

## Laboratory tests for reactive barrier design

Alexandre Duarte Gusmão<sup>a,\*</sup>, Tácio Mauro Pereira de Campos<sup>b</sup>,  
Manoel de Melo Maia Nobre<sup>c</sup>, Eurípedes do Amaral Vargas Jr.<sup>b</sup>

<sup>a</sup> Department of Civil Engineering, University of Pernambuco and CEFET/PE, 52021, Brazil

<sup>b</sup> Pontifical Catholic University of Rio de Janeiro, Rio de Janeiro, Brazil

<sup>c</sup> Federal University of Alagoas and Maia Nobre Engineering, Brazil

### Abstract

Owing to limitations of pump-and-treat, several technologies are being investigated for groundwater treatment. One of the most promising is the treatment of contaminants through the use of reactive barriers installed in situ, especially in the case of aquifers contaminated with chlorinated solvents. This work presents results of batch and column tests with metallic iron and some chlorinated solvents (1,2-DCA, 1,1,2-TCA and TCE). Such tests provided means to evaluate the degradation rates of these compounds and their byproducts. It is concluded that the reductive dechlorination with metallic iron can have different results, depending on the type of contaminant. Some contaminants may not present any degradation, or they have a half-life time so high that the use of the reactive barrier technology may not be practical. Furthermore, the formation of chlorinated byproducts, eventually more toxic than the original contaminant and that are not degradable using this same technology, emphasises that the treatment of aquifers should be sequential.

© 2004 Elsevier B.V. All rights reserved.

**Keywords:** Groundwater; Reactive barrier; Soil remediation; Chlorinated solvents; Zero-valent iron

### 1. Introduction

Groundwater is the unique source of drinking water for a large number of people in the world, especially in rural areas. In Brazil, reliable statistics on the use of groundwater does not exist yet, but it is considered that some 15–20% of the consumed water comes from aquifers. And there is a cognisance that the use of groundwater is increasing more and more. Disordered use and occupation of urban sites has been one of the main causes of aquifers contamination, promoting not just damages to the environment, but also serious negative socio-economic impacts.

Underground contamination with hazardous wastes has been one of the largest environmental problems in several countries, with many industrial sites presenting groundwater contamination. The sources of contamination can be of several types and act together or separately (e.g. septic tanks, landfills, tailing dams and industrial leaks).

In a problem of aquifer contamination, the first engineering remediation measure usually comprises the implementation of control systems, aiming both the immobilisation of the source of contamination and the control of the dissolved plume. Control systems, including pump-and-treat, are effective in the prevention of migration of plumes, through the use of pumping wells (hydraulic barriers), including or not physical contention. Such systems however, have several limitations if used isolated, especially in the case of aquifers contaminated with non-aqueous phase liquids (NAPLs).

The modern conception of aquifer treatment shows that additional techniques of remediation, especially in situ treatments, should be planned, investigated and implemented besides the control systems, seeking to accelerate the process of removal of the mass of contaminants in the groundwater.

In theory, the use of in situ reactors presents a series of advantages in relation to pump-and-treat, especially because of their low operation and maintenance costs. Being a passive type of treatment, they also do not require continuous supply of energy.

Among such techniques, one of the most promising is the use of reactive barriers that have been used in aquifers contaminated with chlorinated aliphatic organic compounds, also known as chlorinated solvents. These substances are

\* Corresponding author. Tel.: +55-81-3241-5964;  
fax: +55-81-3241-7576.

E-mail addresses: gusmao.alex@ig.com.br (A.D. Gusmão),  
tacio@xiv.puc-rio.br (T.M.P. de Campos), manoelmaia@uol.com.br  
(M.d.M.M. Nobre), vargas@xiv.puc-rio.br (E.d.A. Vargas Jr.).

one of the main anthropogenic sources of groundwater contamination in different countries in the world.

This paper presents the results of batch and column tests with metallic iron and some chlorinated solvents (1,2-dichloroethane, 1,1,2-trichloroethane and trichloroethylene), that allowed an evaluation of the degradation rate of these compounds and their byproducts. It is shown that, depending on the type of contaminant, different results occur in response to the reductive dechlorination with metallic iron.

## 2. Passive in situ treatment

Unlike other traditional geotechnical areas, the practice of groundwater on-site remediation started to show some development only in 1970s. Ever since then it has been experiencing an accelerated growth on both information and knowledge on the efficiency and limitations of different applied techniques.

Limitations observed in the use of techniques such as the pump-and-treat, promoted an increase in the development of research and applications of new technologies, especially in situ treatments for use together with systems of control of migration of dissolved plume. Fig. 1 shows a sketch of one of such techniques, more specifically, the use of a passive barrier for groundwater treatment.

