



## Multilayer PRBs - Effective Technology for Protection of Groundwater Environment in Traffic Infrastructure

Joanna Fronczyk\*, Katarzyna Pawluk, Kazimierz Garbulewski

Warsaw University of Life Sciences, Department of Geotechnical Engineering, Nowoursynowska 159, 02-773  
Warsaw, Poland  
[joanna\\_fronczyk@sggw.pl](mailto:joanna_fronczyk@sggw.pl)

One of the crucial environmental problems through the world is the pollution of groundwater by run-off and snowmelt from roads. In the case of incorrect environment protection in the vicinity of roads the pollutants may migrate to groundwater causing hazard to sources of potable water. Imposing the flow of polluted water through a reactive materials filling a multilayer permeable reactive barrier (PRB) is one of the methods to prevent pollutants to groundwater. This paper focus on composition of road run-off samples (water in spring and summer, snow in winter) collected along road network in Warsaw. Moreover, the ability of the zeolite, activated carbon, zero-valent iron and geza rock to immobilize the contaminant sources from de-icing agents is also included. Finally, the analyses of the influence of chemical substances (chloride and lead) on the hydraulic properties of activated carbon (the most suitable reactive material) have been made in adjusted triaxial test equipment. Based on the laboratory test results the general conclusions related to the ability of a reactive materials tested for application in the multilayer PRBs were drawn.

### 1. Introduction

Pollutions from traffic infrastructure (e.g. road, highway networks, petrol station etc.) is one of the sources, which have a distinct and negative impact on the environment, particularly on the groundwater quality. Stormwater run-off contains heavy metals and de-icing agents (rock salt consisting mainly the sodium chloride - NaCl) used to increase driving safety on public roads in the winter. The water with high salinity level runs off into surface waters or storm sewers or infiltrates into the soil and groundwater affecting the groundwater environment (Novotny et al., 2008). Therefore, in the case of high level contamination the remediation method is required (Fronczyk, 2008). The US EPA recommend for the application the Permeable Reactive Barriers (PRB) technology (EPA, 1998). A permeable reactive subsurface barrier is defined as "an emplacement of reactive materials in the subsurface designed to intercept a contaminant plume, provide a flow path through the reactive media, and transform the contaminant(s) into environmentally acceptable forms to attain remediation concentration goals downgradient of the barrier" (EPA, 1998) (Figure 1).

The aim of this paper is presenting results of the study carried out to check the ability of zeolite, activated carbon, zero-valent iron and geza rock as a reactive materials proposed to be applied in the multilayer PRBs for groundwater protection along roads. For this purpose, the analyses of the physical and chemical properties of tested materials have been carried out by using batch tests for de-icing agents. Besides, the research tests of the influence of chemical substances (chloride and lead) on the hydraulic properties of activated carbon (the most suitable reactive material) have been made in adjusted triaxial test equipment.

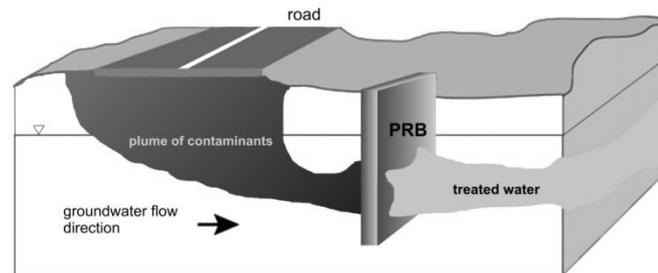


Figure 1: The concept of Permeable Reactive Barrier (PBR) to protect groundwater environment along road

## 2. Contaminants from transport

Urbanization has caused an increase in impervious surfaces like roads, driveways, sidewalks, parking lots etc. and contribute to pollution deposition on the surface. From surfaces of traffic infrastructures the most of contaminants flow into ground by infiltrating the stormwater (Mikula et al., 2006; Norrström, 2005).

The hydraulic conductivity ( $k$ ) of ground decides about intensity of infiltration in soil layers. Many factors influence on the hydraulic conductivity, e.g. any increase in double layer thickness, in electrolyte concentration or in cation valence, which tend to decrease the hydraulic conductivity. However, clayey soils permeated with liquids containing monovalent cations tend to produce low hydraulic conductivity while those permeated with liquids containing polyvalent cations tend to produce higher hydraulic conductivity. Furthermore, turbidity, nutrient content, and microorganisms can also affect hydraulic conductivity (Daniel, 1994).

