentrations (<200 µMol according to Wüst *et al.*, 1999) of contaminants such as chlorinated ethenes. The comprehensive reaction framework describing the dechlorination from perchloroethylene (PCE) to trichloroethylene (TCE), dichloroethylenes (DCE), vinyl chloride (VC) and finally ethane is given by Arnold & Roberts (2000). Within this study**,** a reduced model is used, which focuses on the main hazardous compounds PCE, TCE and *cis*-DCE (Bayer, 2003). For the presented generic study, VC and further DCE isomers are not considered but may play an important role in other cases.

The outflow of the ZVI reactor represents the inflow of the GAC reactor, which is modelled by the pore surface diffusion model described by Crittenden *et al.* (1986). It incorporates the main kinetic processes of single and multiple contaminant sorption on GAC. Competitive sorption, which leads to displacement of less sorbing compounds in favour of better sorbing compounds, is simulated based on the ideal adsorbed solution theory (IAST).

The model toolset is applied to a hypothetic example. The abovementioned four-compound system is to be treated to reach maximum contaminant levels (MCL = $10\ \mu g\ l^{-1}$) at the outlet of the combined reactor.

Influent concentrations of PCE, TCE, and monochlorobenzene are set to C_i = $100\ \mu g\ l^{-1}$. Three cases are distinguished with *cis*-DCE concentrations of $C_{cis\text{-}DCE}$ = 0, 1, 10 and $100\ \mu g\ l^{-1}$ (Fig. 1). These are selected in order to highlight the relevance of

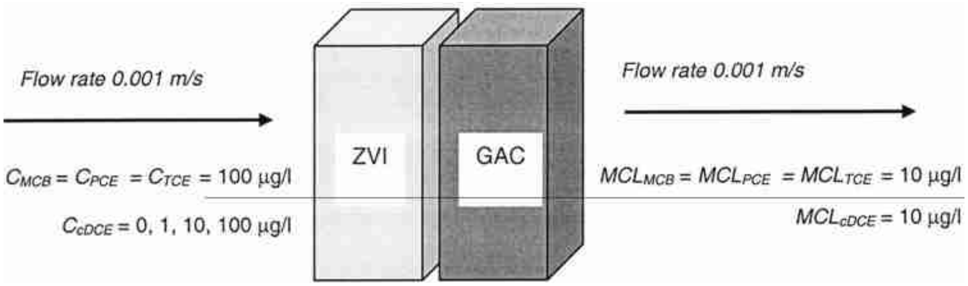

Fig. 1 Configuration of confined reactor with considered contaminant inflow concentrations (C_{PCE}, C_{TCE}, C_{DCE}, C_{MCB}) and target concentrations (MCL_{PCE}, MCL_{TCE}, MCL_{DCE}, MCL_{MCB}).

Table 1 Degradation rate constants, production rates and sorption parameters (Thiem *et al.*, 2000) used in the study.

Contaminant		Rate constant	Freundlich isotherm parameters	
		k_i(h^{-1})	K_F (µmol g^{-1})(l µmol^{-1})^{nF}	n_F
monochlorobenzene	MCB		341	0.4
perchlorothylene	PCE	0.3527	310	0.52
trichloroethylene	TCE	0.5694	111	0.59
cis-dichloroethylene	*cis*-DCE	0.0432	38	0.53
production rates				
PCE → TCE	$^{\kappa}$PCE,TCE	0.137		
PCE → *cis*-DCE	$^{\kappa}$PCE,cDCE	0.015		
TCE → *cis*-DCE	$^{\kappa}$TCE,cDCE	0.262		

this compound, which occurs as a by-product (breakdown product) in the ZVI reactor and has a relatively low sorptivity. The considered degradation and production rates for treatment with ZVI as well as the Freundlich parameters describing the sorption on GAC are listed in Table 1. The volumetric flow rate of the groundwater to be treated is set constant at 0.001 m^3 s^{-1} over a planning period of 10 years.