On the other hand, the great demand for more effective remediation strategies caused the use of emergent technologies without a rigorous and independent evaluation of their application effectiveness. In fact, some techniques presently available in the market have been exposed as being “miraculous”, able to provide complete remediation of contaminated sites. However when there is a mixture of different contaminants in a given site (common situation), any technique may show serious application limitations. Even in cases where the source

comprises only one type of contaminant (particularly an organic one), its byproducts may not be easily eliminated by the same remediation process. Thus, it is evident that an aquifer treatment may require simultaneous or sequential use of different remediation processes, like it happens in the treatment of surface water.

In the case of in situ treatment, a very significant progress has been observed in the research area from the beginning of 1980s, particularly in the adaptation of techniques of treatment of surface water to the treatment of groundwater.

### 2.1. Use of zero-valent metals in the degradation of chlorinated solvents

According to Gillham and O’Hannesin [1], the first registration of the use of zero-valent metals in the degradation of organic contaminants was a patent requested by Sweeny and Fischer [2], in which granular zinc was used for degradation of pesticides. Although the results obtained were quite promising, there was no noticeable advance on such types of research in the scientific community.

At the end of 1980s, the University of Waterloo began studies related to the use of zero-valent metals in the degradation of chlorinated solvents, and its application in the remediation of aquifers. The research included laboratory experiments and instrumented prototype field tests at their experimental site in the Canadian Forces Base at Borden, Ontario.

The first laboratory experiments included batch tests using different contaminants and different metals. Fig. 2 shows the results of degradation of 1,1,1-trichloroethane in the presence of different metals [1]. The shape of the curve suggests that the degradation of the contaminant can be simulated through a reaction of first order. Results obtained for some

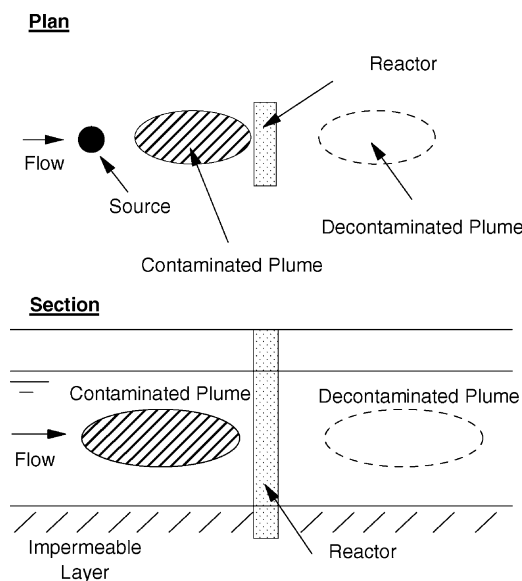


Fig. 1. Passive in situ treatment of groundwater.

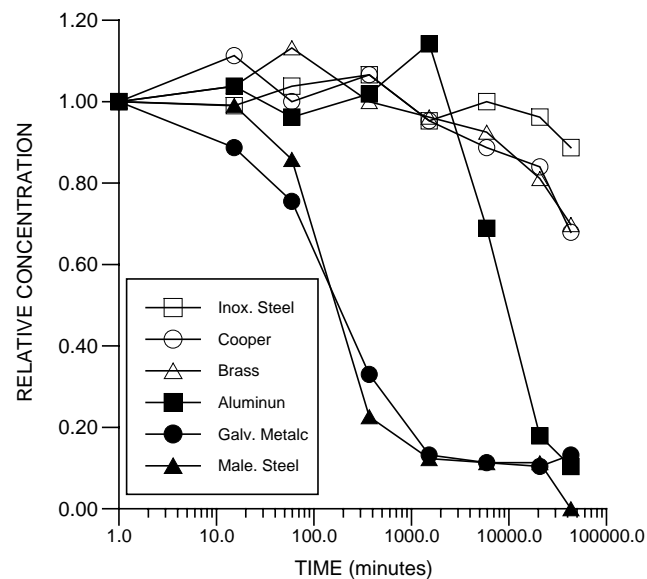


Fig. 2. Variation of the concentration of the 1,1,1-trichloroethane along time [1].

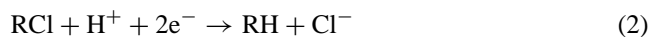
metals showed degradation rates of 3–6 orders of magnitude greater than those observed under natural abiotic conditions, evidencing that the process can significantly accelerate the degradation of chlorinated solvents in groundwater.

In spite of the research involving the use of different metals in reactive barriers, most of the applications have been made with the zero-valent iron. The main advantages of the use of the iron are its readiness in industrial scale, competitive prices and smaller environmental impacts.

Another research line encompasses the use of other metals together with iron in the degradation of chlorinated solvents, such as the iron–nickel mixture and iron–palladium. Some works have shown that this association of iron with other metals can increase degradation rates and decrease concentrations of the chlorinated byproducts.