Road run-off consists of three different flow phases: dry-weather base flows, stormwater run-off and snowmelt. The significance of each depends upon many factors, with the two most important being season and land use. Depending of those factors the stormwater runoff from roads contains a mixture of toxicants such as nutrients, pathogens, total suspended solids, heavy metals, nitrogen oxides, carbon monoxide, hydrocarbons, aldehydes, sulfur oxides, pesticides and chlorides (Mikula et al., 2006; Vijayaraghavan et al., 2009). Most of these substances are originated from emissions and corrosion of vehicles and wear products from the asphalt surface, and also from roadside solids or liquid waste (Norrström, 2005). In contrast to stormwater, snowmelt contains mainly the salts, which are applied to safe driving condition every year. During the winter period about thousands tones of several different types of salts are used to melt ice and snow. The sodium chloride (NaCl) is most common used as the de-icing salt because of its low cost, availability and high effectiveness. The chloride ions are very mobile and promote some substances leaching from roadside soils by a range of different processes. According to Novotny et al. (2008) the snowmelt run-off contains higher level of heavy metals concentration, compared to non-winter run-off, predictable due to the high chloride concentration. Moreover, the high chloride levels proportionally reduce the partition coefficients, causing more metals to be in a dissolved, and more toxic form. Furthermore, the use of de-icing agents to prevent ice formation have been shown to have a toxic effect on plants (Cekstere et al., 2008). The negative impact of salts, especially of sodium chloride on roadside soils and vegetation are well documented (Novotny et al., 2008; Bäckström et al., 2003; Norrström, 2005).

## 3. Materials and methods

The materials used in the tests are divided into two following groups: reactive materials and de-icing agents. The reactive materials were as follows: activated carbon (Hajnówka, Poland), zeolite (Bystre, Slovakia), zero - valent iron ZVI (USA), geza rock (Wrzosówka/Kielce, Poland). The last presented material is not a typical reactive material. This is a sedimentary, compacted, porous, generally a two-component carbonate-quartz rock, which has a sorption properties.

Table 1: Chemical composition of de-icing agent

Product name of the de-icing agent	Chemical composition
Road salt	NaCl min 90.0 %
Mine Salt "Kłodawa" S.A.	Insoluble part 8.0 % H <sub>2</sub> O max 3.0 % K <sub>4</sub> Fe(CN) <sub>6</sub> 40 mg/L

As the de-icing agent sodium chloride from PolSuper Company was used. Chemical composition of de-icing agent is given in Table 1.

The first step of investigations contained the analyzes of chemical composition of snow and run-offs samples collected along the chosen streets in Warsaw. The streets were located at ecologically valuable areas. Eleven snow and run-off samples were taken in January and July 2010. In addition, in December 2011 six soil samples were collected along B. Czecha Str. from a depth of 0.2 m. Snow samples were melted at room temperature and examined to determine the concentration of Cd, Ni, Cu, Zn, Pb, Cl and petroleum ether extracts (PEE). Metals from soil samples were extracted with 1M HCl solution (with soil-to-extractant mixture ratio 1:10), while Cl with distilled water (with soil-to-distilled water ratio 1:10). Metals were analyzed using inductive coupled plasma (ICP), organic compounds using extraction with petroleum ether, while chloride concentrations using Mohr's method. In all samples pH and conductivity were also determined.

The second step of investigations concentrated on the assessment of reactive materials properties: grain size distribution, maximum and minimum dry densities, total specific surfaces, hydraulic conductivity (ASTM, 2000) and ability to chloride retention using the batch tests according to US EPA guidelines (EPA,1992).

The influence of chemical substances (chloride and lead) on the hydraulic properties of activated carbon have been determined in adjusted triaxial test equipment. The specimens tested were 0.07 m in diameter and 0.14 m in height. Samples were permeated first with distilled water and later with the chloride (10 mg/L) and lead (10 mg/L) solutions. The hydraulic conductivity (k) of samples, using constant head procedure, was calculated by measuring the volume of flow for given time interval. In batch equilibrium tests variable chloride concentrations (150, 170, 190, 210, 220, 230 and 250 mg/L) and constant shaking period of time (24 h) were assumed. Specimens consisting of 2 g dry reactive materials and 100 mL of chloride solution were placed in 250 mL flasks. The experiments were performed in duplex at laboratory temperature of 20 - 22 °C. Initial pH and electrical conductivity values ranged from 1.34 to 7.55 and from 0.01 to 80.20 mS/cm, respectively. The ion concentrations, electrical conductivity, pH and temperature in the equilibrium solutions were analyzed.

