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BACKGROUND

The most common technique widely applied for groundwater remediation is „pump and treat", where production wells lift the contaminated water onto the surface where the water is treated and the clean water is injected back to the aquifer. There is always an uncertainty in this process concerning the capturing of the whole contaminated plume, if there are no untreated sources or separated plumes left behind. This treatment process always require a long-term (several months or years long) attended and quite expensive operation. During the time of remediation the real estate development is hindered by the presence of onsite equipments and installations. It is often observed that several months after the remediation method is finished, the groundwater monitoring data show repeatedly high levels of the contamination due to the secondary contamination of groundwater from soil. The average cost level of these remediation techniques varies between 4–7 Euro/m^2 and the operation costs can go even beyond that.

With ongoing activities and operating facilities on site, or when the contaminated site has buildings and infrastructure elements, usually there is no real chance to eliminate the contamination source with these traditional techniques. In such cases the realistic goal of the intervention can only be to eliminate the spreading of the contaminant plume to (1) uncontaminated areas or (2) unaffected environmental media. This is often accomplished by a barrier installed in the way of the moving dissolved contamination. Since the 90s there is a widespread technology for such passive remediation alternatives that is called Permeable Reactive Barriers (PRBs). The remediation is based on a carefully designed permeable barrier installed in the path of the moving dissolved plume that is capable to treat the groundwater. While groundwater moves through the permeable wall the pollutants are precipitated, adsorbed or decomposed and water with acceptable quality leaves the safe side of the wall. The traditional reactive materials applied in such installations are iron and active carbon granulate.

The appropriately selected barriers are capable of cleansing organic and inorganic dissolved contaminants (e.g. hydrocarbons, chlorinated hydrocarbons, pesticides, chromium and other toxic metals, nitrate, sulfate contaminations, and acid mine drainage (AMD). Beyond the above applications there are remarkable technical and business opportunities in the development of new reactive material packs. There are open questions related to the design and planning of complex and transient hydraulic systems and related innovative solutions, such as relative barriers.

The University of Miskolc, Faculty of Earth Science and Engineering has been involved in the research of Permeable Reactive Barriers for more then a decade. The European Commissions Framework Five program supported the EVK'-1999-00186 PEREBAR research program, which was titled as „Long-term Performance of Permeable Reactive Barriers used for the Remediation of Contaminated Groundwater". The Faculty of Earth Science has been involved in this research project as a research partner and its role was to evaluate the aging mechanisms of the reactive materials, and their impact on the hydraulic permeability and design of the reactive materials (Bőhm et al., 2003). Parallel to that the three institutions of this proposal (Institute of Chemistry, Institute of Process Engineering and Department of Hydrogeology and Engineering Geology) jointly with the University of Nottingham launched an innovative research on using high humin-acid containing natural materials, such as lignite or peat as reactive material (OTKA T-031959) (Laktos et al., 2007). During the last year a new multidisciplinary research team was formulated by the same institutions of the University of Miskolc to start the preliminary investigation and innovation on the design of a *new generation of PRBs.*

RESEARCH GOALS

Our goal is to lay the technical foundations of an innovative, passive remediation system, which is a considerably cheaper, and offers faster option for Brownfield rehabilitation and real estate development than the traditional PRBs, while cost-effectively secures the protection of (1) human receptors, (2) ecosystem and (3) environmental media. Our research toolbox contains: laboratory tests, modeling and technical design tools.

The set of innovative technical solutions consist of: the development a new natural reactive material, with high humin-acid content (e.g. lignite or peat), which can be installed and operated cost effectively; a modular design, which enables the operator to easily replace the exhausted reactive module pack with new ones; PRB designed for its full life cycle, incorporating the demands of reclaiming exhausted reactive modules and the energy recovery from its material; full compliance with the latest European and domestic technical standards and legal regulations.

The core of the research contains the (1) development, (2) material processing of the reactive material, its (3) chemical and (4) hydrological analysis and (5) investigation of energy recovery alternatives of the same material. At the end of the three year project we shall provide the technical documentation of a set of innovative solutions that can be applied in a new generation of PRB applications. The technical documentation and design can be the basis of a test operation of such an installation.