## 2.2. Mechanism of degradation

The exact mechanism of degradation of chlorinated solvents in presence of iron or other metals is not fully known. The hypothesis better accepted is that there is a reductive dechlorination of the contaminant coupled with corrosion of the iron (Eq. (3)). The iron is oxidised (it gains electrons) while the contaminant (RCl) is reduced (it wins electrons). The reaction happens with the transfer of electrons from the surface of the metallic iron to the contaminant [3].



It is important to mention that the reaction presupposes the formation of a plume of dissolved iron ( $\text{Fe}^{2+}$ ) downstream of the barrier, besides the increase of the chloride concentration ( $\text{Cl}^-$ ). These environmental impacts should be evaluated properly in the design of the reactive barrier.

## 3. Design of reactive barriers

The passive treatment of contaminants comprises the execution of an in situ permeable barrier (reactor) ahead of the path of the contamination plume. As water passively flows through the reactor and the contaminants are degraded, consequently minimising or avoiding contamination of the aquifer downstream the barrier. This degradation can involve physical, chemical and biological processes.

The reactive barriers are dug to the required depth. The fill should be made with the reactive material up to water table level. From this depth to the surface, the barrier can be refilled with the excavated material. The depth of the barrier depends on the plume contamination. For the case of plumes that extend to the base of the aquifer, as it is the case of the contamination with DNAPLs, the barrier should be constructed to the full thickness of the aquifer. If, however,

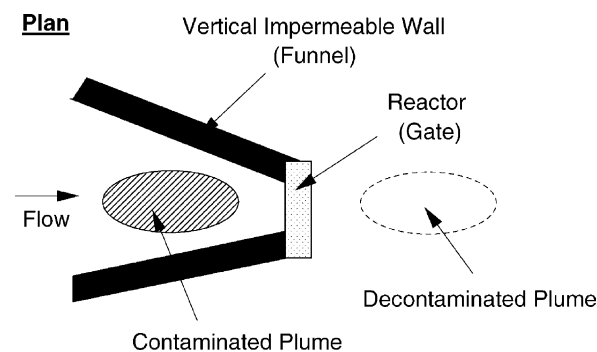


Fig. 3. Funnel-and-gate technique.

the plume occupies the superficial part of the aquifer, as it is the case of contamination with LNAPLs, the barrier does not need to be carried to the base of the aquifer.

The thickness of the barrier depends on the influent and effluent concentration of the contaminant, degradation rate, flow velocity and coefficient of dispersion of the barrier. For the complete remediation of the plume, the reactive barrier should be large enough so that the whole plume can reach and pass through it. Alternatively, the reactive zone or zones can be installed combined with impermeable walls forming what is known as a funnel-and-gate type of barrier (Fig. 3).

The design methodology for a reactive barrier is similar to methodologies used in conventional geotechnical design, with some peculiarities. Gusmão et al. [4,5] discuss a number of geo-environmental aspects related to the design of such barriers.

The design should be based on a good hydrogeological characterisation of the site, laboratory tests for evaluation of the degradation of the contaminants and numerical modelling. Knowledge of the vertical hydraulic gradient (i.e. 3D flow field) is essential to define barrier geometry and its limitations in a case by case basis.

After the identification of potential reagents, the design of reactive barriers should contemplate the execution of laboratory treatability tests, whose main objectives are: (i) selection of a viable reagent for the reactor (for example, the iron), (ii) estimation of the rate of degradation of the contaminants, (iii) evaluation of the working life time of the reactor.

The treatability tests can be performed under no flow conditions (batch tests) or under gravitational or imposed flow conditions (column tests).

In case of complex sites, use of new construction techniques, very costly projects and pilot scale reactive barriers can also be executed and monitored on the site.

## 4. Batch tests

The main objective of the batch test is the preliminary selection of the possible reagents. This test consists of placing a certain mass of the metal (iron, in the case of the present work) in glass (or non-reactive) recipients (with a

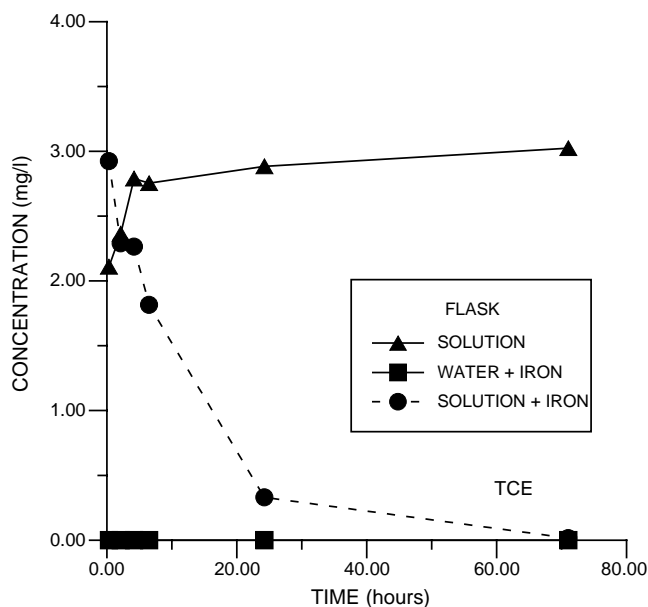


Fig. 4. Variation of the concentration of TCE along the test.

sealing cap), fully fill them with the contaminant solution, leaving the mixture undisturbed in an appropriated agitator (reagent flasks). Recipients filled only with the solution (white flasks), and others only with water and iron (control flasks), are also used.

