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Reactive (Oxygen) Gas Barrier and Zone Technologies

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10.1 Introduction to Reactive Gas Barriers and Zones

Following a decade of investigation and field-scale testing, reactive gas barriers and zones (RGBZ or gas permeable reactive barriers [PRBs]) have been introduced as a state-of-the-art remediation technology for both organic and inorganic contaminants in the groundwater zone.

RGBZ technology is sustainable and can achieve long term and stable attenuation of the negative impacts of these contaminants on groundwater bodies and flow. It requires a modest initial investment and operational costs are very competitive with other alternatives. In addition, RGBZ consumes minimal resources (e.g., energy, materials, land, and manpower). Both the operational risks and risks to human health/and the environmental are low. The RGBZ technology has demonstrated a high efficiency in stimulating the intended transformation and exchange processes, while at the same time showing a low sensitivity to temporal changing geohydraulic and geobiochemical conditions.

Gas PRBs can be implemented as a stand-alone technology; they are also suitable for treatment train applications, which are used to treat complex contaminants (Figure 10.1). There are three basic application methods:

1. In situ gas reactors can operate as full-section gas PRBs (reactive walls) to prevent the breakthrough of contaminated groundwater into a sensible object that is being protected. These are typically used to limit plume propagation or to avoid juridical implications with respect to downstream land owners.
2. In situ gas reactors can operate as pre- and posttreatment zones for lumped reactive barriers (e.g., funnel and gate, grain, and gate) or treatment trains. Pretreatment is defined as the conditioning of a lumped stream of contaminated water (e.g., to remove iron) to guarantee the best technical performance of subsequent treatment steps (Kassahun et al., 2005). Posttreatment is a polishing step following the removal of the main contaminant mass. For this treatment to be optimal, downstream natural attenuation of some remaining or previously inaccessible compounds needs to be stimulated.
3. In situ gas reactors can also operate as reactive gas zones in cases where the objective is to lower the state of damage of a sensible subsurface domain (site decontamination). Reactive gas zones then act as retention or buffering regions against natural dynamic flow changes (e.g., coupled aquifers to river systems), impacts from the top soil (e.g., contaminated overburden or dumps) or from nearby applications of invasive technologies (e.g., construction or mining activities).

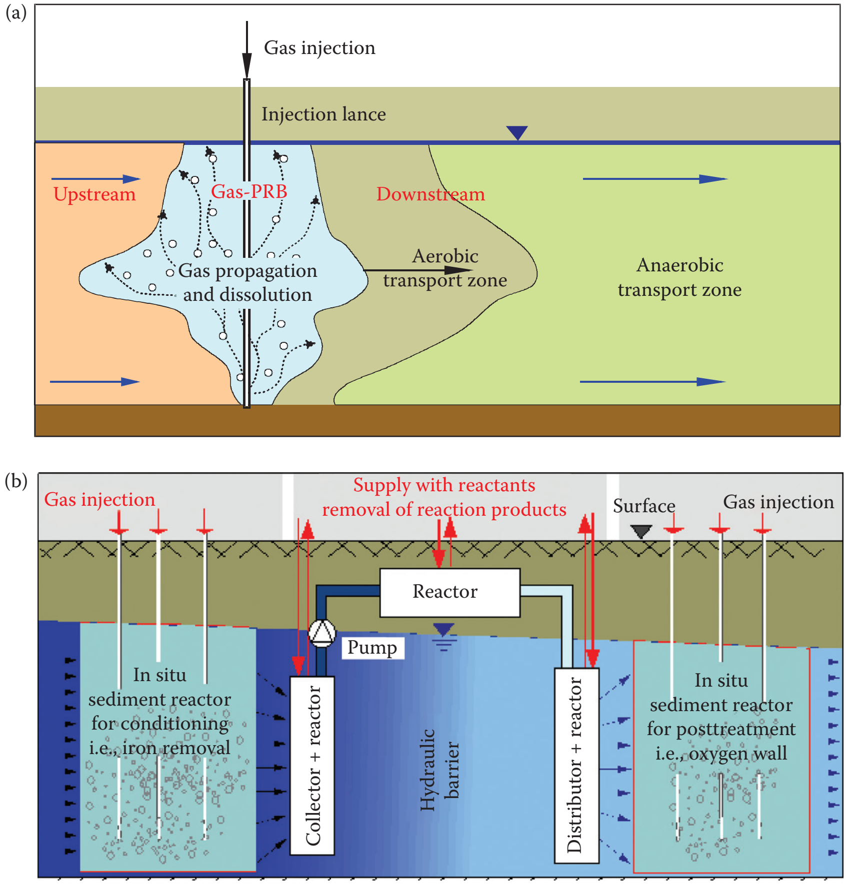


FIGURE 10.1
Technology application variants for RGBZ. (a) Stand-alone full-section gas PRB with sequential reactive zones (patent EP 1550519 "BIOXWAND"). (b) Pre/postreactive gas zones of a drain and gate treatment train for complex groundwater and subsurface decontamination (patent DE 10310986 "GFIadags").

The methods of RGBZ operation used in this research are direct gas injection (DGI) and application options for low-pressure (NDI) and high-pressure injections (HDI), which are discussed. It is noted that the term "sparging" is not used for RGBZ applications, as it is linked to applications that generate a gas which escapes from the groundwater zone and strips groundwater contaminants. Biodegradation is only an additional effect of sparging; a soil gas extraction and treatment system is needed.

The RGBZ technology has been approved by German Environmental authorities (ITVA, 2010) and additional applications in regard to enhanced natural attenuation (ENA) are anticipated.

Gas PRB instrumentation can be installed with minimal effort. Only a limited number of small diameter vertical perforations are needed, and sequential reactive zones can be formed in undisturbed geologic structures. In this way, the invasive effects of groundwater flow are minimized and the RGBZ operates as a hydraulically passive technology. The injection and propagation of a gaseous mixed phase in the subsurface is performed using controllable 3D gas flow networks. Reactants are temporarily stored in trapped gas clusters in the porous matrix adjacent to adsorbed contaminants and biofilms, and the delivery of gaseous reactants into the groundwater flow can be adjusted by controlling the partial pressures of gas components.

Similar to other in situ technologies, RGBZ are strongly dependent on the hydrogeological domain, described by the porous rock or sediment, groundwater flow, and migration properties. RGBZ are additionally dependent on the pneumatic or gas flow characteristics of the subsurface. Thus, the management of a complex heterogeneous multiphase multicomponent flow and migration domain demands that the engineer who is planning and applying the RGBZ displays a high level of professionalism.

RGBZ are ideally applied in horizontal multiple-layered sediment formations of nonuniform fine- to coarse-grained sands and fine gravels. Depths to 50 m below the ground surface are accessible without the use of heavy drilling techniques. Enclosed finer texture lenses or thin layers do not limit the application of RGBZ, as they are typically not continuously shaped and contain weak zones of gas-available threshold pressures. A time scale of 1–3 years is required to complete a stable formation of a gas PRB. The horizontal scale needed for a gas storage domain depends on the geological structure. In the direction of groundwater flow, it is typically in the same order of magnitude as the saturated thickness of the aquifer. Stimulation of intrinsic microorganisms can be achieved when a suitable environment is established (redox, pH) and dominant electron acceptors or donors for the biodegradation of groundwater soluble contaminants are supplied. Variable zones of redox potential can be induced by sequential reactors (Figure 10.1) or rate controlled and time-variable gas injections. Products of precipitation reactions (e.g., iron or manganese oxidation or pH-induced instability of carbonate) do not put the long-term operation of the RGBZ at risk. The well-known effects of bypassing or channelling groundwater flow due to gas clogging can also be monitored and controlled.

The most common RGBZ application uses atmospheric air and pure oxygen gas or its mixture to supply electron acceptors for aerobic biodegradation. Luckner (2001) reviewed the potentially available gaseous reactants and their impacts on biodegradation. Noble gases such as He, Ar, Ne, and SF_6 are used as tracers (Weber, 2007). Electron donor supply due to methane (Zittwitz and Gerhardt, 2006) and hydrogen gas (Bilek and Wagner, 2009) injection have been tested for in situ stimulation of cometabolic CHC degradation and autotrophic sulfate reduction. In situ iron removal can also be forced by oxygen and ammonia gas applications.

Due to insufficient gas storage capabilities, fissured rock domains and unconfined aquifers with a saturated thickness less than 3–5 m are less suitable for gas PRB applications. In addition to the geological domain, the type and complexity of the limiting reactants for in situ transformations, and the ability to deliver them by gas flow can also impose restrictions. A standalone RGBZ is unable to provide vital nutrients (e.g., available phosphorous or trace metals) where they may be deficient. A gas injection-based method to support the natural buffering capability of a subsurface domain against high proton production is still needed.

Care must be exercised when transformation of high volatility migrants (e.g., chlorinated ethenes or short-chained aliphatics) is intended. These substances can be enriched and stored in gas clusters, and even in cases where gases are not allowed to be stripped from the groundwater zone, the substances may become less accessible to biofilms. The presence of nonaqueous phase liquids (NAPLs) will lower the gas storage capability, because residual NAPL blobs occupy the same pore space portions; additional impacts are changes in the wettability or emulsifications. Toxic concentrations of contaminants, but also unfavorable environmental conditions (e.g., sulfide or pH) in the vicinity of NAPL are frequently reported.

Furthermore, the availability of sufficient time and space to achieve the given protection or remediation goals can limit the application of RGBZ.

10.2 Gas-Water-Dynamics in the Groundwater Environment

10.2.1 Basic Phenomena

Gas flow transport phenomena, capillary gas storage, or entrapment and mass transfer between the water and gas phases have been evaluated at both pore and field scales. Gas–water displacement and mass transfer due to gas injection in a water-saturated subsurface domains occur in a different manner to that in the unsaturated soil zone (Figure 10.2).

The transport of a nonwetting gas phase in groundwater environments is mainly driven by pneumatic pressure, capillary, and buoyancy forces. The pneumatic pressure gradient has to overcome the hydraulic pressure head at the injection point, an additional capillary entry pressure required to open a gas channel network, a pneumatic flow resistance that is formed by friction at nonrigid moving gas–water interfaces, and pressure-dependent gas viscosity (Geistlinger et al., 2006). With increasing distance from the injection point, gas volume portions become disconnected due to a decrease of pneumatic pressure, and pore trapping forms incoherent gas bubbles and clusters. Due to the heterogeneous layered nature of sediment domains, bubbly flow in gravel structures or channelling flow in fine-grained media cannot hold for larger distances (Brooks et al., 1999). The propagation of gas clusters is commonly

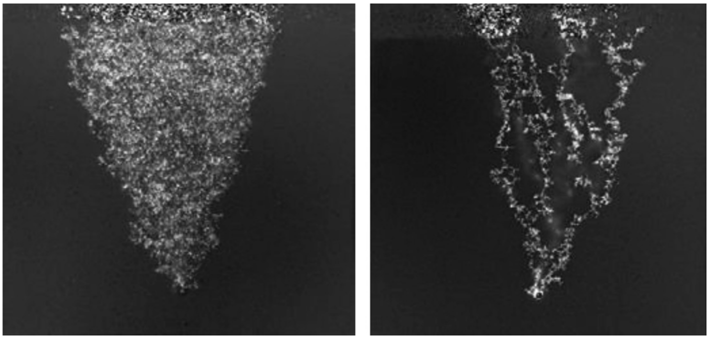


FIGURE 10.2
Basic gas flow types for bench scale direct gas injection in water saturated porous media. Left: incoherent bubbly flow in coarse sand (gas clusters), right: coherent channelized gas flow (viscous fingering). (Geistlinger, H. 2010: Model supported high pressure pulsed Gas Injection (HDI) for in situ Remediation of contaminated Aquifers: Laboratory scale Experiments and Computer Simulations for Optimization of the Technology. Report Nr. KF0011010SB7–2, Helmholtz-Centre for Environmental Research UFZ, 63 p. (in German).)

reported in field applications. These clusters are unstable gas-filled bodies with a magnitude in the order of several pore and solid particle diameters. Their bulk gas pressure can change due to mass transfer and they cannot equilibrate the variable capillary forces at their total water interfaces. Gas clusters are moved upward by buoyancy forces and they are laterally spread by pneumatic cluster displacement when gas is injected. This behavior is defined as pervasive gas flow. Gas propagation stops when the threshold pressure of a given sediment or rock layer cannot be overcome. Following the cessation of propagation, high local gas accumulations and highly coherent gas saturations can be present. This bulk or geological trapping can form reliable gas storage zones, and groundwater conductivity can be lowered significantly.