RATIONALE AND BENEFITS

PRBs has a demanding and complex design preparation phase which is followed by a rather simple installation and an almost unattended operation with minimum energy demand. The reactive wall utilizes the natural groundwater gradient to clean the moving dissolved plume.

Our new and innovative PRB goes beyond its traditional type in several aspect. Traditionally the active carbon reactive pack has excellent absorption capacity and can be regenerated with good efficiency. The natural materials tested in this research project are significantly cheaper than the active carbon, and even though its contaminant retention capacity (CRC) is by far below that of the active carbon but it can reach as much as its 30%. Once exhausted there is no need for the expensive regeneration but rather it can be co-incinerated in coal power plants with energy recovery, and can be replaced by a new reactive pack. In many of our countries there is a significant volume of mining wastes available (e.g. coal dust, and silt) as cheap resources (often with disposal problems) that can be tested for such applications too. In its readily available form or with certain modifications those can be used due to their high ion exchange capacity and complex forming, reducing capacity. The new generation of PRBs is estimated to offer 20–50% cheaper alternatives to the traditional active carbon packs.

Another innovative element of the design is that the reactive packs can be reclaimed after being exhausted. The technical framework and viable design of such an underground installation is a major task of the development project. The exhausted reactive packs must be reclaimed and replaced with new ones if needed. The reclaimed reactive packs can be co-incinerated in traditional coal power plants, which require a "cradle-to-grave" approach right from the first steps of design and material selection. This idea is unique among the PRB applications.

One reactive pack applied in a wide, universal sense for more contaminants is an idealistic plan, which has no any technical and financial legitimacy. The reactive material must be selected by matching it to the investigated dissolved plume and considering the environment of its transport. In case of mixed chemical plumes there is always a demand for compromise in operating the reactive barrier bellow its contaminant specific optimum. The modular design of the PRB can serve for the benefit of this problem too, by coupling several, different material packs optimized for different chemicals within one wall.

There are considerable capacities available from humin-acid rich materials (e.g. lignite, and brown coal), that are potentially applicable as reactive matrixes. Several Hungarian raw material sources (e.g. Bükkábrány) and foreign coals shall be evaluated and compared. These materials and their raw material processing techniques are routinely applied when they are used in coal power plants. There is a considerably different processing technology need when the material is used as a reactive barrier. The required process engineering tasks demanded vary on a wide range, mainly because the reactive material must provide activity on a relatively long timescale. This requires primarily high reactive surface of the lignite grains, which means a relatively small grain size of lignite. The decrease of grain size has an effect on permeability, and other physical conditions within the barrier. In order to reach our goals, for all development modules we must determine the specific parameters of the reactive material, in terms of reaction kinetics, hydrodynamics and energy utilization.

RESEARCH TASKS

The research efforts are grouped into four modules:

Reactive material development — chemical compatibility

The research project will focus on the treating of dissolved heavy metal plumes. There are three available principles in removing metal ions, such as cementing, precipitation and sorption. Iron is the primary option for cementing, which does not cause environmental threat when dissolved in groundwater. There is a limit in its application though, because this method is only effective for those metals to the left side of irons electrode potential rank. As precipitating materials the basic oxides can be considered or the sulfide generation. Such biological barriers with sulfate reducing bacteria have been applied already. The third option: sorption offers much greater variability than the previous two, because there are various known sorbents among organic and inorganic materials. The (1) selectivity of the material, its (2) compatibility with the environment and its (3) price are the three main parameters in determining applicability and competitiveness. The price of the sorbent has a major impact on the treatment of the exhausted pack. When using expensive sorbents regeneration is recommended, but it further raises the price of the operation. When using cheaper sorbent material, regeneration is avoidable and the exhausted reactive pack can be integrated to an appropriate waste stream and its management. The selectivity of the sorbents to contaminants is a very important factor when choosing the material. The PRB must operate in a geochemical environment where dissolved plume in balance with the geological environment. The elements of the geological environment are represented in the groundwater according to the solubility balance.

The low quality mineral coals such as lignite forms may very well comply with all three criteria listed above, so primarily this material shall be investigated in detail as potential sorbent. Preliminary tests on model barriers show promising contaminant retention capacity under various concentrations and flow rate. Parallel to that, several other parameters must be determined to support the modeling task, such as sorption capacity as a function of pH and ion composition, and sorbtion rate. Beyond these, also as a part of reactive material development, research shall cover the efficiency check of simple surface alteration methods too, such as: modification of quantity and type of functional groups, modification of pore structure, and finally the effect of ion exchange on the reactive material. For this later one pH control and anion removal might be needed.