RESULTS

Feasible designs of the sequenced ZVI-GAC reactor are determined for a range of ZVI volumes, V_{ZVI}, from 0 to 750 m^3. If V_{ZVI} is insufficient to properly reduce the concentrations of the chlorinated ethenes, GAC can be used to collect the surplus. This means that for every V_{ZVI} a GAC volume V_{GAC} exists, which is necessary to reach the MCLs at the combined reactor outlet. At first glance this aspect seems to be an advantage of the combined system.

Figure 2(a)–(d) depicts the V_{ZVI}–V_{GAC} trade-offs for each contaminant. The envelope of all contaminant-specific trade-off curves defines the required V_{GAC} for any given V_{ZVI}. Figure 2(a) reveals that the relatively low sorptivity of *cis*-DCE controls the V_{GAC} over a wide range of given V_{ZVI}. It is evident that due to the high production rate of *cis*-DCE this appears even if this contaminant is not in the influent water. Raising the influent concentration of *cis*-DCE beyond 1 µg l^{-1} (Fig. 2(c)–(d)) leads to a significant rise of V_{GAC} if the ZVI unit ahead insufficiently decreases the concentration of *cis*-DCE before it reaches the GAC reactor.

One central aspect for the design of the combined reactor is illustrated for the case with no *cis*-DCE in the groundwater to be treated. Figures 3(a–d) show concentration breakthrough curves within the operation time of $T = 10$ years and for a constant GAC volume of $V_{GAC} = 1$ m^3. Increasing V_{ZVI} from 0 m^3 to 35 m^3 results in less pronounced and delayed breakthroughs of the higher chlorinated PCE and TCE. Contaminant *cis*-DCE, produced in the ZVI unit, surmounts the given MCL of 10 µg l^{-1} after approximately one year. A significant further rise of V_{ZVI} to 178 m^3 can mitigate the *cis*-DCE concentration at the ZVI-outlet to MCL, but due to competitive sorption in the GAC reactor the attained degradation is still insufficient. Contaminant *cis*-DCE is desorbed in the GAC due to the occurrence of the better sorbing MCB and consequently shows concentrations beyond MCL at the GAC outlet after nearly 2 years. Though in

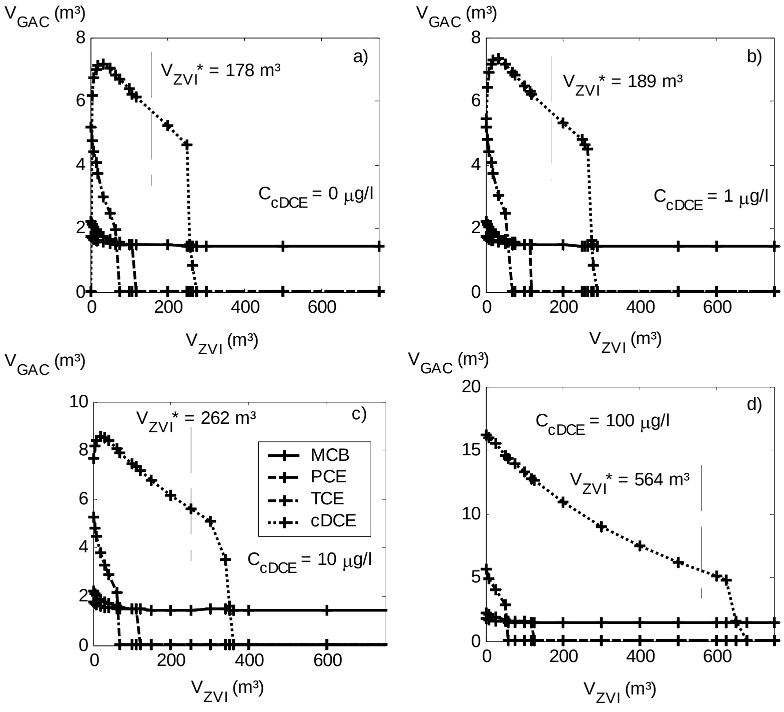

Fig. 2 Required Volume of GAC (V_{GAC}) as a function of ZVI volume (V_{ZVI}) and contaminant influent concentrations ($C_{MCB} = C_{PCE} = C_{TCE} = 100$ µg/l, $C_{cDCE} = 0, 1, 10, 100$ µg l^{-1}) for an operation time of 10 years and a constant flow rate of 0.001 m^3 s^{-1}. Vertical dashed lines indicate threshold values, V_{ZVI}^{*}, for which all contaminant MCLs are met at the ZVI outlet.

