

EN-Z-LITE TECHNOLOGY

The reclamation of groundwater is usually carried out via a so-called *pump&treat* process. The water is first extracted from the groundwater table (*pump*), then purified *on site* in a plant purposely installed on location (*treat*).

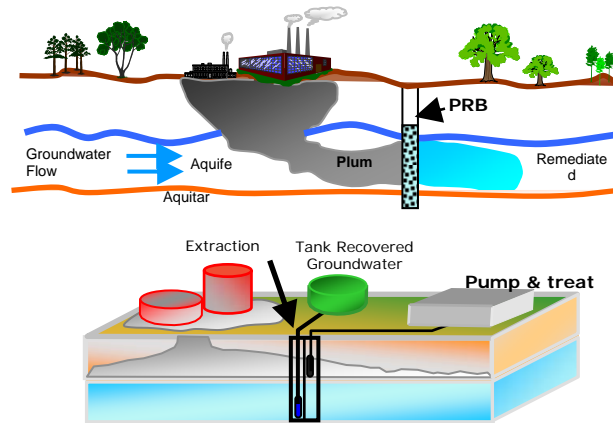


Figure 1: Scheme of groundwater treatment according to Permeable Reactive Barrier (top) and *pump&treat* (bottom) technologies

An innovation in this area is represented by the Permeable Reactive Barrier (PRB), in which the initial stage of *pump&treat*, technically extraction and phase separation, is eliminated: where the conditions allow the system for the treatment directly in the underground, the contaminated water does not need to be pumped to reach the surface, but is transported to the treatment *in situ* through natural flow in the aquifer and the surface of the site remains available for other desired use.

In *on site* as well as *in situ* treatment, the critical element is constituted by the performance of the employed reactive material. The *pump&treat* process is normally based on the use of granular active carbon (GAC), which has a wide range of action, but more innovative systems utilize ion exchange resins on polymer supports or specific adsorbents.

PRBs are equipped with various materials: metals, mainly iron, absorbing materials such as GAC and natural zeolites. It can still be considered an emerging technique that to date counts few more than a hundred *full scale* implementations, in large part in the USA and about a dozen in Europe.

PRBs can be classified essentially based on the reaction that eliminates the contaminant, which can be adsorption or chemical transformation.

The most representative of the adsorbing materials, which is also utilized in PRBs, is GAC, efficient above all for apolar organic compounds. Its major limit resides in the scarce specificity which, while allowing the removal of various contaminants, cause however interferences on the part of the components commonly present in groundwater, such as humic acids and inorganic ions. This inconvenience is at the base of its fast saturation and difficult regeneration, and constitutes the most consistent limitation.

The chemical processes adopted in PRBs are based on the transformation of the contaminants into less hazardous compounds and usually do not require the regeneration of the reactive material, unless there is a loss of reactivity due to processes of passivation or of the obstruction of active sites. The transformation inside the reactive barrier is commonly a redox reaction which oxidizes or reduces the contaminant; the reactive medium may supply electrons for the reduction, as in the case of metallic iron. The limits of PRBs based on uncharged metals regards the field of application, at present circumscribed to chemically reducible compounds, such as some heavy metals (for instance

Cr^{VI}) and many chlorinated aliphatic compounds. Another critical factor is the endurance of efficiency with time, for applications that can last even for decades, concretely conditioned by the geochemical reactions in the aquifer.

The En-Z-Lite process allows to overcome the points of weakness of the materials usually adopted for the treatment of groundwater, in both *pump&treat* and PRB procedures. Synthetic hydrophobic zeolites constitute a particularly efficient reactive system with a wide range of action capable of delivering suitable results to the demand of decontaminating polluted aquifers from complex mixtures of organic compounds, such as those derived from petroliferous and petrochemical activities.

The peculiarity of zeolites consists of their chemical-physical properties, which can be modulated in a way to select the structure that has optimal *shape selectivity* and polarity. In this manner only the molecules whose dimensions and polarity are compatible with the characteristics of the zeolite can penetrate the nanoporous structure and be accommodated stably in the channels. The different molecules dissolved in the groundwater are thus discriminated on the basis of dimensions and polarity. All considered, the hydrophobic zeolites behave like a solid solvent which selectively extracts the apolar contaminants.