When applying the low-pressure NDI method to natural consolidated sediments, matrix and pore restructuring does not occur. Multiphase flow characteristics of the sediments remain stable over a large range of total mechanical stress (Giese et al., 2003). The high-pressure method HDI focuses pneumatic sediment cracking in the vicinity of the injection point. In addition, local structure reorganization is needed to generate preferential flow paths for gas pulse propagation.

10.2.2 Example Test Facilities

A *pore to bench scale* gravimetric-optical measurement system (Figure 10.3) was developed using coupled cameras to detect overall gas saturations (stationary camera) and local moving gas bubbles or clusters (dynamic camera) in a 2D acrylic glass chamber (0.40 m × 0.45 m × 0.01 m). The system allows for a high resolution in time and space and for simultaneous observations of

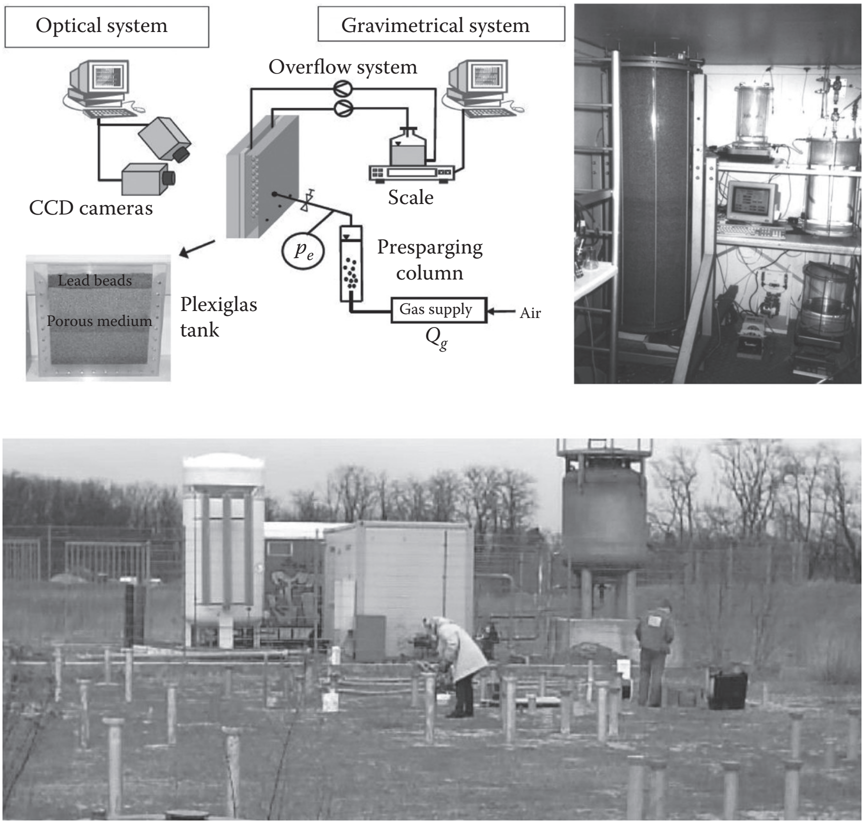


FIGURE 10.3
Test devices and sites for DGI studies. Upper left: gravimetric-optical system. (Geistlinger et al. 2006: Direct Gas Injection into glass beads: Transition from incoherent to coherent gas flow pattern. *Water Res. Research*, 42, paper W07403, 12 p.) Upper right: pressurized rotatable column with gravimetric balancing system, bottom image: field-scale test site BIOXWAND.

pore to local scale phenomena (10^{-5}–10^{-1} m). Uniform sand fractions and glass beads were used as sediments and effective mechanical stress is induced by hydraulic pressure being applied to a rear-side membrane and an overburden or gravimetric load (leaden spheres). A gravimetric phase balancing system was installed for saturation measurements.

A *bench to pilot scale* research test site for gas-based remediation techniques was installed at the Dresden Groundwater Centre (Figure 10.3). Test columns and tanks (0.3 m–3.0 m in diameter) were used to evaluate the effective parameters for gas injection, storage, and dissolution for upscaling to field applications (Weber, 2007). The test devices operated under near-to-field conditions. 1D and 3D total stress and system pressures of 300 kPa (using a 20 m column of water) were applied to the columns and tanks. The temperature of the system was set at 10–15°C, which are temperatures typical of groundwater. Multiphase water and gas flow interactions were studied using parallel flow, counterflow, and cross-flow (horizontal, vertical). A phase balancing system runs under system pressure conditions. A 2D tank test device was used for imaging and the bulk estimation of trapped gas lenses in layered sediment formations. The influence of gas trapping to a stationary groundwater flow was evaluated using in situ sensor arrays and noninvasive geophysical gas monitoring systems (e.g., geoelectric-induced polarization) as discussed in Boerner et al. (1996). Bulk parameters for the field-scale NDI application were preliminary estimated by pilot scale testing.

Typical gas injection rates for the bench to pilot scale testing of the NDI were 10^{-3}–10^{-1} m^3/h STP, and the flow sections ranged from 10^{-2} to 10^{-1} m^2.

Field-scale research test sites (up to 500 m^2 of treatment area and 5–50 m in depths) were operated by the Berlin Water Company (Figure 10.3) and the Helmholtz-Centre for Environmental Research UFZ. Several field-scale test applications were run with DGI technology (NDI and HDI methods) in sediment environments. There was also an application of NDI in fissured sandstone bedrock (Schinke, 2008). The field sites were equipped with conventional and state-of-the-art injection and monitoring techniques, and high-resolution site investigations were performed. From these field-scale tests, best available technologies and strategies for site characterization, injection, and monitoring system operation, and control of RGBZ were derived (Ehbrecht and Luckner, 2004; Beckmann et al., 2007). An integral balancing algorithm for gas injection and biodegradation and a tracer test method using noble gases was also developed.

Typical gas injection rates for the field-scale testing of NDI were $1 \times 10^{-1} - 2.5 \times 10^{0}$ m^3/h STP and the flow sections ranged from 10^1 to 10^2 m^2.

10.2.3 Gas Injection and Gas-Water Displacement

There is a difference in the gas-water-displacement effects of low pressure (NDI) and high pressure (HDI) DGI methods. In particular, the effects of interest are the injection pressure gradient, gas injection rate, and apparent gas propagation velocity.

In the NDI system, the placement or mixing of a low amount of immobile (gaseous) reactants in a natural groundwater flow and their dissolution are typical of full-section PRBs. Following this, the desired in situ reactions occur in downstream aquifer regions. In addition, a stationary gas channel network is typically formed. The same gas flow paths are used multiple times, even when a pulsed injection is applied. The density of a gas channel network and the volume of gas clusters are functions of texture in homogeneous sediment regions. The coarser the material, the lower the gas network density; however, the mean dimension of moving gas clusters is higher. Typical cluster diameters in the order of <2 mm in fine- and nonuniform-grained sands and >20 mm in coarser sands bubbly clusters have been reported (Weber, 2007).

A natural groundwater domain is characterized by multiple gas transport barriers caused by the horizontal layering and compaction of sediments. The transport of gas clusters is highly sensitive to these structures and heterogeneities. Gas accumulation occurs, and regions of coherent mobile gas saturations can result. These structures must be explored during a gas-hydrogeological surveying.

There is a weak interaction between gas and water flow during NDI; pervasive and bubbly gas propagations facilitate the simultaneous use of macropore structures for water and gas flow. There is some rearrangement of the path of water flow during gas injection due to local gas accumulation in capture zones. Subsequent conductivity changes are limited to the local scale and a degree of homogenization of the water flow can be achieved by temporary clogging of coarser high-permeability zones.

An effective displacement of mobile water by mobile gas in a near flow region is induced using HDI. The displacement results from high-gradient, high-frequency pulses with injection periods in the range of seconds to minutes. HDI is applied when source zone or soil matrix decontamination is required and it has been used in combination with NDI (NDI–HDI) for local gas storage homogenization in the large scale BIOXWAND application. HDI has reported to cause more significant changes to groundwater flow in terms of flow direction, velocity, and dispersivity (Selker et al., 2007; Geistlinger et al., 2006). Applications in bedrock and other low permeable environments (e.g., sandstone structures or silt barriers) may generate gas accessible pore networks.

There is evidence from field-scale gas tracer applications that the mutual displacement of gas flow networks can occur during simultaneous injection at locally distributed lances (Uhlig, 2010 and Schinke, 2008). The effect can be explained by applying the pervasive gas flow concept of moving incoherent clusters where effective mixing of cluster flow paths is not possible. The practical outcome is that the determination of the ROI of an array of gas lances must be performed by complex lance array testing.

10.2.4 Gas Propagation and Storage

Gas storage in aquifers mainly appears as either mobile gas capturing or accumulation below geological barriers or the residual pore-trapping of gas clusters. Gas saturation (volume of gas per volume of pore space) is used to characterize storage.

During NDI in sandy sediments, typical gas saturations are 1%–5% for residual gas, 5%–10% for mobile gas (during injection periods), and greater than 15% for mobile gas capture zones (Weber, 2007 and Engelmann et al., 2010). Texture and mechanical stress only exert minor influences on these means of gas saturation. It has been reported that pervasive incoherent cluster flow can occupy a denser pore channel network than coherent flow over large distances, and can be maintained for hours after gas injection has ceased. It can also lead to redistribution of subsurface gas storage. Effective pervasive gas propagation is in the range of 10^{-2}–10^{-1} m/h.

When applying HDI, local increases in, as well as the homogenization of, gas saturation are induced in a near region with an ROI <3 m (Geistlinger, 2010). In this case, gases can be effectively supplied to the bottom zone of an aquifer (which is of special interest in unconfined aquifers), and when a density-driven plume propagation is under consideration (e.g., a dissolved CHC plume). With increasing distance and due to gas viscosity and compressibility characteristics, the HDI injection pressure transforms almost completely into high gas propagation velocities in coherent channelized networks. There is no additional gas saturation effect of HDI at greater distances from the injection point and the effective gas propagation of channelized flow is of $>1 \times 10^0$ m/h. A wide velocity range indicates the instability of this transport behavior with a few dominating macroflow paths.