Reactive barrier and its environment — hydrodynamic compatibility

Although the good material composition of the reactive barrier is necessary, the fulfillments of other conditions are also required to achieve effective remediation of underground contaminants. The hydrodynamic design and the environmental settings of the elaborated reactive barrier materials are inevitable for effective applications. Complex hydrogeological modeling can play a significant role to design the permeable reactive barrier properly involving all information concerning the contamination properties of the geological environment. As a first step, it is important to investigate the influence of the applied reactive barrier on the groundwater flow system at the targeted site. In order to achieve hydrodynamic compatibility, changes in geometry and permeability conditions of the barrier system, based on the modeling simulation results can help to avoid any unfavorable effects, like flooding the shallow groundwater system or the movement of the contamination plume beside the barrier.

As a second step, the underground contamination transport, and the change of physical and chemical processes in space and time between the plume and the reactive barrier material can be described with the help of reactive transport modeling. These transport simulations can also explain how the effectiveness of barrier material changes in time concerning the actual physical, chemical and possible biological processes. Based on the proposed complex hydrodynamic and transport modeling activity, the appropriate design of reactive barrier systems can be realized more effectively than by the earlier practice. The simulations can determine whether the contact time inside the reactive barrier is long enough to absorb the contaminants or not. The simulations can also predict how frequently it is necessary to replace the barrier material.

One of the key issues is to determine the hydraulic conductivity of the elaborated reactive barrier material. To support the hydrogeological modeling activity, laboratory hydraulic conductivity and permeability tests will be implemented to derive reliable information about the hydrodynamic properties of the different barrier materials. Then, based on the modeling simulation results, new laboratory investigations can help to set the required hydraulic conductivity parameters for given environmental problem.

Technical design — compatibility of the individual modules

One major research task of the innovative PRBs is the framework development of the modular design which facilitates the reclaiming of exhausted packs. The modular design enables the operator to construct the barrier from different reactive packs, without mixing their material streams. This arrangement of the packs has a major role in designing the order of chemical processes taking place in the barrier. This technical feature guarantees clean material streams to make the utilization of exhausted reactive packs much easier. The reclaiming the exhausted packs for this purpose is a new concept in the PRB remediation, which requires a more complex installation than the traditional slurry wall technique. The technical framework of accommodating and reclaiming reactive modules requires a new innovative technical solution, to be described in this module.

The harmonization of the individual design modules and investigation of their impact on each other is also a major task in this module. Each single step of the design has its impact on the technical feasibility of the PRB, in fact there are interactions among each modules. Within this module we shall develop a harmonized set of technical parameters in terms of chemistry, hydrogeology and technical design.

Utilization

One of the great advantages of carbon based reactive matrix materials over against other type of reactive materials is the relatively easy feeding into carbon based plant processes for energetic utilization after the end of their lifetime. However it must be determined which properties of the reactive material are going to be altered during the groundwater remediation process (heavy metal concentration, humidity, heating value,...). It is also important to determine the method, the altered matrix material can be modified for implementation into carbon based energetic operations. It is known, that application of gasification or incineration of coal requires different raw material quality. The required coal quality can be produce from the used matrix material using process engineering methods, however the technology has to be determined and the costs of the technology and regeneration process as well as the financial feasibility have to be investigated too.

The alteration of the reactive media and the appearance of the bounded contaminants are going to be estimated by the "accelerated model" carried out in module 1 and using reaction – kinetic models. Using the estimated data, regeneration, utilization and disposal methods, the applied technology and its cost can be determined.

Focusing on thermal utilization, it has to analyze how the heating value of the carbon material is changing during groundwater remediation process. It is also very important to determine the phase in which the pollutants are concentrating as the effect of thermal processes or gasification. Next to calorific properties, thermo–analytic and selective extractive techniques are going to be used to track the bound metal ions and their alteration, their stabilization process during recycling and disposal practice. These analyses support the evaluation of the alternatives and the selection of the least risky one. It is important to compare the costs of the promising methods to clear weather they are cost effective and competitive against conventional and feasible solutions (e.g. disposal).

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