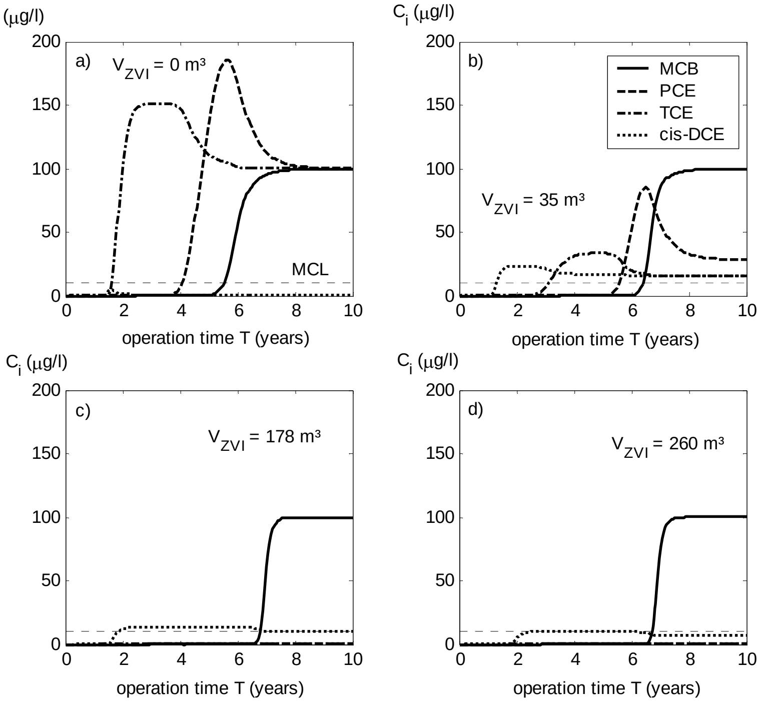

Fig. 3 Concentration breakthrough of contaminants at the GAC reactor outlet for volume of GAC $V_{GAC} = 1$ m^3 and variable volumes of ZVI $V_{ZVI} = 0, 35, 178,$ and 260 m^3.

this case the concentration of *cis*-DCE is only slightly above MCL over the rest of the operation time, V_{ZVI} has to be raised further to 260 m³ in order to meet the MCL. The threshold values, V_{ZVI}^*, for which all contaminant MCLs are reached at the ZVI outlet are given in Figure 2 for all scenarios considered. It is obvious that independent of the influent *cis*-DCE concentration the ZVI reactor has to be overdesigned to ensure that *cis*-DCE is not critical to the required GAC volume. The results indicate that the additional volume of ZVI needed is approximately independent of the influent concentration of *cis*-DCE and amounts to about 80 m³.

ECONOMIC CONSIDERATIONS

In order to determine the cost-optimal reactor configuration, i.e. the lowest price $V_{ZVI} – V_{GAC}$ combination, a main decision variable is the desired lifetime of the GAC reactor. The required GAC volume has been calculated for lifetimes of 1, 2.5, 5 and 10 years (number of fillings: 10, 4, 2 or 1, respectively). Figure 4 shows the corresponding $V_{ZVI} – V_{GAC}$ trade-offs (envelopes subsuming the contaminant-specific design curves). The resulting total volume of GAC required within a planning period of 10 years is not exactly the same for all strategies as depicted in Fig. 5. Lower lifetimes mean a minor accumulation of *cis*-DCE in the GAC, which effects a slightly lower GAC volume V_{GAC} if given V_{ZVI} is below 100 m³. For $V_{ZVI} > 100$ m³, the reduction of V_{GAC} is attributed to the marginal flattening of the concentration breakthrough curves with raised GAC life.