Figure 10.4 and Table 10.1 summarize the current knowledge of gas storage and propagation phenomena during DGI into sediments in the groundwater zone. Assuming an injection area of 10^{-2} m² for bench scale testing and 10^1 m² for field applications, observed injection pressures and gas propagation velocities during rate controlled field testing of NDI and HDI (Weber, 2007, Geistlinger, 2010 and Zittwitz et al., 2012) are very similar. The gas injection pressure difference due to the hydrostatic level typically increases during NDI from $<5 \times 10^0$ kPa to 3×10^1 kPa when the injection rate is increased from 0.5 to 2.5 m³/h STP. This indicates a change to channelized flow and a

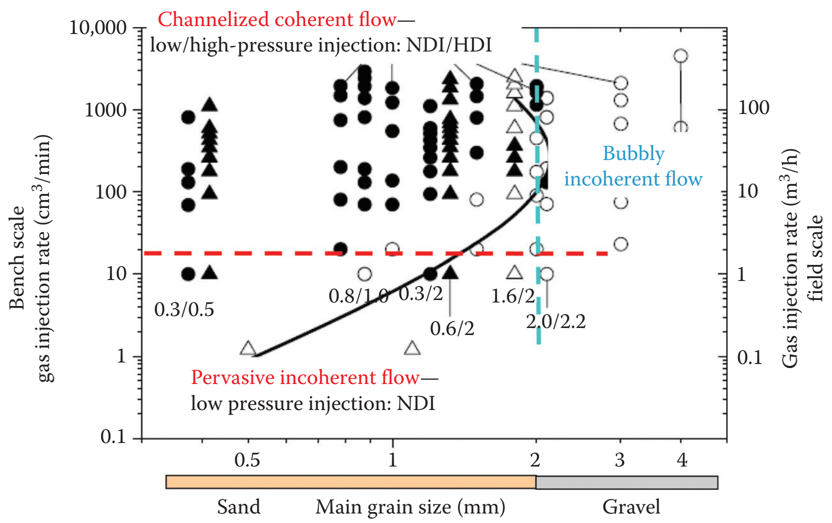


FIGURE 10.4
Gas flow classification scheme of bench to field-scale DGI. (Adapted from Geistlinger, H. et al. 2006: *Water Res. Research.* 42, paper W07403, 12 p.; basic scheme and data from bench scale testing.)

TABLE 10.1

Field Parameters for NDI and HDI Gas Injection (Sandy to Gravel Sediments)

	Pressure Difference at Injection Point	Flow Rate (STP) at Injection Point	Mean Propagation Velocity over ROI	Flow Type/ Injection Type, Frequency
	Δp_{IP} (kPa)	$Q_{g,IP}$ (m³/h)	$v_{g,ROI}$ (m/h)	–
NDI, low	<30	<1.0	0.01–0.1	Pervasive or bubbly/ continuous or pulsed f < 1/d
NDI, high	30–100	1.0–3.5	0.1–10.0	Channelized or bubbly/ pulsed f < 1/h
HDI	>300	>5	>5.0	Channelized or bubbly/ pulsed f > 1/min

subsequent higher gas propagation is observed. It is noted that Figure 10.4 is somewhat similar to the findings of Wang et al., (1998) who analyzed the flow instability of immiscible displacement in the vadose zone during water and NAPL infiltration.

High gas saturation can be achieved using surfactant enhanced NDI (Giese and Reimann, 2003). Foam formation will lower the gas propagation velocity and the mass transfer coefficient and gas stripping can be completely avoided. There is evidence of a reliable mass transport of dispersed solid substances (e.g., bacteria, nutrients) through sediments by gas-in-water-foams pilot scale. Using surfactants, a complete local drainage of pore space can be induced, enabling up to 70% of gas saturation. Surfactant-enhanced NDI is difficult to control under field-scale conditions and is still being investigated. Potential applications of induced pH buffering and in situ gas-induced impermeable walls to optimize dewatering of construction pits are also currently being investigated.

10.2.5 Gas Dissolution and Degassing

The dissolution of gaseous components from a trapped gas phase into groundwater flow has been investigated using pore- to field-scale test facilities (Figure 10.3). Conceptually, it is understood to be a bidirectional kinetic multicomponent mass transfer of moving gas–water interfaces of multisphere gas clusters. This leads to bubbles shrinking or growing (variable volume model), and subsequently to dynamic interface areas and partial pressures of gaseous compounds. Heterogeneous gas saturation at field scales can be taken into account through coupling the multisphere distribution to a hydrogeological (e.g., water flow velocities) or geometrical (e.g., pore sizes) distribution function (Geistlinger et al., 2005).

Mass transfer is driven by partial pressure gradients of gaseous compounds in groundwater flow. A primary problem is the determination of an effective mass transfer coefficient and its scale dependency (Luckner and Schestakov, 1991). Estimation of active gas–water interface areas and water diffusion lengths are also needed. Estimates of hydraulic conductivity changes due to residual gas storage cannot easily be derived from well-known functions of vadose zone modeling due to the nature of gas-water-displacement near saturation (Giese, 2012).

A lot of experimental and modeling work to determine the mass transfer coefficients at the pore to bench scale has previously been reported; an overview of this work is presented in Geistlinger et al. (2005). Best practice scalable mass transfer calculations take into account the dimensionless numbers: the Peclet number (Pe: relates water flow velocity to diffusion), Sherwood number (Sh: relates mass transfer to Pe), and Damkoehler number (Da: relates hydraulic resistance to mass transfer times). State-of-the-art modeling techniques were tested and further developed, and field-scale modeling capabilities of multiphase multicomponent reactive transports were demonstrated for operation control of RGBZ (Horner et al., 2009, Geistlinger, 2010, Weber et al., 2013) using adapted codes of PHT3D, TOUGH2, and MIN3P. It has been reported that for the practical purposes of RGBZ control, first-order transfer functions can be applied to residual gas dissolution.

Balanced experimental data sets (Geistlinger et al., 2006; Weber, 2007; Ehbrecht and Luckner, 2004), and field-scale balance and sensing estimates (Engelmann, 2010; Ehbrecht and Luckner, 2004, Beckmann et al., 2007) are available for pure oxygen gas dissolution. Residual oxygen gas saturations of 2%–4% in sandy sediments can completely dissolve when 2–3 pore volumes of gas-free groundwater have passed. This measure is used in practice to periodically reload storage zones of the PRB BIOXWAND. Mass transfer rates decrease when inert gases are present (e.g., during air injection or in presence of high-dissolved nitrogen concentrations in natural groundwater).

Degassing in conjunction with DGI is defined as the reduction of gas caused by gas stripping and/or diffusive degassing from groundwater. Stripping occurs as a bulk gas escape (buoyancy and convection driven) of mobile gas clusters reaching the phreatic groundwater surface and capillary fringe. A multicomponent gas volume is injected into the coherent gas phase of the vadose zone, and the entire mass of the gas mixture is transferred. Mixing in the soil gas is only limited by gas diffusivity and the partial pressure gradients of the gaseous components. Stripping may also be generated when a gas flow network connects to unsealed technical or natural macropores (e.g., boreholes, wells, and other observation installations), or natural fissures in overlaying gas barriers. Partitioning of volatile compounds such as volatile organic compounds (VOCs) and short-chained alkanes to the gas flow and their escape to the soil gas is of concern due to safety implications.

Diffusive degassing of dissolved compounds from groundwater is a substance-specific mass transfer through the capillary fringe, and is driven by specific diffusivity and fugacity according to Raoult's law. Flux limitations typically arise from dispersivity and fluctuations in groundwater flow.

Stripping is probably the dominant degassing effect during DGI application; however it is difficult to quantify diffusive degassing due to natural soil gas fluctuations. Until recently, sensors for the direct measurement of degassing fluxes have not been available. Stripping needs to be limited by gas injection control, and should be monitored by soil gas monitoring. Best practice for flux estimation includes stationary model-based balancing of the gas injection mass, and gas tracer testing (Weber, 2007). Some light gas escape in the range of 10%–30% of the injected mass often can be tolerated to ensure a sufficient efficiency of reactant supply to the upper (near-fringe) groundwater flow region. If oxygen gas is used, aerobization of the vadose zone can be a desired additional treatment effect of immobile soil water and of leaches from the topsoil. A low-cost soil venting technique can effectively support soil gas mixing and minimize safety implications.

10.3 Techniques and Devices for RGBZ Formation

10.3.1 Set of Available Technical Tools

The first step in the technical implementation of RGBZ is a detailed gas-hydrogeological site investigation. In addition, biogeochemical and contamination information need to be obtained as part of the investigation. The best practice depth-oriented soil core sampling includes low-diameter drilling with liner sampling or percussion core probing, and direct push methods including CPT, pneumatic percussion, and Sonic® vibration sounding (e.g., Geoprobe®). A conceptual gas-hydrogeological site model is required, and can be developed using sample analysis and geophysical and hydraulic survey data. Such a model is presented in Figure 10.5. Borehole logging can include gamma (γ-γ), neutron (n-n), and electric conductivity logging and thermal and permeability flow metering. Hydraulic and immission pumping and infiltration tests can support the establishment of treatment region dimensions.

RGBZ require specialized gas injection and monitoring methods and devices; techniques to efficiently control gas dynamics and their impact on in situ transformation processes are also required. The formation and control of a homogeneous gas distribution and flow-oriented gas dissolution must be enabled, and excessive gas emission from the groundwater zone must be avoided.

A gas injection system consists of four main components: injection lances, a gas delivery and mixing station, an injection control system (pressure, flux, and time control), and a warning and safety system adapted to the expected field gas compositions.

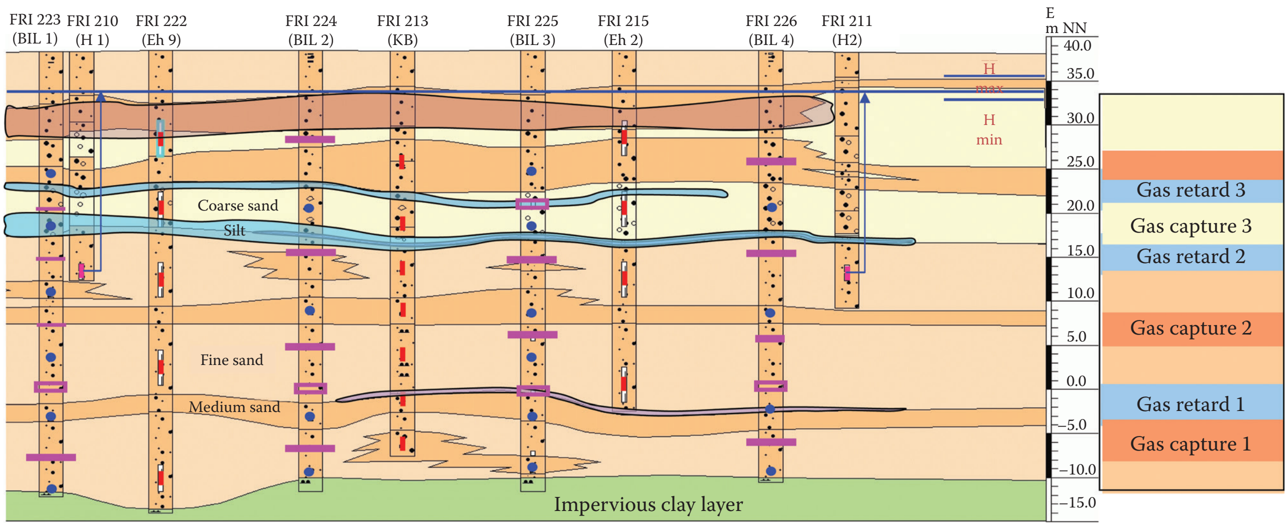


FIGURE 10.5
Cross section of a gas PRB domain as gas-hydrogeological structure model (BIOXWAND).

