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Application of permeable reactive barriers near roads for chloride ions removal

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Abstract: *Application of permeable reactive barriers near roads for chloride ions removal.* One of the most critical sources of pollutants are road run-offs. Road run-off is a complex mixture of toxicants e.g. heavy metals, de-icing agents, organic compounds and water suspensions of solid substances. One of the most negative impact on the environment has sodium chloride which is used as de-icing agent. In the case of incorrect environment protection in the vicinity of roads pollutants may migrate to groundwater causing hazard to sources of potable water. One of the methods to prevent the migration of pollutants to groundwater is imposing the flow of polluted water through a reactive material filling a permeable reactive barrier (PRB). This paper examines the feasibility of selected reactive materials for the reduction chlorides concentration in road run-offs. Four different reactive materials: zero valent-iron, activated carbon, zeolite and geza rock have been chosen for studies. The tests results indicated that the most popular reactive materials used in PRB technology, activated carbon and zero-valent iron, removed exhibited the highest efficiency in chloride ions removal. Moreover, the composition of road run-off in samples collected along roads in Warsaw was determinated.

Key words: Permeable Reactive Barrier, reactive materials, remediation, contamination, de-icing agents.

INTRODUCTION

Process of degradation and destruction of the environment is in mostly caused by human negative activities, especially in view of generating sources of pollution.

Road infrastructure is one of the sources of this type of contamination. Transport has a highly negative impact on surface- and groundwater, soil and air in the vicinity of roads. Pollution can be caused by the emission of fuel gases, evaporation of media, breaks and tires usage, as well as de-icing agents (Merkisz et al. 2005). The most widely used de-icing material is sodium chloride NaCl, which dissociates in water to Na^+ and Cl^- thereby reducing its freezing temperature.

Although natural attenuation processes occur in the soil reducing the concentration of contaminants (by degradation, dilution or sorption), of high contamination of soil and groundwater necessitates the application of remediation methods (Yong and Mulligan 2004). One of technical methods which are used to reduce concentrations of substances contaminated groundwater is Permeable Reactive Barriers (PRB) (Fig. 1). “A permeable reactive barrier is a wall built below ground to clean up polluted groundwater. The wall is permeable, which means it has tiny holes that allow groundwater to flow through it. Reactive materials in the wall trap harmful chemicals or change the chemicals into harmless ones. Clean groundwater flows out the other side of the wall” (EPA 542-F-01-005 April 2001).

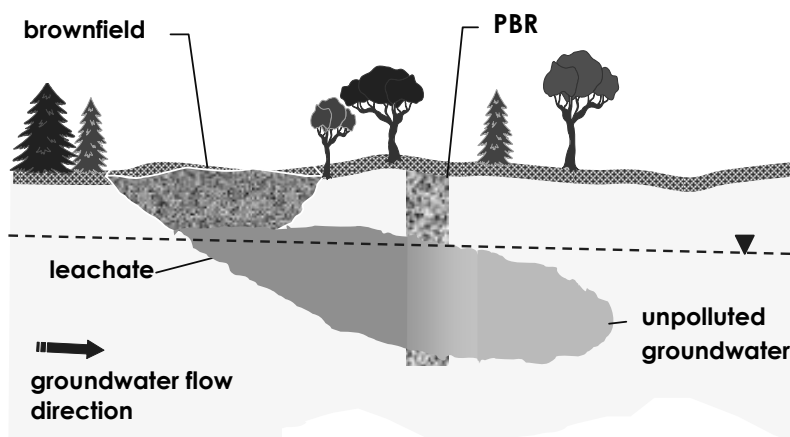


FIGURE 1. The concept of Permeable Reactive Barrier (Fronczyk 2008)

PRBs are widely used in contaminated areas (like brownfields) and have a lot of advantages such as relatively low costs, the usage of naturally occurring processes in groundwater, low impact on the environment and the possibility of implementation in urbanized areas. However, the PRBs have disadvantages like: long remediation time, changes the properties of reactive material in time and the need for regeneration or exchange of reactive materials.