Discounting future costs gives net present values accounting for interest earnings. Assuming a discount rate of 5%, expenditures decrease especially for high number of refills, where payments occur in later stages of the planning period. We express these savings through V_{GAC} equivalents reflecting the required total V_{GAC} minus the relative discount (Figure 6). The ideal combined system is then given by the relative material costs for ZVI and GAC. Due to the characteristic form of the $V_{ZVI} – V_{GAC}$ (equivalent) curves, a threshold value u of the unit costs ratio r = (price of ZVI per m³)/(price of

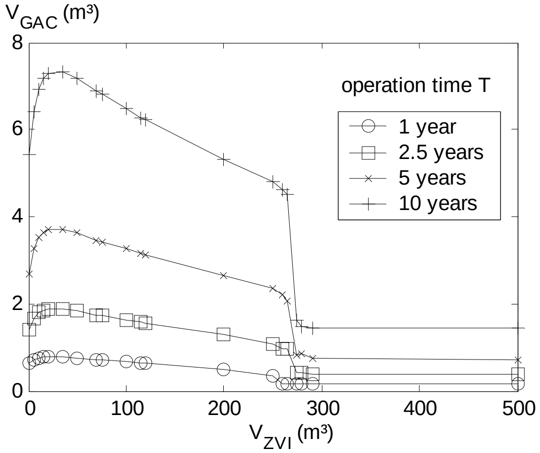

Fig. 4 Required volumes of GAC and ZVI to comply with target concentrations of all contaminants at the combined reactor outlet for four different operation times T, i.e. life times of GAC reactor (1, 2.5, 5, 10 years).

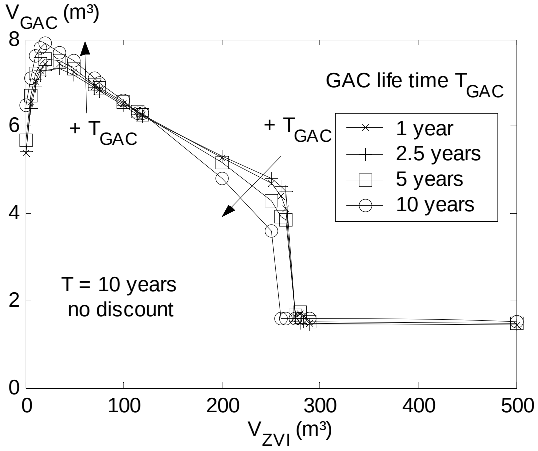

Fig. 5 Summarized total volume of GAC, V_{GAC}, for operation time of 10 years depending on the number of fills (i.e. life time of GAC reactor). Results given for the combined reactor.

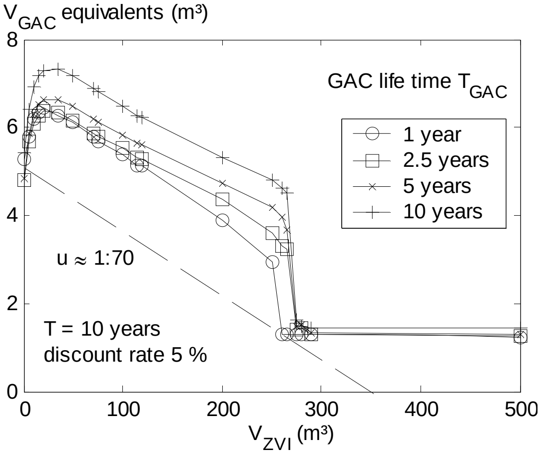

Fig. 6 Summarized total GAC volume equivalents for an operation time of 10 years if discounting is considered (see Fig. 5 for results without discounting). Dashed line represents cost isoline for a given ratio of unit ZVI costs and unit GAC costs of 1:70.

GAC per m³) can be derived which distinguishes between two alternative reactor configurations. If *r* is below *u*, the use of a single GAC unit is favourable. Higher values yield a combined system as the optimum, which should be designed such that the least sorbing compound (*cis*-DCE) is not critical at the GAC reactor outlet. For the selected example, *u* scores 1:70 which virtually prefers the use of solely GAC.