An RGBZ monitoring system is comprised of a combination of five elements. These are groundwater observation and sampling points or wells, an in situ sensing array for detection of the dissolved gas distribution domain, a detector set for estimation of pneumatic and hydraulic gas propagation, a measurement system to quantify dynamics of gas saturation in the gas storage zones, and finally, a soil gas composition control system.

Techniques that can be used to efficiently control the performance of a gas PRB and optimize the impact to in situ transformation processes are available as an integral mass balancing method for injection gases, and as an algorithm for performance optimization. Modeling techniques can be used for the planning and evaluation of gas PRB applications. Due to their reactive multiphase multicomponent nature, they are normally too complex and the uncertainty is too high, rendering them of questionable value as a decision making tool.

10.3.2 Gas Injection Devices

10.3.2.1 Gas Lances

Lances can be installed by drilling and sounding or direct push methods (Figure 10.6). A number of technical requirements must be met: (1) prevention of ground loosening during installation; (2) high-precision depth-oriented positioning of filter elements to 50 m below the surface, including in heavy ground penetration conditions; (3) a gas-tight vertical sealing of the injection

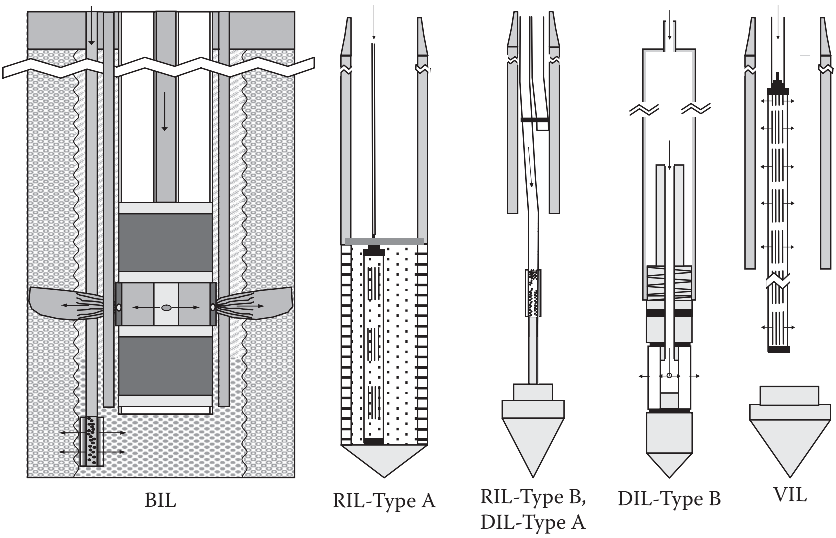


FIGURE 10.6
Variants of injection lance installations for DGI applications. BIL—drilling; RIL—percussion sounding; DIL—CPT-based penetration sounding; and VIL—vibration sounding.

filter tubing; (4) an appropriate pressure, diffusion, and reaction-resistant casing or tubing material; and (5) a gas filter backfill construction that permits homogeneous horizontal gas flow coupling to the subsurface layers.

Drilling Injection Lances (BIL) can be installed in heavy or variable layered sediment and bedrock environments using dry and hydraulic drilling using diameters <250 mm. There are typically no depth restrictions and multilevel injection filters can be positioned in one borehole (Schinke, 2008). The main disadvantage is that the extraction of subsurface material up to 2 m in diameter cannot be avoided (Engelmann et al., 2004). Following the installation of lances, the measurement of material extraction during the drilling process and tight grouting of the casing annulus and the loosening zone are required, even under bedrock conditions. Special grouting valve casings are available for high-pressure injection of sealing suspensions (e.g., bentonite clay). Injection volumes must be balanced and controlled, and a multistep grouting procedure has to be planned with intermittent testing of the sealing effect. Care has to be taken during grouting, as undesired clogging of the main gas transport layers or gas filters can occur. Suffusion-protected gas filter zones are built-up by gravel or coarse sand. Gas injections via multilevel filters can be performed using casing packers.

There are three types of *Sounding Injection Lances*. During direct-push installation, displacement and compaction of the rock material take place, and an autosealing effect is gained between the casing and the borehole walls. Borehole diameters are approximately 30–80 mm.

Percussion Sounding Injection Lances (RIL) can be installed in sediments to a depth of 10 m using 2–3 in casings (e.g., HDPE) with a filter tip and sealing packers between the casing segments (Figure 10.6—RIL-type A). The casing remains in the borehole and gas injection tubing and gravel fillings are placed into the filter zone, which is sealed by a compacted clay layer. In addition, sensors and multilevel filters can be installed. RIL are installed in medium-compacted sediments using heavy pneumatic percussion tools (e.g., Geoprobe®, up to 100 kN). Depths of 30–40 m can be reached, although care must be exercised when pushing down a cone tip with fixed injection tubing as the milling of soil material can lead to filter sealing or destruction. After reaching the planned depth, the hollow casing is drawn back and can be used multiple times. An additional hollow drilling auger can help to lower the penetration resistance of highly compacted or very coarse layers by preloosening. High pressure sealing of the borehole can be done during withdrawal of the casing (Figure 10.6—RIL-type B). It is recommended that up to 2 months consolidation time be given for the installed lances before starting lance operation, particularly for HDI applications (Engelmann, 2010).

Continuous hydraulic cone penetration tools (CPT) with up to 200 kN are used to install *Penetration Injection Lances* (DIL). Thinner casing walls allow for the installation of larger diameter tubing. The maximum depth is in the same magnitude as for RIL and predrilling or stabilizing casings are required in heavy soil layers. A filter casing injection lance (Figure 10.6—DIL-type B) can be used multiple times as the CPT is able to withdraw the complete system. There are a number of sensing, additional testing, and sampling tools available for both percussion sounding and CPT, which give the advantage of flexible multifunctional applications (Dietrich and Leven, 2006). Lances of DIL-type B allow for pressure-controlled groundwater sampling, permeability testing, and in situ groundwater screening of dissolved gases.

High-quality direct push lances can be installed up to 80 m at a moderate cost using the Sonic® sounding technology. *Vibration Injection Lances* (VIL) are good alternatives to classical dry drilling in sediment environments in terms of depth and core probing, and both multilevel and coupled sensing installations are available. Another advantage is grouting and sealing of the lances or filters is done by sonic withdrawal of the casings, which results in autocompaction and consolidation (Engelmann et al., 2009). VIL lances are preferred, even for HDI gas injections.

10.3.2.2 Gas Supply, Gas Mixing, and Distribution

Injection gases used in RGBZ include pure gases (e.g., oxygen), or gas mixtures. Air is typically used as a carrier gas to achieve high ROI, and partial pressure can be controlled with a few lances and oxygen. Inert trace gases (e.g., He, Ar and Ne or reactive gases such as methane and carbon dioxide) can be mixed with the injection gas.

Pure gases are economically stored in pressurized tanks, and additional gas compression is not required for injection. Oil-free compressors are used for the injection of atmospheric air mixtures, and a postdrying step for compressed air is necessary.

Mass flow controllers and flow meters are recommended for the mixing and distribution of injection gases as they allow the balancing of injected gas amount for each lance. These devices require calibration to the specific gas mixtures (Figure 10.7). Pressure meters and magnetic valves enable effective gas distribution and dynamic injection intervals.

Gas injection is performed as either low-pressure (NDI) or pulsed high-pressure injection (HDI). Continuous NDI injection is applied in the initial formation period for a gas PRB when there is a high demand for reactants (e.g., oxygen), and it results in full ROI formation, preconditioning, and preoxidation of the rock matrix. It can also lead to some emission of gas into the unsaturated zone. Constant injection pulses over a few hours are used during a regular RGBZ operation, and these pulses are interrupted by periodic break periods. HDI injection consists of high frequency, high-flow rate gas pulses in the range of seconds to minutes. Gas breakthrough to the unsaturated zone is avoided by the time limitation of coherent gas flow periods. HDI can be used for formation of local gas storage zones with higher gas saturations, and for repairing of clogged gas lances. While a gas supply system for NDI has to resist a total pressure of approximately 500 kPa, an HDI supply system (including lances) needs to be operated at >1000 kPa.

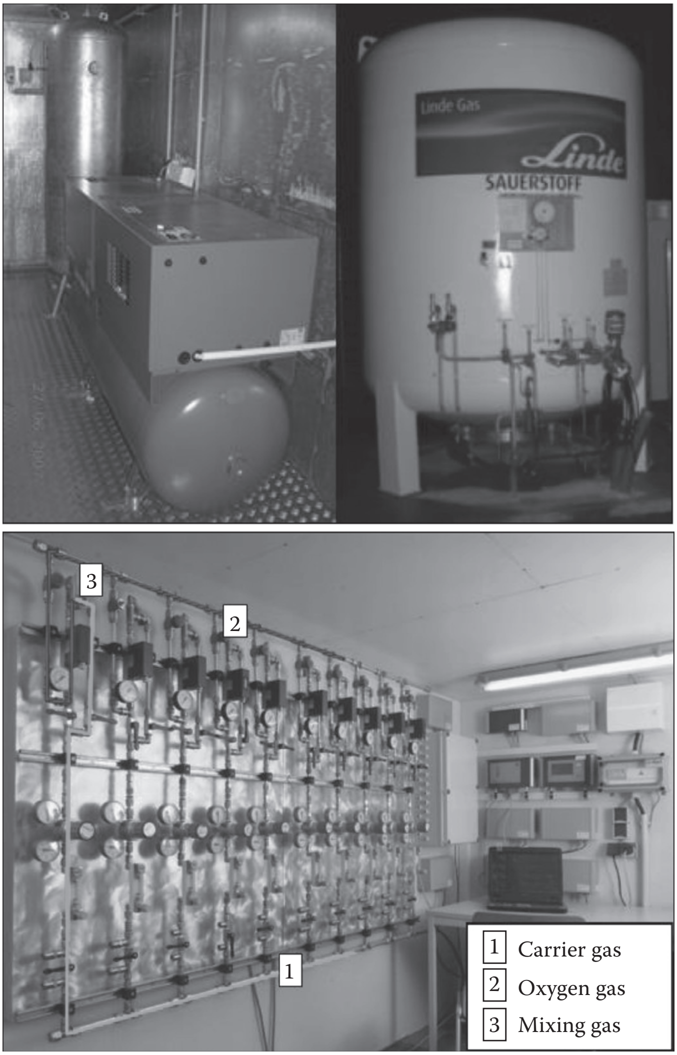


FIGURE 10.7
Technical equipment used for DGI (left to right): Gas compressor or blower; pressurized or liquid gas tank; and gas injection and mixing station. (From Schmolke, L.P. et al. 2007: *Proc. Dresden Groundwater Research Centre*, Nr. 31, pp. 135–146 (in German).)

10.3.2.3 Safety Precautions

The materials used in the gas supply system have to be chosen in accordance with the reactive gases used. Also, technical precautions for pressurized systems need to be taken into account. Leaks in the gas supply system can be automatically monitored using gas-specific sensors, pressure transducers, and smoke detectors. Limiting access, remote control systems, and an automatic off switch are needed for the gas tanks and supply system. When dealing with volatile hazardous contaminants or potentially explosive gas mixtures, gas warning devices and a soil gas venting system are required.

10.3.3 Monitoring Devices

The main functions of a RGBZ monitoring system are: (1) the detection of gas emissions at geological weak points, nontight boreholes, and soundings; (2) representative sampling of groundwater and soil gas; (3) detection of gas distribution and dimensions (ROI) of the RGBZ; (4) estimations of injection gas propagation and dissolution; and (5) estimation of local gas saturations in crucial regions and layers.