#### 4. Results and discussion

The results of chemical composition of snow and run-offs samples are presented in Tables 2 and 3. Ion concentration depends on the sampling sites (different type of road, traffic density and amount of used de-icing agents) and sampling time (winter and summer). The results indicate the increased values of some indicators and their variability over time. The pH of samples ranged from 6.84 to 8.16, while the electrical conductivity from 0.057 to 22.900 mS/cm. The highest exceedance of limit values was noted for nickel and lead concentrations, as well as for chloride concentrations in snow samples. It may be due to the fact that the samples collected in January were taken six weeks after first snowfall. During this time numerous snowfalls and frequent de-icing of roads were observed. The presence of heavy metals in the samples tested could result from contamination of materials used to maintain roads in winter or from exhaust and dust emissions from various sources (e.g. thermal-electric power station, corrosion of the railings and road signs). The concentrations of cadmium in run-offs and snow samples as well as copper in snow samples were smaller than the limit of detection, which was 0.002 and 0.02 mg/L for cadmium and copper, respectively.

The results of soil samples analyses are summarized in Table 4. Soil samples were collected in December before snow falls. It might cause low chloride concentrations in soil, because chloride ions are highly mobile in soil. The highest concentrations were obtained for zinc and lead and the lowest

for cadmium. However, even for zinc and copper the limit values specified for environmental protected areas were not exceeded. According to Polish standards and requirements the limit values are as follows: 30 mgCu/kg, 100 mgZn/kg, 1 mgCd/kg, 35 mgNi/kg and 50 mgPb/kg.

The physical properties of reactive materials are presented in Table 5. Relationships between hydraulic conductivity of activated carbon and pore volume of flow (PVF) obtained from the tests using the constant head test method are shown in Figure 2.

Table 2: Analysis of snow samples - January 2010

Sampling place	pH	Conductivity [mS/cm]	Cl <sup>-</sup> [mg/L]	Cu <sup>2+</sup> [mg/L]	Zn <sup>2+</sup> [mg/L]	Cd <sup>2+</sup> [mg/L]	Ni <sup>2+</sup> [mg/L]	Pb <sup>2+</sup> [mg/L]	PEE [mg/L]
Estrady Str.	8.28	5.58	1297.6	0.250	0.031	0.084	0.630	0.556	7.64
Wybrzeże Gdyńskie Str.	7.37	22.90	6856.6	0.279	0.110	0.081	0.579	0.632	14.52
Solec Str.	6.84	10.71	2446.3	0.276	0.948	0.080	0.572	0.799	19.61
Belgradzka Str.	8.16	12.87	3148.2	<0.020	0.023	<0.002	0.607	5.000	13.34
Moczydłowska Str.	7.65	8.38	2063.4	<0.020	0.137	<0.002	0.567	0.088	8.63

Table 3: Analysis of run-offs - July 2010

Sampling place	pH	Conductivity [mS/cm]	Cl <sup>-</sup> [mg/L]	Cu <sup>2+</sup> [mg/L]	Zn <sup>2+</sup> [mg/L]	Cd <sup>2+</sup> [mg/L]	Ni <sup>2+</sup> [mg/L]	Pb <sup>2+</sup> [mg/L]	PEE [mg/L]
Estrady Str.	7.81	0.079	14.181	0.043	0.30	<0.002	0.007	0.012	5.93
Wybrzeże Gdyńskie Str.	7.55	0.057	2.836	0.03	0.18	<0.002	<0.005	0.016	3.9
Lucerny Str.	8.02	0.083	6.382	0.028	0.14	<0.002	0.005	0.012	11.65
B. Czecha Str.	7.39	0.106	9.927	0.048	0.15	<0.002	0.005	0.009	3.53
Belgradzka Str.	7.4	0.093	14.89	0.096	0.19	<0.002	<0.005	0.010	1.6
Gąsek Str.	7.51	0.205	48.216	0.024	0.12	<0.002	<0.005	0.005	4.60

Table 4: Analysis of soil samples

Sample No	pH	Conductivity [mS/cm]	Cl <sup>-</sup> [mg/kg]	Cu <sup>2+</sup> [mg/kg]	Zn <sup>2+</sup> [mg/kg]	Cd <sup>2+</sup> [mg/kg]	Ni <sup>2+</sup> [mg/kg]	Pb <sup>2+</sup> [mg/kg]
1	6.42	0.094	0.6	5.730	19.168	0.326	0.814	16.293
2	6.38	0.109	0.6	12.084	35.321	0.457	1.347	37.480
3	6.34	0.057	0.4	7.599	58.307	0.363	1.110	22.099
4	6.29	0.057	0.8	9.206	6.859	0.367	0.94	22.522
5	6.55	0.055	0.4	14.133	10.044	0.526	1.425	36.373
6	6.59	0.049	0.2	8.318	7.272	0.478	1.123	29.241