At chosen times, samples of solutions from all recipients are collected and submitted to chemical analyses to determine concentration changes and to obtain physical–chemical parameters (e.g. pH, redox potential, electric conductivity).

Fig. 4 shows the results of a batch test of trichloroethylene (TCE) in the presence of iron [6]. This metallic iron is known as TRIFER EL200. It is a powder of pure and atomised iron, used mainly in the production of chemical products (with an effective grain diameter  $D_{50} = 60 \mu\text{m}$ ). It is observed that the TCE degraded during the time of the test. The half-life time of TCE was 9.3 h using first order kinetics model.

Figs. 5–7 show the variation of pH, redox potential and electric conductivity along the batch test of TCE, respectively. It is observed that pH increased in the beginning of the test and then remained constant until the end of the experiment. The reactive and control flasks showed reducing conditions throughout the experiment with values of approximately  $-500 \text{ mV}$ . Finally, it is also observed that the electric conductivity increases in the test due to the dechlorination of TCE.

Figs. 8 and 9 show results of batch tests of 1,2-dichloroethane (1,2-DCA) and 1,1,2-trichloroethane (1,1,2-TCA), respectively in the presence of iron [6]. It is observed that the 1,2-DCA did not degrade during the time of the test (the white and reactive flasks presented similar results), while the 1,1,2-TCA presented degradation signs, but with a much low degradation rate than that of the TCE test (half-life time of 1,1,2-TCA was 74.1 h).

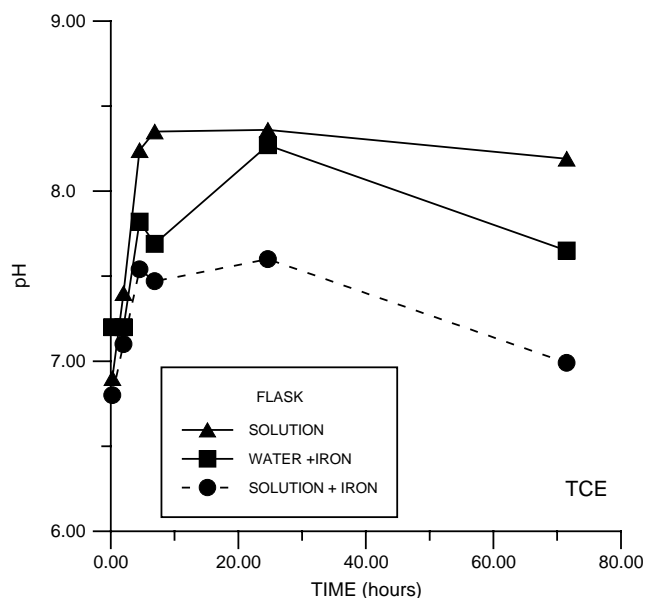


Fig. 5. Variation of pH along the test.

These results showed that the technique of reductive dechlorination using metallic iron can present fairly different results, depending on the contaminant in question. Some contaminants do not present degradation or have so high half-life time that the use of reactive barriers (with iron as reagent, as usually considered) may prove to be unfeasible, at least in the case of chlorinated aliphatic organic compounds.

The information on the non-degradation of the 1,2-DCA is considered to be quite relevant. Besides the indication that the technique here considered does not apply to any chlorinated solvent, it also shows that its use for other contaminants that have the 1,2-DCA as byproduct (such

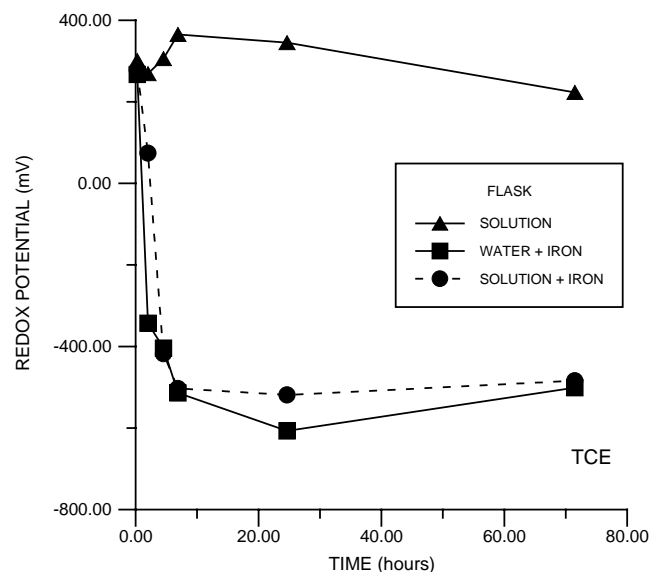


Fig. 6. Variation of redox potential along the test.