10.3.3.1 Groundwater and Dissolved Gas Monitoring

Groundwater sampling equipment can be installed using self-grouting direct push technology. Special filters and pumps are required due to small diameters and gas-protected filter screens (Figure 10.8). Sampling using

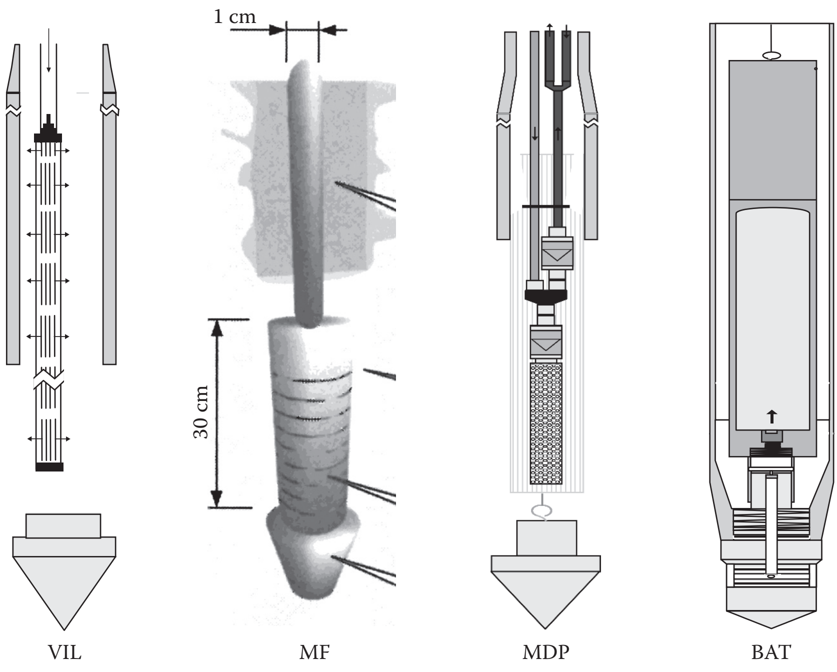


FIGURE 10.8
Groundwater monitoring devices for RGBZ. (VIL—loosen sonic lance filter; MF small diameter observation well; MDP—loosen double-valve pneumatic pump; BAT pressure conserving bailer shuttle).

peristaltic (at shallow groundwater levels) or double-valve pneumatic pumps (MDP) and shuttle systems (BAT) give point information due to small sampling volumes and short filters. MDP and BAT can be used for a pressurized groundwater sampling without degassing losses.

Modified RIL-type B and DIL-type A lances can be used to install 25-mm groundwater filters. Local-scale integrated samples can be obtained using packers and either multiple MDP or button valve pumps (Uhlig, 2010 and Zittwitz et al., 2012). When using a Sonic®-system, 50-mm direct push filters can be installed. In addition to these pumps, mobile bailing systems (e.g., BAT) can be applied. Hydraulic and immission pump tests are then performed to obtain volume integrated groundwater information. In a gas injection zone, it is necessary to cover wells with a gas-tight cap.

The sampling of dissolved gases can be performed by pressure conserving bailing devices and the use of trace gases (Ehbrecht and Luckner, 2004). A headspace gas phase can be brought into equilibrium with the water sample and pre- and postsampling can be undertaken using gas chromatography. Inert gas flushing, volume and mass balancing, and multiple pressure controls are needed in order for confidence to be placed in the results obtained.

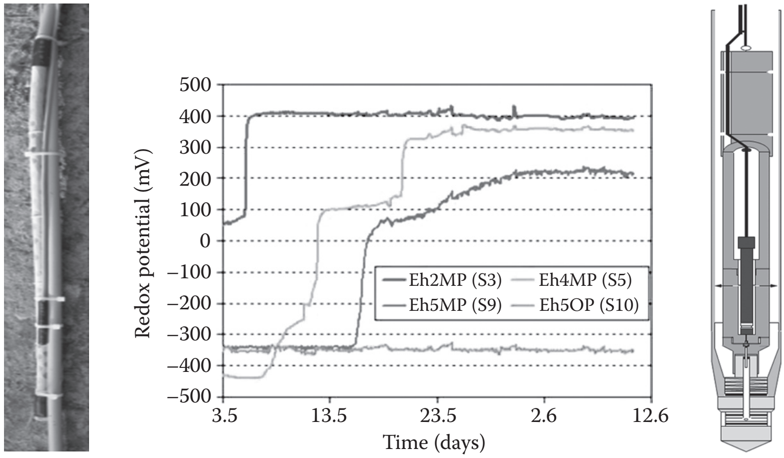
10.3.3.2 Gas Monitoring

It is advisable to install an array of in situ gas sensors in the gas injection zone of an RGBZ. The distribution of gases and ROI dimensions can be obtained, along with an estimation of injection gas propagation and the dissolution of the gas phase. Combinations of sensors are placed and grouted to the main gas-permeable layers using the direct push method. They can also be installed in small-diameter observation wells if packers and an automated pumping system are used. A shuttle-sensing tool MIDZ (Figure 10.9) can detect high concentrations of dissolved gases. MIDZ uses a pressurized flow chamber with integrated sensors, and is installed with CPT technology.

The interpretation of gas sensor signals is based on the gas-hydrogeological model. Currently, the best available sensors for oxygen gas are in situ redox electrodes and oxygen optodes (Engelmann, 2010). Carbon dioxide optodes are recently developed too. Flow-through monitoring systems (e.g., MIDZ or packer-sealed filters) can provide meaningful information about in situ pH and electrical conductivity conditions.

Starting a gas injection, initial gas sensor values are typically widespread. However, after matrix preoxidation and homogenization by water flow, sensor signals become meaningful. The signals can serve as a measure of the change in the heterogeneity of the reactive zone during operation of an RGBZ.

In situ redox sensors and oxygen optodes can be used to estimate gas propagation and dissolution due to their short reaction time. The travel times for coherent gases and clusters are measured as the time required for the breakthrough reactions of each sensor, and gas flow paths can be elucidated. The



VIL + Eh   Change of redox signals due to oxygen gas injection   MIDZ

FIGURE 10.9
Gas monitoring devices for RGBZ and gas sensing signals (data from BIOXWAND). (VIL + Eh—loosen sonic lance filter with redox sensor; MIDZ—flow-through shuttle).

sensor value changes on the cessation of gas injections can be interpreted as the propagation of incoherent gas clusters and gas dissolution.

Another method for the estimation of gas propagation is trace gas testing; currently the best available are found to be noble gases (e.g., He, Ne, and Ar). Trace gases are mixed with a carrier gas and injected at low partial pressures. Due to a lack of interaction with soil and groundwater, environmental authorities have accepted the use of noble gases. Care is needed during trace gas sampling due to their high volatility. The use of pressurized samplers or bailers is also recommended (Uhlig, 2010 and Schinke, 2008).

10.3.3.3 Gas Saturation Testing

To estimate the amount of stored reactive gaseous substances, a gas saturation test that takes pressure dependency into account is required. The best available techniques for gas saturation estimations are (1) gas-hydrogeological balancing injection gas models, (2) direct gas profiling, and (3) local pumping tests in gas storage regions. Aqueous and partitioning trace gas infiltration methods are time-consuming and are currently still under evaluation.

Oxygen gas balance models can be parameterized using laboratory tests and gas monitoring. These models are suitable for the estimation of mean gas saturations in large gas storage zones, or layers during stationary operation periods (Ehbrecht and Luckner, 2004; Weber, 2007). The first step is to estimate the geometry of the storage zones, using gas-hydrogeological

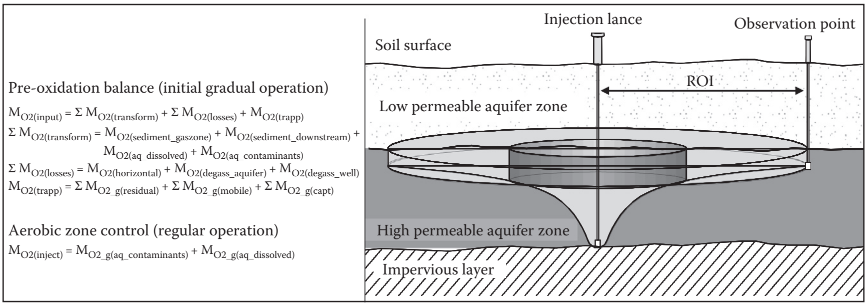


FIGURE 10.10
Example of a balance model scheme for NDI operation of an RGBZ. (From Weber, L. 2007: *Proc. Dresden Groundwater Research Centre*, Nr. 30, 151 p. (in German). With permission.)

surveying. Distributed gas input values; gas transfer (dissolution and consumption by groundwater and sediment), gas losses (horizontal escape from ROI and degassing) and gas storage (trapping) can be calculated or estimated (Figure 10.10). The complexity of the balance model is reduced during the regular operation of gas PRBs.

Direct gas profiling can be performed using borehole logging and sounding methods. Geophysical borehole logs are well known and evaluated (Dietrich and Leven, 2006). Calibration using a reference system (pilot or bench scales) is required. Gamma (γ-γ) logs detect the subsurface mean density distribution, while neutron (n-n) logs are sensitive to the presence and mass of hydrogen (water). The best results are achieved using the neutron method where gas saturations of 4% are significant and penetration radii are of >0.15 m.

The best resolution gas saturation data can be acquired using time domain reflectometry (TDR). TDR traces changes in the dielectric state of a domain, which is sensitive to the water content. TDR logging tubes (50 mm) can be installed by Sonic® technology. Adapted TRIME® sensors (Fundinger et al., 1996) were tested in a balanced pilot scale column device (Engelmann, 2010), and they have been used for continuous profiling. Changes in saturation of approximately 2% are significant, as are penetration radii of 0.30 m. TDR systems are recommended for identification of gas capture zones (Figure 10.11).

Hydraulic pumping tests can evaluate the impact of gas storage zones to groundwater flow. A field demonstration showed local lowering of conductivity from 4×10^{-3} to 1×10^{-3} m/s in gravel sediment near the tested well, and gas saturations of 7%–10% were reported.

10.3.3.4 Soil Gas Monitoring

Due to safety requirements, monitoring the continuous gas distribution and composition in the unsaturated zone is obligatory for RGBZ operations. A

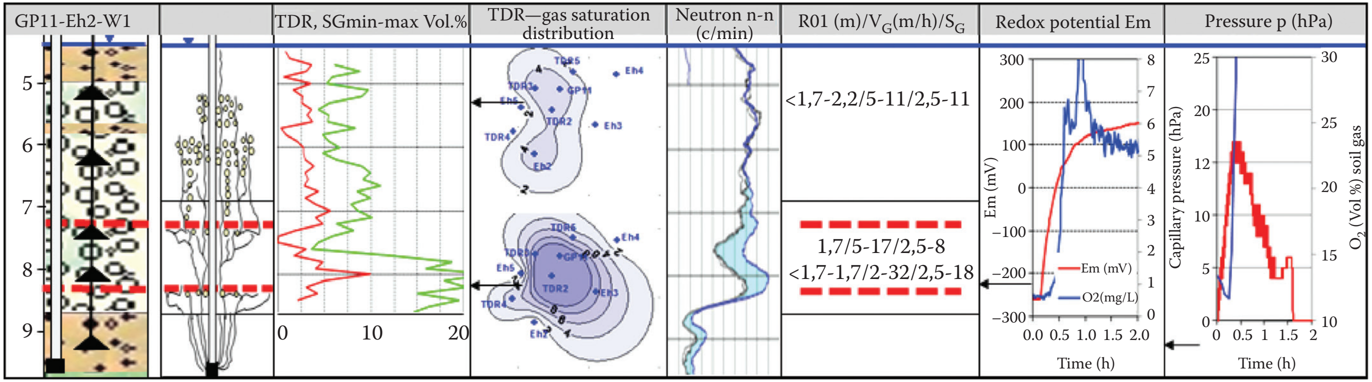


FIGURE 10.11
Combined gas sensing of storage zones with TDR, n-n-log, redox, O_2-optodes, and pressure detectors for gas reloading decisions. (From Engelmann, F.I. 2010: Model supported high pressure pulsed Gas Injection (HDI) for in situ remediation of contaminated aquifers: Technology for a controlled operation of gas storage zones and development of a measurement system of in situ gas saturation and a gas injection technology. Report Nr. KF0011010SB7–1, Sensatec, 46 p. (in German).)

large number of gaseous substances of interest and mixtures can be detected by sensors or on-site analyzers. Small diameter (25 mm) soil gas probes are installed at specified depths by direct push or manual electric ramming. Low flow pumping and on-site analysis is the preferred sampling method. In situ diffusive sensors are available; however the absorption rates are not as consistent or reliable.