The aim of this paper is to study the suitability of some chosen materials (activated carbon, zeolite, zero-valent iron, geza rock) as fillers for PRBs designated for protection of groundwater along roads.

CONTAMINANTS FROM TRANSPORT

Transport is one of the sources of environment pollution. The highest concentration of contaminants occurs in the vicinity of roads. The level of contamination depends on some factors,

e.g. physicochemical properties of soils, amount of absorbed chemical substance, distance from emission source and size of contaminant plume.

Properties of soils decide about intensity of natural attenuation processes and contaminants migration in soil layers. One of the most important factor is hydraulic conductivity k . In subsoils, many factors can influence the hydraulic conductivity, e.g., any increase in double layer thickness produces a decrease in hydraulic conductivity, also any increase in electrolyte concentration or an increase in cation valence will tend to decrease 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 of clayey soils. On the other hand, turbidity, nutrient content, and microorganisms can also affect hydraulic conductivity (Daniel 1994). In case of non-cohesive soils, there exist two transport mechanisms: advection and dispersion. There is also third

transport mechanism, diffusion, which appears in case of cohesive soils (but no occurs advection process). Migration of pollutants in soils causes contamination of water and air, as well as has negative impact on plants and animals. Moreover, the sorption capacity of soils influences intensity of contaminants migration: the highest sorption capacity, the lowest migration intensity.

Main contaminants from transport are (Polkowska et al. 2007):

- nitrogen oxides,
- carbon monoxide,
- hydrocarbons,
- particulate matter PM,
- sulfur oxides,
- aldehydes,
- salt.

Most of these substances are connected with engine gases, in contrast to salt which is used to safe driving conditions during winter season. The rate of salt application is about thousands of tones per year. The most common de-icing material is sodium chloride (NaCl) because of its low cost, availability and high effectiveness. NaCl can be used in form of

dry salt but also as brine, pre-wetted salt or mixed with calcium chloride (IBDiM 2006). Furthermore, there are standards recommending the exact dose of NaCl which should be adjusted depending on weather conditions. In the compact city environment with high traffic density, street trees commonly are stressed due to a harsh microclimate and soil conditions (e.g. inhibition of membranes functions, ion deficiency, decrease of enzymes activity, salt-induced water stress). The use of de-icing salts on roads also leads to deposition in the greenery environment (Cekstere et al. 2008).

MATERIALS

Materials used in the research are divided into two following groups:

- reactive materials,
- de-icing agents.

The reactive materials used should provide facilitate the reduction of concentration harmful substances. In conducted investigations four materials were taken into account (Fig. 2):

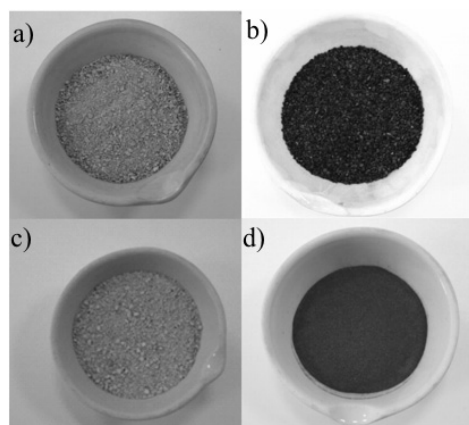


FIGURE 2. Reactive materials used in the research a) geza rock, b) activated carbon, c) zeolite, d) zero-valent iron

- a) geza rock (Wrzosówka/Kielce, Poland),
- b) activated carbon (Poland),
- c) zeolite (Bystre, Slovakia),
- d) zero – valent iron ZVI (H200 Plus™, HEPURE TECHNOLOGIES USA) .

In laboratory tests as a de-icing agent sodium chloride from PolSuper company was used. Chemical composition of de-icing agent is given in Table 1.

TABLE 1. Chemical composition of de-icing agent

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

METHODS

The first step of laboratory investigations was the analyze of chloride concentrations in snow samples collected along

the streets in Warsaw, which were taken in January and February 2010. Location of sampling sites is presented in Figure 3.