Table 5: Physical properties of reactive materials

Reactive material	Min. dry density $\rho_d$ min [t/m <sup>3</sup> ]	Max. dry density $\rho_d$ max [t/m <sup>3</sup> ]	Specific surface area [m <sup>2</sup> ]
Activated carbon	0.370	0.527	201.61
Geza rock	1.410	2.258	2.47
Zeolite	0.867	1.230	33.34
Zero – valent iron	2.760	4.879	77.26

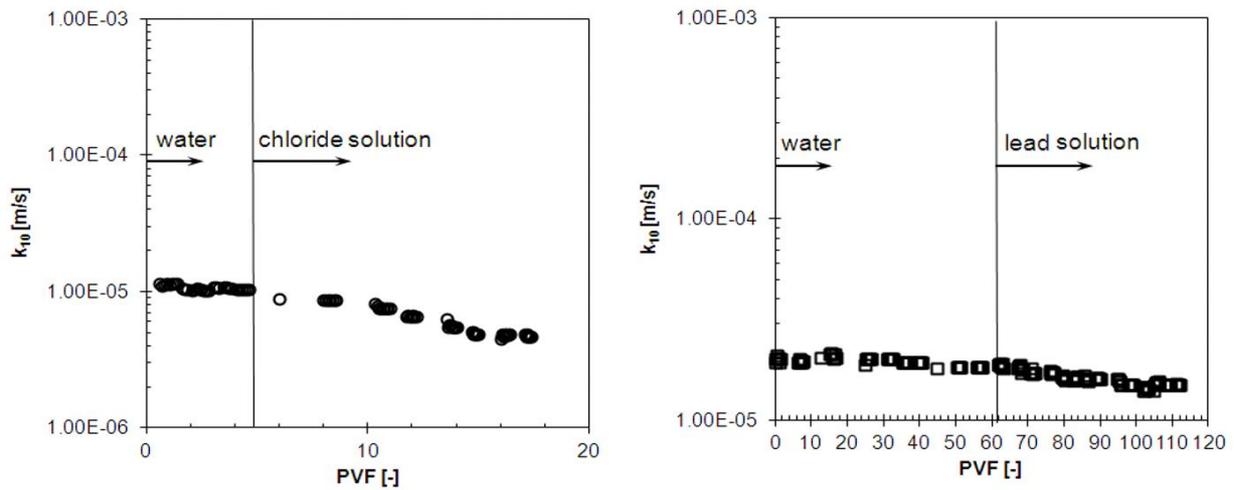


Figure 2: Hydraulic conductivity of activated carbon permeated with distilled water, Cl, and Pb solutions

Hydraulic conductivity of activated carbon determined during permeation of distilled water stabilized at the value of  $(1.0 - 1.9) \cdot 10^{-5}$  m/s. After the distilled water was preplaced by ion solutions, the hydraulic conductivity of samples gradually decreased depending on permitted solution. After 17 PVFs of chloride solution permeation, the hydraulic conductivity of activated carbon have decreased to the value of  $4.7 \cdot 10^{-6}$  m/s and after 100 PVFs of lead solution permeation to the value of  $1.5 \cdot 10^{-5}$  m/s.

All materials tested reduce chloride concentration, however with low intensity. These materials are widely used as reactive materials fulfilling PRBs, and they have ability to heavy metals and organic compounds retention, also in the vicinity of roads. Results of batch equilibrium tests are presented in Figure 3. Chloride concentration reduction is presented as a relationship between initial and equilibrium concentrations. Sorption models such as Freundlich, Langmuir or Henry isotherms do not describe well the chloride retention processes on chosen materials. The highest chloride concentration reduction up to 38 % was observed for zeolite, while the lowest reduction up to 5 % for zero valent iron. Based on the test results it can be concluded that the ability to chloride concentration reduction of other two materials (activated carbon and geza rock) is similar to the ability of zeolite and assumes a value of 35 %. The pH and electrical conductivity of equilibrium solutions ranged from 1.35 to 6.91 and from 0.081 to 72.200 mS/cm, respectively. During the test reduction of pH and increase of electrical conductivity was observed, which was related to the concentration of chloride in solution.