Gas sensing and sampling near the capillary fringe can support the estimation of gas distribution and propagation in the groundwater zone. The initial signals of soil gas sensors are interpreted as breakthrough times and possible locations of gas emission from the groundwater domain. Soil gas sensors are used to check the sealing result of grouted injection lances. Additionally, gas consumption (e.g., oxygen, methane) or production (e.g., carbon dioxide) can be estimated by soil gas sampling, and the unsaturated zone can be included into an RGBZ treatment system (Uhlig, 2010).

10.3.4 Techniques for PRB Performance Control

Once reactive gases are dissolved into the groundwater flow, there are several measures or techniques that can be used to evaluate and control transport and the in situ transformation of dissolved compounds in the aqueous phase. These methods can also evaluate the interactions with reactive sediment surfaces (ENA). Sophisticated reactive modeling tools and techniques for site characterization and the identification of transformation process are also available. A number of these techniques require a site and contamination-specific application.

Given all of the possible methods to control the reactive zones of gas PRBs, an algorithm was constructed to take into account adaptive performance and optimization measures, and evaluated at the BIOXWAND gas PRB. The algorithm is site specific and given as an example in Table 10.2.

10.4 Example Applications of the RGBZ Technology

Three example applications have been chosen to demonstrate the capabilities of gas PRBs. First, the results of a full-section PRB (BIOXWAND) that has been operating for 5 years to treat an ammonium plume are presented. A homogenized nitrification effect was reached using injections of variable oxygen gas and air concentrations. The PRB was scaled up to a length of 800 m. In the second example, an oxygen gas PRB was used to naturally attenuate an organic contaminant plume containing aliphatic and aromatic hydrocarbons. The PRB technology has been accepted by the mining industry and environmental authorities as a method that can be used to prevent the future plume propagation or deviation due to mining activities using

TABLE 10.2

Algorithm for Optimization of the Performance of Gas PRBs

Performance Limitations	Risk Lowering Measures	Optimization Actions
Distribution of reactants	Refining the injection array density by gas analysis-hydrogeological model	Horizontal ROI dimensions and overlapping Injection gallery sequences in flow direction Identification of gas retardants Injection below treatment layer
	Variation of the injection rate and pulses	Injection rate (NDI) or pressure (HDI) change Pulse frequency change HDI–NDI combination
	Use of carrier gases	Hydraulic autoregulation by nitrogen clogging Short-term reloading of reactants (e.g., oxygen) Gas mixture supply (e.g., trace gases, methane-air)
	Use of a downstream reaction zone	Macrodispersion mixing of reactants Amplification of reaction length and time
Gas dissolution	Forcing gas supply to fine to medium grained sediments	Formation of dense gas networks with high mass transfer interfaces Homogenization of gas distribution
	Limiting gas supply to coarse sediments and capture zones	Prevention of inactive gas capture zones
Dissolved concentration range of reactants	Limiting reactant concentrations	Lowering gas saturation Partial pressure variation of reactants
	Optimization of the geochemical state	Aerosol or foam injection to control, e.g., pH, Hardness and cometabolic degradation Supply of higher oxidizers (e.g., H_2O_2)
	Nutrient supply	Supply of gaseous and solid nutrients (e.g., CH_4, CO_2, phosphate)
Clogging, permeability losses	Periodical redox state changes (aerobic/anaerobic)	Lowering the injection cycle time Increasing break periods Avoiding the carrier gas supply Demand-oriented reactant supply
Bypassing of groundwater flow	Forcing autoregulation	Hydraulic forcing of bulk groundwater flow due to local pumping or drainage

Source: Internal document of Sensatec GmbH, Kiel. With permission.

aerobic enhancement of biodegradation. The third example is an in situ drain and gate technology (GFIadags®) which included two RGBZs as a treatment train for a plume of a complex inorganic and organic contaminant containing ammonium, phenols, aromatics, DOC). A zone for the removal of iron by oxygen and ammonia gas and a polishing downstream oxygen gas reactor for the degradation of ammonium and DOC were formed.

10.4.1 The BIOXWAND Technology for Ammonium Elimination

Since the 1990s, the Berlin Water Company (BWB) has been working to safeguard a groundwater resource with a capacity of 10,000 m³/d, which is used for drinking water production (reference). Approximately 200 million m³ of groundwater was contaminated with 2200 tonnes of ammonium and organic trace cocontaminants including CHC (*cis*-DCE, vinyl chloride) and pesticides as a result of waste water infiltration and drainage from an unsealed sludge storage area of an upstream sewage field. A protection well gallery is being used to capture the contaminated stream, and groundwater with mean ammonium and organic trace substance concentrations of 10–20 and 0.02 mg/L respectively, are pumped out and treated at a nearby waste water plant. The extent of the contamination of the aquifer matrix is estimated to be 3000 tonnes of adsorbed ammonium, with approximately 2200 tonnes accessible to treatment using ion exchange (Ehbrecht and Luckner, 2004).

After the German Federal Ministry of Education and Research funded an evaluation of in situ cleanup approaches, the reactive gas barrier technology BIOXWAND (EP 1550519) was chosen as the best available method for the remediation and protection of the groundwater resource and therefore, the best option to replace the pump-and-treat system (Figure 10.12) (reference). Since 2007, a permeable oxygen gas barrier (length = 200 m, depth = 40 m, thickness = 25 m) has been installed approximately 500 m upstream of the drinking water well gallery A (Engelmann and Schmolke, 2014). The final length of the barrier is planned to be 800 m, and it was predicted that up to 200 kg/day of ammonium will be oxidized in situ.

Based on a mass balance approach and supported by reactive transport modeling (Horner et al., 2009), the initial annual oxygen demand for the performance of a 100 m barrier segment is approximately 64 tonnes. Approximately 28 tonnes/year of oxygen is needed to treat the inflowing groundwater (20 tonnes/year for nitrification, 8 tonnes/year for iron removal). A total of approximately 36 tonnes/year of oxygen is needed for the partial sediment matrix treatment of 22 tonnes/year of sulphide and 14 tonnes/year of adsorbed ammonium. The total oxygen demand declined with time due to gradual matrix oxidation.

The hydrogeology of the site is characterized by layered glacial sandy sediments to a depth of 50 m. Enclosed loamy lenses and sublayers in addition to sand layers which have been compacted to varying amounts act as retardants of the vertical gas propagation. In this way, there were four gas storage horizons within the unconfined aquifer (Figure 10.5).

An in-line injection gallery of sealed gas lances of types BIL, DIL, RIL, and VIL supplied the gas. The distance between the lances was 25 m and two injection filter depths (15 m and 40 m below groundwater level) were used. The low-pressure method (NDI) was applied, and gas injection rates were 0.5–2.0 m³/h STP. The radii of influence (ROI) for effective horizontal gas propagation were approximately 10–25 m. In addition to the ROI and the

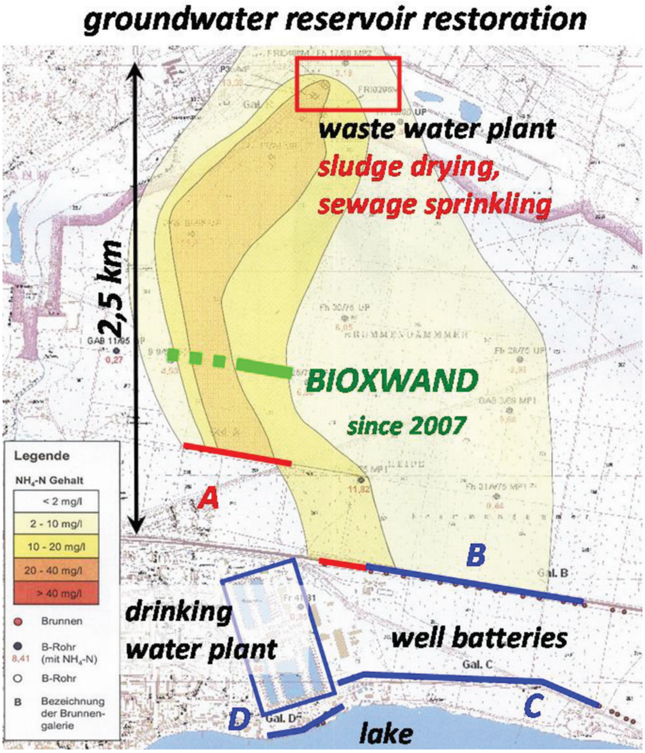


FIGURE 10.12
Site map of the BIOXWAND application area.

local variations in the injection regime based on hydrogeological profiling, monitoring was used to achieve a full-section PRB effect. The oxygen content of the injection gas varied between 20% (e.g., same as the atmosphere) and 100%. Gas injection cycles of 1–2 h were followed by breaks of 3–5 h, and coherent gas flow velocities >1 m/h were detected next to the injection lances. Vertical gas escape into the unsaturated soil zone was monitored as it occurred (e.g., when it exceeded the local aquifer gas storage and retardation capacities). In this case, stripping did not occur due to a lack of volatile solutes in the groundwater.

The BIOXWAND performance showed that it was impractical to aim for a quick remediation (e.g., satisfying the entire oxygen demand of 64 tonnes per 100 m) during the first year of barrier operation. This can lead to decreased operating efficiency with high gas losses mainly due to heterogeneous gas distribution, diffusion-limited gas dissolution, the variable and developing kinetics of matrix to groundwater exchange, and biochemical transformation processes. In the case of BIOXWAND, an initial 3-year operating regime was conducted, during which a total oxygen mass of 100 tonnes was supplied. The oxidation of the sediment matrix and nitrification rates were increased slowly during this time and a reliable homogenization of dissolved oxygen distribution of 5–50 mg/L were achieved. Groundwater redox potential was increased from approximately—200 mV to +500 mV after 3 years.

In situ gas storage monitoring was used to optimize the performance of the BIOXWAND. The mean gas saturation of 2%–4% was found to be an appropriate range for effective operation (Figure 10.13), however this was just the range of residual gas saturation in the sediment. The amount of time required for complete dissolution and consumption of such oxygen gas was estimated to be equal to that it required exchanging 1.5–2.0 pore volumes of groundwater. Local saturations of up to 17% were detected in some coarse sandy layers. This was linked to a localized reduction in hydraulic conductivity from 4×10^{-3} to 1×10^{-3} m/s. In this case, a hydraulic self-regulation and homogenization of the groundwater flow occurred. High groundwater fluxes in the coarser sections were decreased by preferential gas storage, whereas low fluxes in the finer-grained sections were increased with an increase in the local hydraulic gradients. Monitoring and control of the hydraulic flow homogenization in gas PRBs at the field scale are subjects of research, as they are important factors in the cost-effective operation of PRBs and their increasing acceptance from the point of view of the authorities.