CONCLUSIONS

The results for the $V_{ZVI} - V_{GAC}$ trade-offs for the selected example case illustrate the interference of ZVI- and GAC-specific processes. Chlorinated ethenes can be degraded by ZVI or sorbed in the subsequent GAC reactor, enquiring which material is ideal to be used for each specific contaminant. Apparently, the answer is governed by the given (relative) values of degradation rates and sorption parameters. If the treatability of contaminants is similar for both materials such as in the presented study, some secondary reactor-specific processes appear to be relevant design criterions. In the selected example both treatment options are less suited for *cis*-DCE than for the other ethenes, denoting that the occurrence of *cis*-DCE as a byproduct in the ZVI reactor determines required material volumes even if it is not in the influent groundwater. Since the sorption capacity of this contaminant is lower than for the competing compounds, accumulated *cis*-DCE may be desorbed in the GAC and exhibit critical breakthrough concentrations above the given target levels although its concentration was uncritical at the interface between ZVI and GAC. Obviously, the combination of ZVI and GAC would be more effective if opposite treatability trends exist, e.g. if degradation rate constants of the compounds decline and sorptivity rises with increasing chlorination.

Since the modelling results considerably depend on the material-specific conditions, the derived economically optimal system is only valid for the presented individual case. The demonstrated concept based on unit prices, however, is a straightforward and generally applicable method to identify low cost options. In practice, further aspects such as expenditures for reactor construction and material replacement need to be considered.

Acknowledgements Funding for this study has been provided by the German Department of Education, Science, Research and Technology (BMBF), Contracts no. 02WT0019 and No. 02WR0195.

REFERENCES

Arnold, W. A., Roberts A. L. (2000) Pathways and kinetics of chlorinated ethylene and chlorinated acetylene reaction with Fe(0) particles. *Environ. Sci. Technol.* **34**(9), 1794–1805.

Bayer, P. (2003). *Modelling, economic assessment and optimisation of in-situ groundwater remediation systems*. PhD thesis, Center for Applied Geosciences, University of Tuebingen., Germany.

Bell, L. S. J., Devlin, J. F., Gillham, R. W. & Binning, P. J. (2003). A sequential zero valent iron and aerobic biodegradation treatment system for the degradation of nitroaromatics. *J. Contam. Hydrol.* **66**, 201–217.

Crittenden, J. C., Hutzler, N., J., Geyer, D., Oravitz, J. L. & Friedman, G (1986): Transport of Organic Compounds With Saturated Groundwater FLOW: Model Development and Parameter Sensitivity. *Water Resour. Res.* **22**(3), 271–284.

Fiorenza, S., Oubre, C. L., Ward, C. H. (2000). *Sequenced Reactive Barriers for Groundwater Remediation*. Lewis Publishers, Boca Raton, Florida, USA.

Köber, R., Schäfer, D., Ebert, M. & Dahmke A. (2001) Coupled in-situ reactors using Fe^0 and activated carbon for the remediation of complex contaminant mixtures in groundwater. In: *Groundwater Quality: Natural and Enhanced Restoration of Groundwater Pollution* (ed. by S. F. Thornton & S. E. Oswald). (Proc. Third Int. Conf., Sheffield, UK), 435–439. IAHS Publ. 275. IAHS Press, Wallingford, UK.

Kouznetsova, I., Bayer, P., Birk, S., Liedl, R. & Finkel, M. (2003) Numerical modelling of the sequenced use of zero valent iron and activated carbon for in-situ groundwater remediation. In: *FZK/TNO Conference on Contaminated Soil* (Proc. Eighth Int. Conf., Gent, Belgium), 932–941.

Tiehm, A., Schulze, S., Böckle, K., Müller, A., Lorbeer, H. & Werner, P. (2000) Elimination of Chloroorganics in a Reactive Wall System by Biodegradation on Activated Carbon. In: *FZK /TNO Conference on Contaminated Soil* (Proc. Seventh Int. Conf., Leipzig, Germany), 924–931.

Wüst, W. F., Köber, R., Schlicker, O. & Dahmke, A. (1999) Combined zero- and first-order kinetic model of the degradation of TCE and cis-DCE with commercial iron. *Environ. Sci. Technol.* **33**(23), 4304–4309.