The second step of conducted investigations concentrate on assessment of reactive materials physical properties (sieve analysis, maximum and minimum dry density tests and total specific surface analysis SSA). Tests were conducted according to polish standard (PN-88/B-04481, 1998).

Three types of laboratory retention tests were conducted in the studies. The first was focused on the identification of the chloride reduction ability of the reactive materials. Each of reactive materials (50 g) was mixed in flasks with NaCl solution (1500 mg·dm⁻³) for 48 hours. Chloride concentration, conductivity, pH and temperature were examined at the beginning and at the end of the experiment. Based on this studies two reactive materials with highest affinity to chloride ions were selected. Thereafter, in pre-



FIGURE 3. Location of sampling sites: 1) Estrady St., 2) Wybrzeże Gdynskie St., 3) Solec St., 4) Lucerny St., 5) B. Czecha St., 6) Belgradzka Str, 7) Moczydłowska St. 8) Gąsek St.

vious type of studies on chosen materials batch kinetic tests and batch equilibrium tests were carried out (2nd and 3rd type of retention studies). These tests were conducted to quantify and qualify the mechanism of chloride uptake by reactive materials. The batch kinetic tests were based on shaking 2 g of reactive material with 100 ml of 150 mgCl·dm⁻³ solution for 1, 3, 6, 10, 34 and 58 hours. In batch equilibrium tests variable chloride concentrations (150, 170, 190, 210, 230 and 250 mg·dm⁻³) and constant shaking period of time (24 h) were assumed. The concentration, conductivity, pH and temperature of chloride in the initial and equilibrium solutions were analyzed.

In order to establish the adsorption isotherms were analyzed the batch tests results using Solver program. In parametric analysis following models (adsorption isotherms) were used:

– Freundlich equation

$$\frac{x}{m} = K_F \cdot C_R^{N_F} \quad (1)$$

– Langmuir equation:

$$\frac{x}{m} = \frac{K_L C_{a \max} C_R}{1 + K_L C_R} \quad (2)$$

– Henry equation:

$$\frac{x}{m} = K_D \cdot C_R \quad (3)$$

where: x/m – the reactive material phase concentration [mg·g⁻¹], K_F , N_F – Freundlich constants [dm³·g⁻¹], $[-]$, C_R – equilibrium concentration of chloride in the liquid phase [mg·dm⁻³], K_L – Langmuir constant [dm³·g⁻¹], $C_{a \max}$ – maximum sorption capacity [mg·dm⁻³], K_D – Henry constant [mg·dm⁻³].

RESULTS AND DISCUSSION

Composition of snow samples

The results of chloride concentration in snow samples are presented in Tables 2 and 3. Chloride concentration depends on the sampling sites (different type of road, traffic density and amount of used de-icing agents) and sampling time (heavy snowfalls and low temperature in first sampling time, low snowfalls

TABLE 2. Analysis of snow samples – January 2010

Sampling place	pH	Temperature [°C]	Conductivity [mS·cm ⁻¹]	Chloride concentration [mg·dm ⁻³]
Solec St.	6.84	5.1	10.71	2446.3
Wybrzeże Gdynskie St.	7.37	6.3	22.90	6856.6
Estrady St.	8.37	6.7	4.32	999.8
	8.28	10.1	5.58	1297.6
Belgradzka St.	8.16	8.9	12.87	3148.2
	7.57	5.6	8.07	1808.1
Gąsek St.	7.65	10.1	8.38	2063.4
Moczydłowska St.	8.14	8.5	13.83	4112.6