It is reported in the literature that the supply of oxygen gas causes pyrite oxidation. Dissolved ferrous iron is predominantly precipitated as ferric iron hydroxides. Mass and volume balances for the in situ iron removal and field observations indicated that there was no significant risk of long-term pore clogging to groundwater flow or gas storage. Iron hydroxides precipitated mainly in the low-pore diameter regions (Figure 10.14).

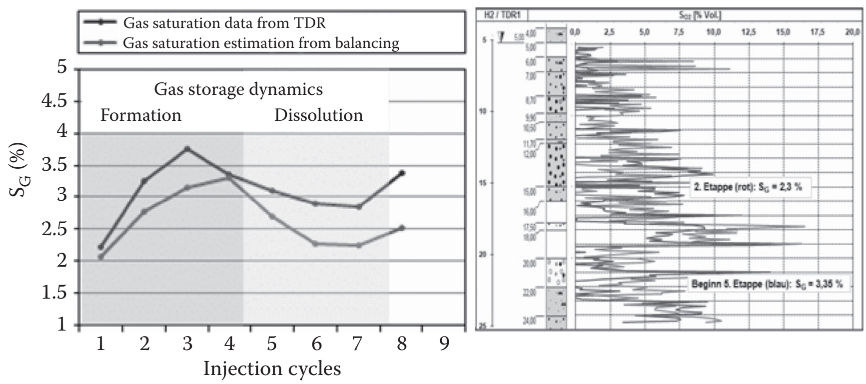


FIGURE 10.13
Gas storage control during BIOXWAND operation: changes of residual gas saturation (left) and local TDR gas sensing results (right).

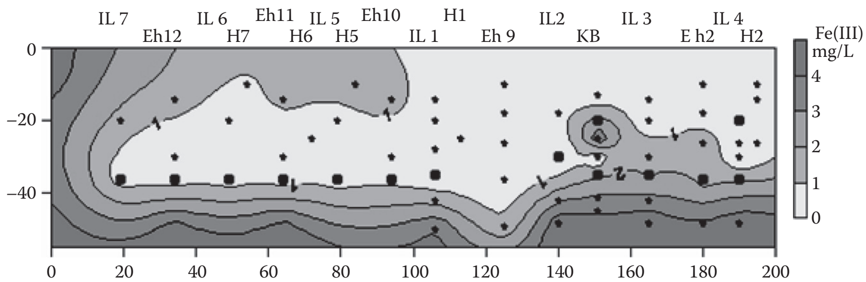


FIGURE 10.14
In situ iron removal in the gas storage zone after 3 years of the BIOXWAND operation.

Pyrite oxidation is accompanied by sulfate and proton production respectively. As a result of implementing the gradual barrier operation regime, production was limited and subsequent sulfate concentrations increased by 100–150 mg/L in fine-grained sands, and by 50–75 mg/L in coarser regions with lower pyrite content. The results showed that proton production due to pyrite oxidation was a reliable, but time-limited indicator of acidification potential during the initial operation period. The proton production was adjusted to the calcite buffering capacities of the aquifer matrix and the inflowing groundwater respectively, and the pH was stabilized at a mean value of 6.7, after it was decreased by 0.5–0.7 units. Calcite dissolution was accompanied by a slight hardening of the groundwater, and calcium ion exchange forced desorption of monovalent ions (e.g., sodium, potassium, and ammonium). This caused an initial increase in the ammonium concentration of 10–15 mg/L in the gas barrier zone.

Dissolved ammonium is transformed to nitrate by autochthonous microbes under aerobic conditions. The main species were *Nitrosomonas europaea*, *Nitrosomonas eutropha*, *Nitrosomonas halophila*, and *Nitrosococcus mobilis*. A lag-period of 30–50 days was needed for their activation after aerobic conditions were established. Laboratory tests indicated that an upper oxygen limit for nitrification was verified during the operation of the BIOXWAND. A significant inhibition was found when oxygen concentrations exceeded 50 mg/L. During the nitration step, no self-inhibition by nitrite was found. Proton production caused by nitrification occurred simultaneously with pyrite oxidation. It was estimated that the buffering capacity of the BIOXWAND would be lowered to approximately 90% of the initial value after 40 years of operation.

After 3 years of BIOXWAND operation, the ammonium concentration was reduced to <5 mg/L in the first 200 m-section (Figure 10.15). The nitrate was reduced to nitrogen by autotrophic denitrification under downstream anaerobic conditions. A slight lowering of DOC by approximately 1 mg/L indicated the transformation of organic compounds. CHC were completely degraded in the aerobic gas barrier zone.

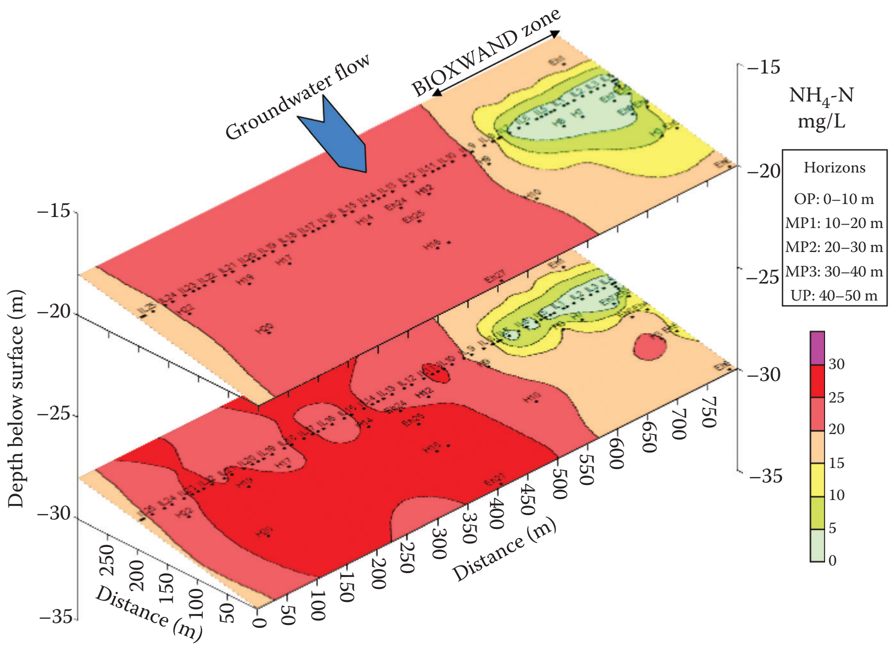


FIGURE 10.15
Results of ammonium degradation after 3 years of BIOXWAND operation.

10.4.2 Oxygen Gas PRB for Risk Coverage of MNA of an Organic Contaminant Plume

An unconfined aquifer in the vicinity of a former lignite processing site was impacted by organic pollutants (aliphatic, aromatic) and a 600 m long contamination plume had formed. Restoration of the site is conducted by a federal administration company specialized in postmining sites (the Lausitzer und Mitteldeutsche Bergbau-Verwaltungsgesellschaft mbH [LMBV]) under the supervision of the mining authority. Following a pump-and-treat decontamination, the Profen site was treated by monitored natural attenuation (MNA). The risk prognosis of the plume behavior was based on delineation of the damaged aquifer region, groundwater flow analysis and prediction, balancing of inventory and mass flow rates of contaminants, and identification of biodegradation processes. The results of the MNA showed that contaminant concentrations were reduced.

A primary protection goal was the prevention of contaminated groundwater impacts from the downstream active lignite mining. The groundwater flow is controlled by mining area drainage and a postmining pit lake. In this way, the cooperation with the mining company was needed in order to ensure an efficient long-term site restoration (Giese et al., 2012).

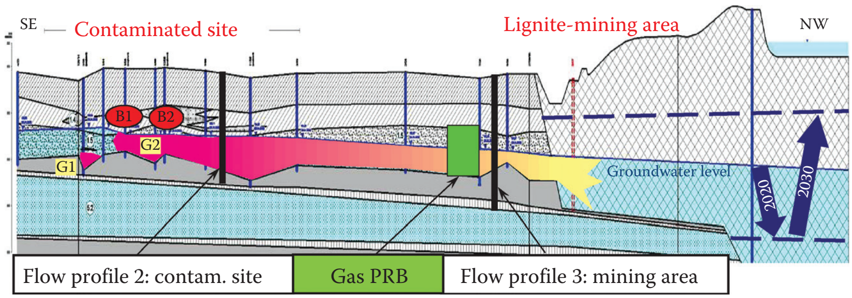


FIGURE 10.16
Cross section of the Profen site (in flow direction): plume propagation from the damage zones (B and G) is toward an active lignite mine pit.

The risk coverage of long-term MNA behavior was demanded by the mining authority. A technical measure was required in order to ensure risk prevention in the event MNA would fail, and to support and stabilize the accorded MNA prognoses. An oxygen gas PRB was identified as the best available technology for this purpose. A schematic representation of the PRB application is presented in Figure 10.16.

A field-scale demonstration and optimization of the gas PRB was performed over 12 months. The goals of the optimization were

- Determine the ability of the DGI to naturally attenuate the contaminants (e.g., forcing the aerobic biodegradation rates of contaminants in the plume)
- Plan a full-scale gas PRB technology that could be implemented as a risk coverage measure in the future (e.g., including owner and authority permission, evaluation of costs and time)

A 450 m² test site that included part of the plume center and a lateral inflow region was chosen. The average aquifer thickness was a 5-m saturated and a 4-m vadose zone (Figure 10.17). The upper aquifer was formed by highly permeable layers of gravel with sands, and the average groundwater velocity in the plume center was 0.8 m/day. A loamy top-layer acted as a gastight sealing. Typical BTEX, naphthalene, and petroleum hydrocarbon concentrations in the plume center were 3, 0.7, and 3 mg/L, respectively (Figure 10.18).

The groundwater level of 1.5 m fluctuated, and subsequent variations in the flow rate occurred due to a high recharge in summer and autumn 2010. Despite these fluctuations, the flow direction did not change. Soil core analysis during the site investigation indicated that there were still high concentrations of adsorbed contaminant in the plume center sediments, and in the

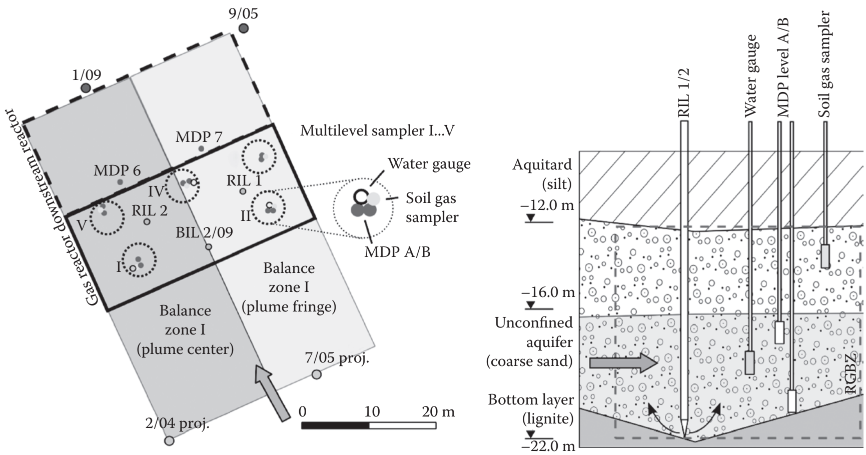


FIGURE 10.17
Test site scheme (left) and cross section (right) of the Profen gas PRB.

underlying impervious lignite layer. In this case, mass balancing of contaminants was limited.