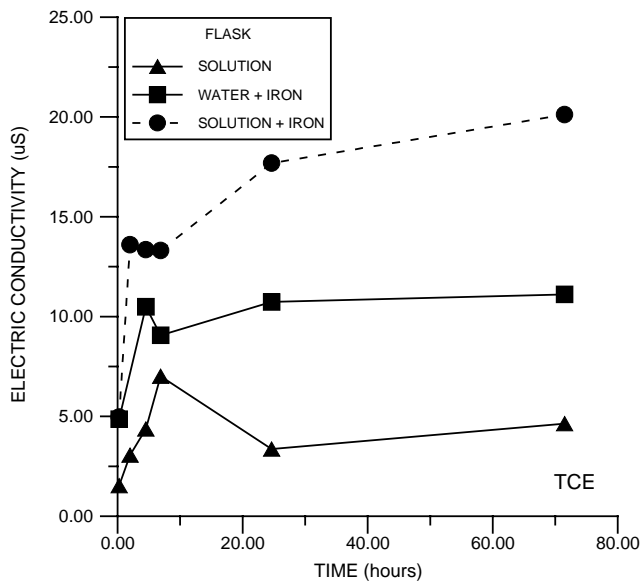


Fig. 7. Variation of electric conductivity along the test.

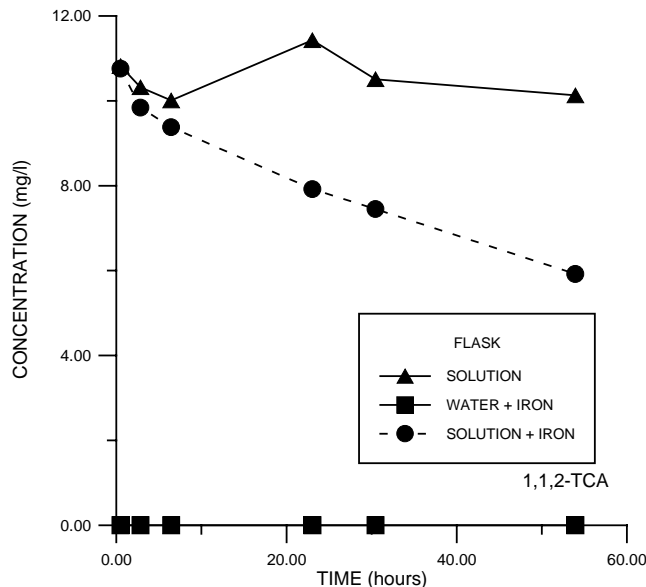


Fig. 9. Variation of the concentration of the 1,1,2-TCA along the test.

as the 1,1,2-TCA), will demand other additional type of treatment to avoid downstream accumulation of 1,2-DCA.

The main problem on the use of zero-valent metals as degradation solvent is the production and accumulation of chlorinated byproducts, that can be more toxic than the original contaminant [7]. For example, at the end of the test with the 1,1,2-TCA, there was an accumulation of vinyl chloride (MVC), which is more toxic than the 1,1,2-TCA. This, shows the need of a careful evaluation on the need of sequential treatments in problems of aquifer remediation.

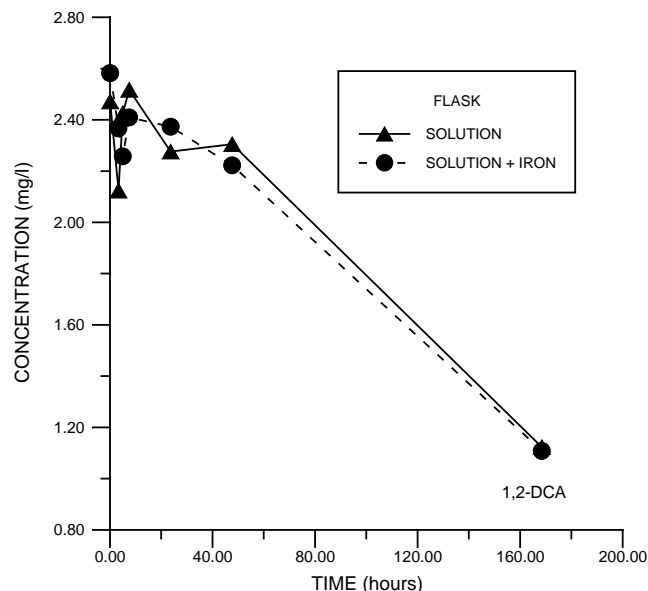


Fig. 8. Variation of the concentration of the 1,2-DCA along the test.