Finally, the zeolites display extremely fast adsorption kinetics, which makes them utilizable not only in PRBs, but also in *pump&treat* applications, where reduced contact times with the reactive element and the attainment of particularly rigorous objectives are generally required.

The contaminants which best represent the advantages derived from employing hydrophobic zeolites in the treatment of polluted aquifers are two: methyl-tert.butyl-ether (MTBE) and 1,2-dichloroethane (1,2-DCA).

MTBE has replaced lead tetraethyl in gasoline due to its elevated octane number. It is substantially soluble in water and even small losses from the tanks have brought about a widespread presence in the soil underneath filling stations and deposits. In order to remove it from water, unsustainable quantities of GAC are necessary and nonetheless inefficient in restoring the always more rigorous levels of imposed admissibility.

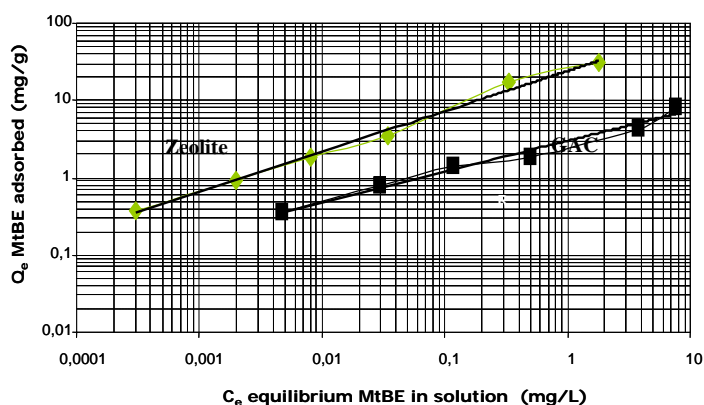


Figure 2: Comparison between MTBE adsorption isotherms onto Zeolite (green) and Granulated Active Carbon (black)

1,2-DCA is a chlorinated solvent, present in the aquifers underlying the sites of many petrochemical companies, which is not reducible by metallic iron, the reactive material generally used in PRBs for such a typology of products.

ON SITE APPLICATIONS: PUMP&TREAT

The zeolites were utilized for the treatment of an aquifer underlying the filling station “Garda Est” where a fuel spill happened. After two years of fruitless attempts, the service company in charge of the decontamination tested technologies such as GAC filters, biological treatment on percolated filters and chemical oxidation with hydrogen peroxide, but without consistently obtaining the limit of 10 µg MTBE/liter of purified water (imposed by the public authorities in a session of the Services Conference).

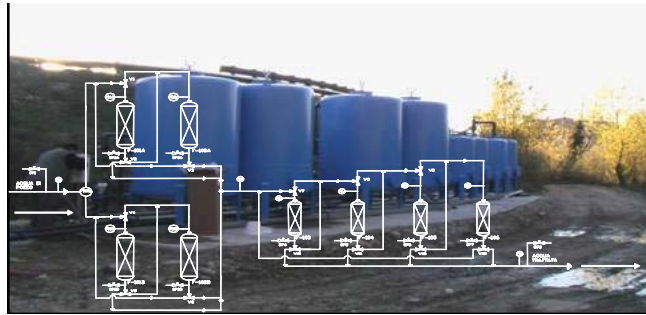


Figure 3: Treatment plant based on GAC + Zeolites running in gasoline station “Garda Est”

In December 2004 a *pump&treat* plant was started using adsorption on GAC followed by zeolites. This sequence was chosen for reasons of efficiency and economics. Basic data obtained during the operation of a pilot installation on the same site in the period June-July 2004 were used for the size-up of the plant. Today the plant is still running and the concentration of hydrocarbons as well as MTBE in the purified water has always been below the limit of 10 µg/l. The figure shows the fluctuation of the flow rate and the variations in inlet concentration of the contaminants over a period of more than two years of operation.

In the ambit of a commercial agreement, by which STA s.r.l. has acquired the rights to offer the En-Z-Lite process on the market external to the ENI group, two more *pump&treat* plants are at the moment operating at another two gasoline filling stations.