The construction of the test site is presented in Figure 10.17. Packer separated double-valve pneumatic pumps (MDP 6/7) were used for the semi-integrated groundwater sampling of 25-mm mini filters (MF) (Figure 10.8).

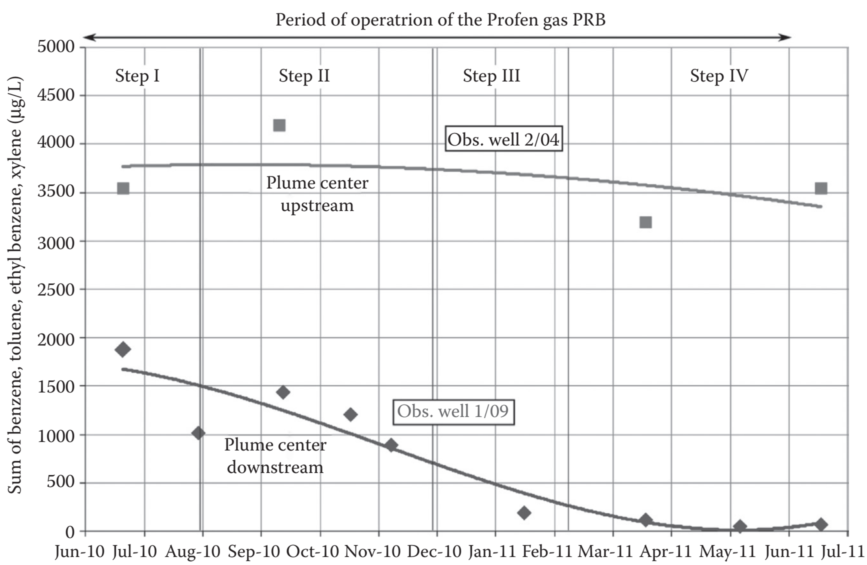


FIGURE 10.18
Impact of the Profen gas PRB to the groundwater load of balance zone I (plume center). The downstream trend was maintained about 6 months after PRB operation stopped (not shown).

During pump testing, the radii of influence were found to be 0.3–0.5 m. Upstream and downstream groundwater monitoring wells were used for an integrated mass flow evaluation using a 3D groundwater flow model. More wells in the vicinity and their long-term monitoring data were taken into account to determine the influence of the gas PRB on ongoing natural attenuation processes.

Neon and helium trace gases were used to determine an initial ROI of the coherent gas flow and gas escape to the vadose zone. These tests were repeated during a subsequent stationary period. An average ROI of gas flow of 5–8 m was detected in the groundwater zone; oxygen gas storage and dissolution efficiency of oxygen at approximately 60% was found using mass balance modeling. The slight aeration of the vadose zone was anticipated during the short-term testing of the gas PRB, and the effects of stripping and the safety implications were monitored in the vadose zone.

The operation of the Profen oxygen gas PRB consisted of three stages. Gas injection rates at lances were in the range of 0.25–0.5 m^3/h STP.

Period I (116 days):	Pre-oxidation by continuous injection of 26 kg O_2/day
Period II (77 days):	Forced sediment conditioning and initiation of biodegradation by continuous injection of 37 kg O_2/day
Period III (128 days):	Stabilization of biodegradation by pulsed injection of 21 kg O_2/day

In periods I and II, almost the entire dissolved oxygen mass was needed for pyrite oxidation. Initial high sulfate production rates led to a temporary decrease in downstream pH and increased iron and manganese dissolution. During period III, the conditions for an optimized biodegradation of pollutants were established and pH >6.5 were found. Approximately, 20% of the dissolved oxygen was consumed in the transformation of contaminants. Additional details are reported in Zittwitz et al. (2012).

Aerobic biodegradation rates were estimated from mass balances, and were proven by laboratory testing and field-scale transport modeling. First-order rate coefficients of 0.07/day^{-1} for benzene and 0.04/day for naphthalene were found. Degradation ratios for the total mass flows of benzene and naphthalene were approximately 96% and 80% respectively.

In summary, the implementation of the oxygen gas PRB at the Profen site was performed during an ongoing MNA application. The ability to enhance natural attenuation potentials in a plume of dissolved aliphatic and aromatic hydrocarbons was demonstrated. No meaningful interference to the accorded MNA prognoses outside the PRB zone was found, due to miminal impacts on the groundwater flow. However, the efficiency of oxygen gas storage and dissolution should be increased significantly in order to optimize the cost effectiveness of a full-scale application.

The gas PRB technology was found to be suitable for the technical risk coverage of MNA. The full-scale application was based on groundwater flow and transport modeling of potential failing scenarios of MNA, due to advancing lignite mining. The mining company supported the planning by providing data regarding the anticipated water management of the lignite mine pit and by facilitating access to a PRB reservation area. The costs and safety issues were also evaluated. The mining and environmental authorities confirmed the treatment targets and the operation chart, and the gas PRB technology became part of a long-term operating closure plan for the Profen site.

10.4.3 Reactive Gas Zones as Part of the GFIadags®-Technology

Reactive gas zones were integrated in a drain and gate technology for the sequential plume treatment of deep aquifers. The treatment train technology was demonstrated at the Schwarze Pumpe site, a former gasification plant. A plume containing high concentrations of phenols (30 mg/L), DOC (100 mg/L), and ammonium (150 mg/L) required treatment in a 37 m deep multilayered aquifer. The thickness of the saturated zone was 20 m, and average groundwater velocity was approximately 0.12 m/day. The gate treatment (zone B) consisted of stripping and chemical oxidation of groundwater contaminants in collector and distributor well reactors (Kassahun et al., 2005). Gas injection zones were established to perform iron removal (zone A: treatment area of 900 m^2) and posttreatment of ammonium and DOC (zone C: treatment area of 1.800 m^2). The treatment train is presented in Figure 10.19. The construction of the gas injection zones followed the principles discussed in Section 10.3. Additional details are reported in Uhlig (2010). Due to high contamination, partial decontamination of the soil matrix was addressed to form in situ buffer zones against breakthrough of fluctuating contaminant streams.

In zone A, in situ iron removal was first induced by oxygen gas injection. As seen in Figure 10.19, the competitive effects of matrix oxidation limited the success. Carbonate precipitation of dissolved iron by ammonia gas injection was shown to be more efficient, as matrix oxidation did not exert an influence. Ammonia demand depended mainly on the buffering capacity of the groundwater flow. A conditioning pH of >7.5 was required, and injection rates were controlled by mixing ammonia gas to a nitrogen carrier gas flow of 0.5–1.0 m^3/h STP. The ammonia injection approach was found to play a part in contaminated site restoration; however, in situ processes require further investigation.

An oxygen gas PRB for bio-oxidation was established in zone C, and was operated over a period of 550 days. Gas lances and observation elements of the types MDP and MF were installed by CPT (see Chapter 3). A 3D gas-hydrogeological model was constructed for groundwater flow and reactive zone balance modeling. Gas injection rates of 0.6–1.2 m^3/h STP were applied, and ROI of single lances were identified using noble trace gas (Ne, He) in the range of 15 m. A downstream reactor was not monitored.

Due to high contamination and the natural pyrite content of the matrix, almost all of the 20 tonnes of injected oxygen gas was consumed by matrix

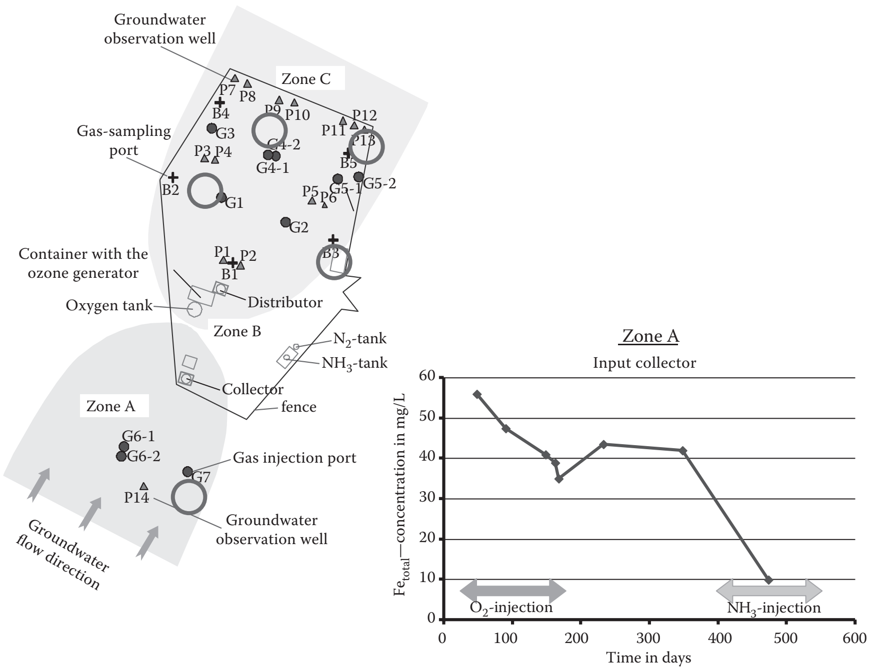


FIGURE 10.19
Left: map of the Schwarze Pumpe drain and gate test site with the reactive zones A to C; right: evidence of iron removal by gas injection in zone A at the collector well.

oxidation (36%), or transferred and consumed in the vadose zone (51%) without provoking a dominant stripping of VOC. With a 150-day lag time, enhanced aerobic biodegradation of the complex organic and inorganic contaminant plume was initiated and reached up to 11% of consumption of the total oxygen gas supply. Simultaneous heterotrophic and autotrophic biodegradation was found (Figure 10.20) and chemical oxidation from the initial excess supply of oxygen gas was also found. However, nitrification in zone C remained limited as the required chemical preoxidation of the hydrocarbon mass by ozone in the gate reactor of zone B was not turned on during the test period. Degradation rates were found to be 0.05–0.1/day for benzene and short-chained alkyl phenols (Uhlig, 2010).

The Schwarze Pumpe site example demonstrated the suitability of gas PRBs in treatment train applications, particularly when a complex contamination situation is present. Often, site restoration and impact reduction targets cannot be achieved or conducted economically by stand-alone applications of a main treatment technology (e.g., a pump and treat). The application of gas PRBs offers a wide range of aerobic and anaerobic conditioning. Posttreatment or polishing measures are required (e.g., for final degradation of CHC, hydrophilic alcohols [in situ flushing] or phenols [MPPE] extraction).

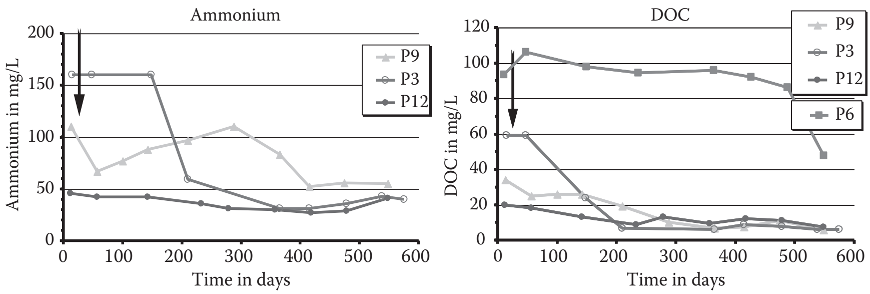


FIGURE 10.20
Posttreatment effect of the reactive gas zone C at Schwarze Pumpe site.

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