### 5. Column tests

The second type of treatability test used in the design of reactive barriers is the column test. This test generally complements the preliminary evaluation of the degradation of the contaminants obtained through the batch tests, as it can simulate flow conditions in the porous media.

The test consists in the percolation of the solution of the contaminant through a cylindrical column filled with the reagent material. Concentration variation and physical–chemical parameters are typically monitored in the effluent (column base) and in different points along the height of the column, at distinct testing times. Hence, the profile of concentration of the contaminant and of its byproducts along the column is obtained. Furthermore, distinct degradation rates can be determined for every value of flow rate [7].

Gusmão [6] presented results of a test with an acrylic cylindrical column of 60 mm of internal diameter and 515 mm of height. The column had seven ports along its height, allowing the collection of fluid samples inside the column.

Fig. 10 shows a sketch of the apparatus used in the test. As required, all the materials from connections, valves and tubes were chemically compatible with the studied contaminants.

The test was performed with a solution of 5 mg/l of TCE and the column was filled with the iron powder EL200. After set-up, it percolated with a volume of water equivalent to 2.7 times the pore volume of the sample in the column. During this period, samples of the influent and effluent fluids were collected for chemical and physical–chemical analyses.

Figs. 11 and 12 show the results of electric conductivity and redox potential along the column test with TCE, respectively. It is observed that the electric conductivity is greater in the effluent port, because there was a dechlorination of

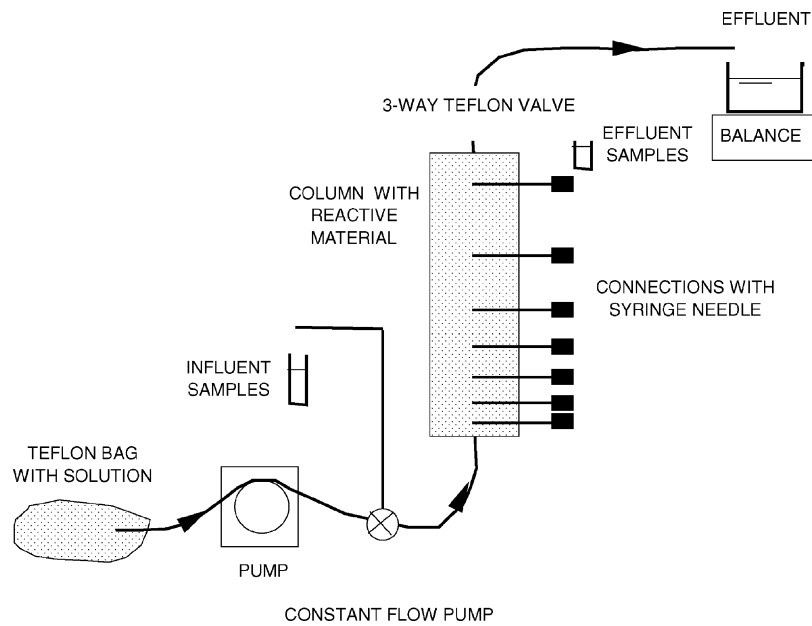


Fig. 10. Schematic drawing of the column test apparatus.

TCE into column. The redox potential values in the effluent port showed reducing conditions.

Following the water saturation, it was initiated the percolation of the TCE solution into the column. The average flow rate during the test was equal to  $55.14 \text{ cm}^3/\text{h}$  which corresponds to a velocity of  $3.79 \text{ cm/h}$ . The test, under percolation of the contaminant, lasted about 66 h. During this period, samples of the influent and effluent solutions were collected for chemical (chromatographic) and physical–chemical (pH, redox potential and electric conductivity) analysis.

Fig. 13 presents the profile of concentration of TCE along the column at the end of the test. It is observed that the TCE was degraded inside the first 30 cm of the column.

The effluent samples did not show the presence of TCE, confirming its full degradation.

Assuming that dispersion in the column can be neglected [7], the time of reaction can be obtained by the flow velocity of the contaminant and the distances inside the column. Thus, a curve of concentration of TCE versus time is obtained, allowing the computation of its degradation rate. Considering that the degradation corresponds to a reaction of first order, it was computed a rate of degradation of  $0.429 \text{ h}^{-1}$ , which corresponds to a half-life time ( $T_{50}$ ) equal to 1.62 h.