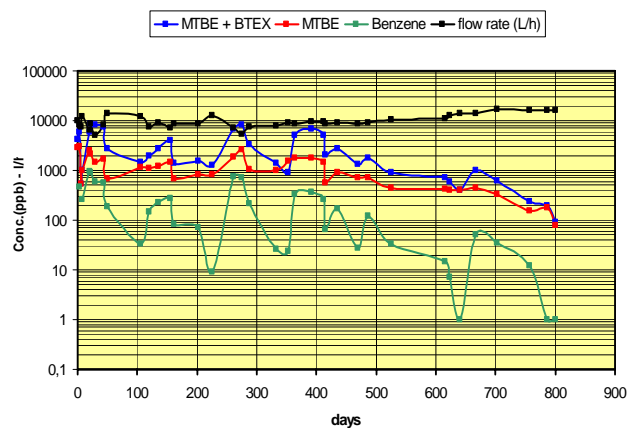
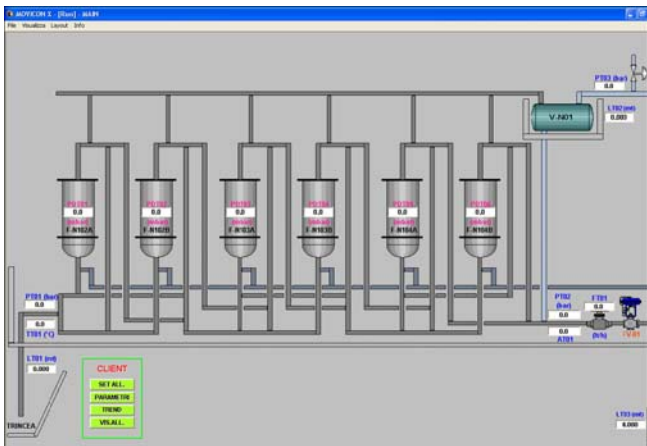


Figure 4: Inlet contaminant concentration and flow rate to Garda Est En-Z-Lite plant

IN SITU APPLICATIONS: PERMEABLE REACTIVE BARRIER



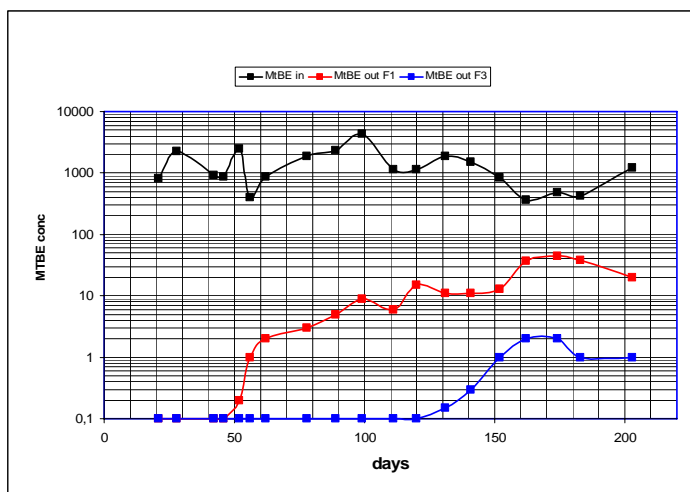
Since July 2006 a functioning PRB is in demonstration at the refinery of Taranto (project realized thanks to financing from the Italian Ministry of Instruction, University and Scientific Research), to treat a plume of contamination, containing MTBE, aliphatic hydrocarbons, BTEX and arsenic, intercepted by a draining trench which forms part of the system of security set-up at the site.

Figure 5: Taranto pilot PRB - synoptic diagram of the data logger and remote control system

Appropriate reactive materials for the treatment of the contaminants, at the revealed concentrations and in the presence of high salinity, were identified in the laboratory, imposing the attainment of the most rigorous regulatory limits (DM 471/99) and 10 µg/l for MTBE. Two types of hydrophobic zeolites, with comparable polarity but different channel dimensions, were employed. One was more adapted to adsorb BTEX, the other more suitable for MTBE and larger sized hydrocarbons. Instead for arsenic commercial materials based on $\gamma\text{-Al}_2\text{O}_3$ and $\text{Fe}_2\text{O}_3 \cdot 9\text{H}_2\text{O}$ were adopted.



Figure 6: Taranto pilot PRB - the gate containing zeolites and material for As sorption



The figure shows the MTBE concentration at the outlet of the PRB in demonstration; it is well below the 10 µg/l objective.

Figure 7: Taranto pilot PRB: MTBE concentration at inlet (black), after first zeolite filter (red) and at the exit (blue)