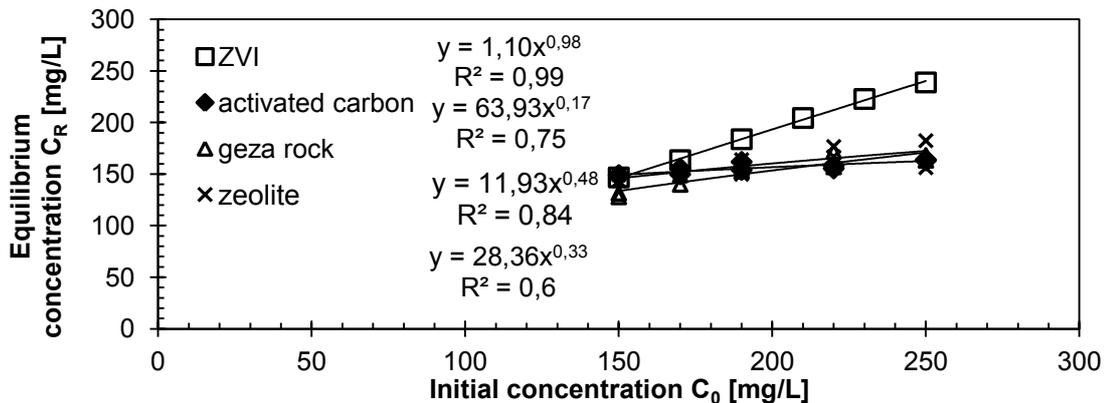


Figure 3: Chloride retention on reactive materials

## 5. Conclusions

Considering the test results obtained including chemical composition of run-offs, snow and soil samples as well as physical, hydraulic and reactive properties of activated carbon, zero valent iron, zeolite and geza rock the following conclusions can be drawn.

1. Chloride and heavy metals concentrations in collected samples are considerably varied even on the same sampling sites. The differences are dependent on sampling time, frequency and intensity of snowfalls. These factors are closely affected by the amount of salt used to ensure safe driving conditions.
2. The mean hydraulic conductivity of activated carbon is  $1.45 \cdot 10^{-5}$  m/s for distilled water and  $4.7 \cdot 10^{-6}$  for chloride solution m/s and, moreover value of hydraulic conductivity  $1.83 \cdot 10^{-5}$  m/s for distilled water and  $1.49 \cdot 10^{-5}$  m/s for lead, was observed.
3. The zeolite, activated carbon and geza rock seem to be the most suitable materials for the reduction of chlorides. The lowest ability to chloride retention has zero valent iron.

## Acknowledgments

This research was supported by Grant no. NN523 561638 from Ministry of Science and Higher Education. Warsaw. Poland

## References

- ASTM (The American Society for Testing and Materials), 2000, Standard test methods for measurement of hydraulic conductivity of saturated porous materials using a flexible wall permeameter, Annual Book of ASTM Standards, Section 4 Construction, Volume 04.08 - Soil and Rock (I), ASTM:D 5084 – 00.
- Bäckström M., Nilsson U., Håkansson K., Allard B., Karlsson S., 2003, Speciation of heavy metals in road runoff and roadside total deposition, *Water, Air, and Soil Pollution* 147, 343-366.
- Cekstere G., Nikodemus O., Osvalde A., 2008, Toxic impact of de-icing material to street greenery in Riga. *Latvia, Urban Forestry and Urban Greening*, 7, 3, 207-217.
- Daniel D.E., 1994, State-of-the-art: laboratory hydraulic conductivity tests for saturated soils. In: Daniel D.E., Trautwein S.J., *Hydraulic conductivity and waste contaminant transport in soil*, ASTM 04-011420-38, Philadelphia, United States: 30-78.
- EPA (Environmental Protection Agency), 1992, Batch-type procedures for estimating soil adsorption of chemicals, EPA/530/SW-87-006-F
- EPA (Environmental Protection Agency), 1998, Permeable reactive barrier technologies for contaminant remediation, EPA/600/R-98/125.
- Fronczyk J., 2008, Zeolite-sand mixtures in permeable reactive barriers in landfill's surrounding. Ph.D. Thesis, Department of Geotechnical Engineering, WULS, Warsaw, Poland (in Polish).
- Mikula JB., Clark SE., Baker K.H., 2006, Modeling zinc and sodium chloride migration in vadose zone soils beneath stormwater infiltration devices, *Proceedings of the Annual International Conference on Soils, Sediments, Water and Energy*, <<http://scholarworks.umass.edu>> accessed 20.12.2011.
- Norrström A. C., 2005, Metal mobility by de-icing salt from an infiltration trench for highway runoff, *Applied Geochemistry* 20, 1907-1919.
- Novotny E.V., Murphy D., Stefan H.G., 2008, Increase of urban lake salinity by road deicing salt, *Science of the Total Environment* 406, 131-144.
- Vijayaraghavan V., Arun M., Umid Man J., Balasubramanian R. 2009, A comparative study of seven materials as sorbents for removal of metal ions from real storm water runoff, *Chemical Engineering Transactions*, 17, 379-384, DOI: 10.3303/CET0917064