The degradation rate of the TCE in the column test was greater than that obtained in the batch tests. Differences such

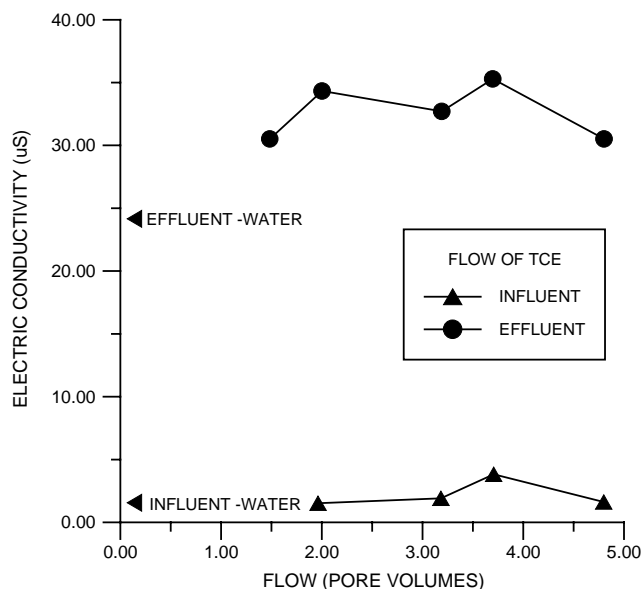


Fig. 11. Variation of the electric conductivity along the column test.

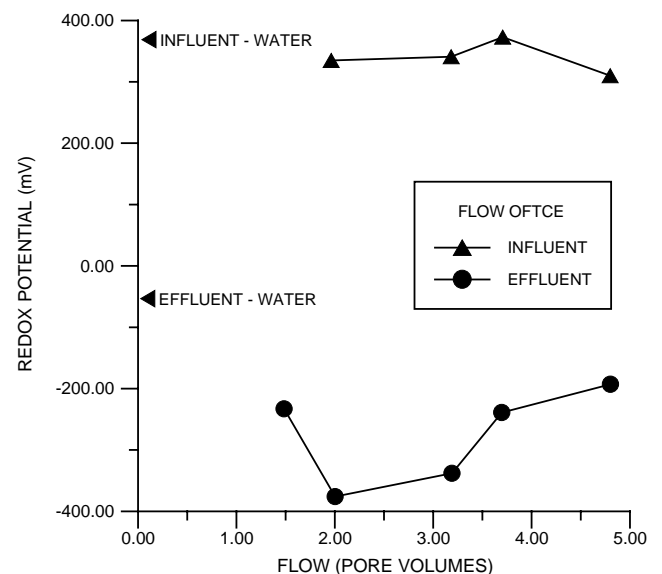


Fig. 12. Variation of the redox potential along the column test.



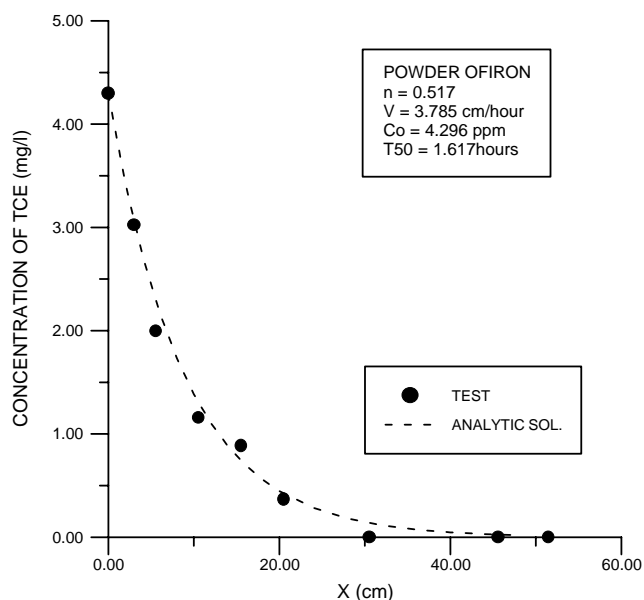


Fig. 13. Profile of concentration of TCE along the height of the column ( $X = 0$  is at the base of the column).

as that were also observed in other works [1,8]. A possible explanation for this is that, in the batch tests, byproducts of the reaction accumulate in the recipient (including inorganic substances) and fix on the surface of the iron, decreasing its reactivity.

Fig. 14 shows the concentration of the byproducts of the TCE degradation along the column at the end of the test. It is observed that the concentration of MVC was of 36  $\mu\text{g/l}$ . This result indicates a need of further treatment of the aquifer. In order to achieve it, if a solution based on the use of reactive barriers is to be pursued, sequential treatment, comprising

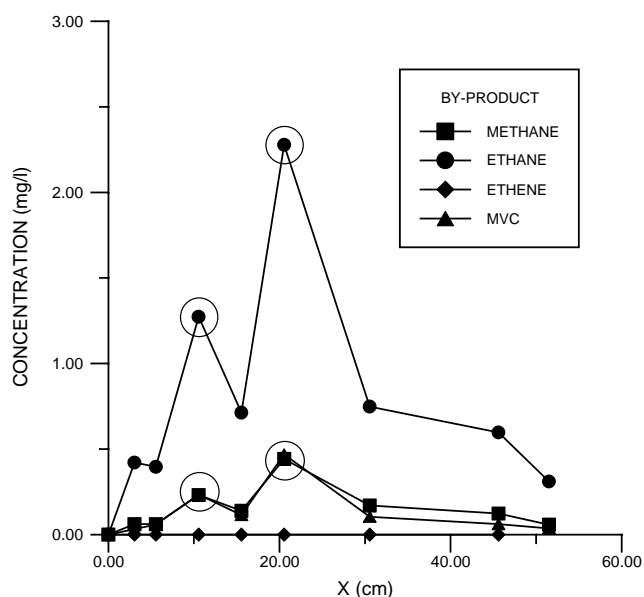


Fig. 14. Profile of concentration of byproducts of TCE degradation along the column.

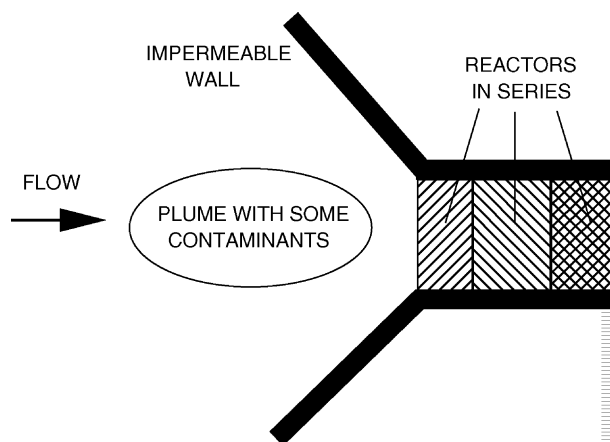


Fig. 15. Sequential treatment through reactors in series.

the use of reactors placed in series, should be considered. In Fig. 15, each reactor would have to be designed to provide full degradation of byproducts generated in the preceding reactor [9].

## 6. Conclusions

The use of zero-valent metals such as iron for in situ passive treatment of groundwater (through reactive barriers) has been considered and may constitute a promising alternative to the commonly used pump-and-treat remediation technology, depending on the type of the contaminants.

As in the case of other technologies of aquifer remediation, the isolated use of the technique of reductive dechlorination through metals may not, however, solve the environmental problem. Some contaminants do not present any degradation or, in other cases, have very high half-life times which may turn this technology not an effective one.

Finally, the formation of chlorinated byproducts, which are more toxic than the original contaminant and do not fully degrade within a given barrier, indicates that the treatment of aquifers should be sequential requiring different steps to eliminate all contaminants.

## References

- [1] R.W. Gillham, S.F. O'Hannesin, Metal-catalysed abiotic degradation of halogenated organic compounds, in: Proceedings of the IAH Conference Modern Trends in Hydrogeology, Hamilton, 1992, p. 9.
- [2] K.H. Sweeny, J.R. Fischer, Reductive Degradation of Halogenated Pesticides, US Patent No. 3.640.821, (1972).
- [3] L. J Matheson, P.G. Tratnyek, Reductive Dehalogenation of Chlorinated Methanes by Iron Metal, *Env. Sci. Technol.* 28 (1994) 2045–2053.
- [4] A.D. Gusmão, T.M.P. Campos, E.A. Vargas Jr., M.M.M. Nobre, Studies on the Performance of Reactive Barriers: Hydraulic Dimensioning, *Rev. Geotecnia* 80 (1997) 5–23 (in Portuguese).
- [5] A.D. Gusmão, T.M.P. Campos, E.A. Vargas Jr., M.M.M. Nobre, Studies on the Performance of Reactive Barriers: Mass Transport, *Rev. Geotecnia* 80 (1997) 25–42 (in Portuguese).

- [6] A.D. Gusmão, Use of Reactive Barriers in the Remediation of Contaminated Aquifers, D.Sc. Thesis, PUC, Rio de Janeiro, 1999, (in Portuguese).
- [7] A.D. Gusmão, T.M.P. Campos, E.A. Vargas Jr., M.M.M. Nobre, Evaluation of some factors affecting the design of reactive barriers, in: Proceedings of the Third international congress on environmental geotechnics, Lisbon, 1998, Vol.2, pp.435–441.
- [8] W.S. Orth, Mass Balance of the Degradation of Trichloroethylene in the Presence of Iron Filings, M.Sc. Thesis, University of Waterloo, Ontario, 1992.
- [9] A.D. Gusmão, Groundwater: Contamination and Remediation Aspects, first ed., EDUPE, Recife, 2002, 193 pp. (in Portuguese).