TABLE 3. Analysis of snow samples – February 2010

Sampling place	pH	Temperature [°C]	Conductivity [mS·cm ⁻¹]	Chloride concentration [mg·dm ⁻³]
Solec St.	7.80	17.0	106	10.63
Wybrzeże Gdynskie St.	7.51	16.7	157	3.55
Estrady St.	7.64	16.4	71	7.09
Lucerny St.	7.46	16.5	151	28.36
B. Czecha St.	7.47	16.4	101	26.94
Belgradzka St.	7.37	16.4	118	11.35
Gąsek St.	7.20	16.4	81	19.85
Moczydłowska St.	7.51	16.4	65	10.64

and higher temperature in the second sampling time). The analyses of snow samples indicated a large difference in chloride concentrations between January and February. The samples from February were collected two weeks after single snowfall, therefore the lower chloride concentrations were detected. However, during this period single road de-icing was applied. The samples col-

lected in January were taken six weeks after first snowfall. During this time numerous snowfalls and frequent de-icing of roads were observed.

Physical properties

The grain size distribution of tested reactive materials are shown in Figure 4 whereas maximum and minimum dry

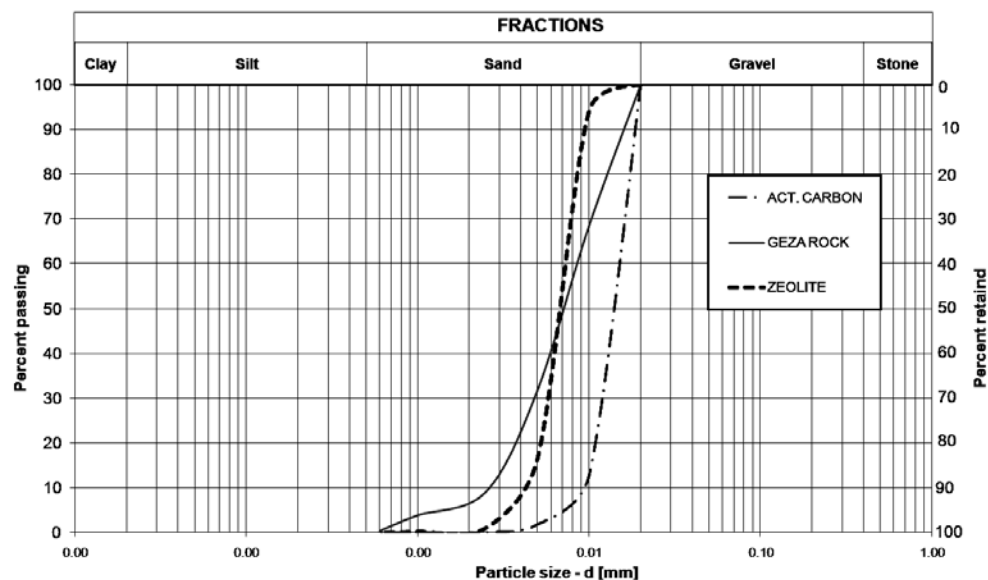


FIGURE 4. Grain size distribution of reactive materials

density are presented in Table 4. The highest maximum dry density has zero-valent iron and the lowest – activated carbon. Results of total SSA (Tab. 5) showed that the highest SSA has activated carbon and zero-valent iron. The smallest SSA was determined for geza rock

Retention tests

The first type of retention tests have shown, that all tested reactive

materials reduce chloride concentration, but the most effective are activated carbon and zero-valent iron. This two reactive materials, widely used in PRB technology, were chosen for further retention tests (Tab. 6).

In 3rd type of retention tests equilibrium times, assumed on the bases of batch kinetic tests, were: 24 hours for activated carbon and 48 hours for zero-valent iron (Fig. 5).

TABLE 4. Maximum and minimum dry densities of reactive materials

Reactive material	ρ_d min [$t \cdot m^{-3}$]	ρ_d max [$t \cdot m^{-3}$]
Activated carbon	0.370	0.527
Geza rock	1.410	2.258
Zeolite	0.867	1.230
Zero – valent iron	2.760	4.879

TABLE 5. Specific surface areas of reactive materials

Material	Dry mass [g]	MBC	Specific surface area [$m^2 \cdot g$]
Activated carbon	10.00	9.63	201.61
Geza rock	10.00	0.12	2.47
Zeolite	10.00	1.59	33.34
Zero – valent iron	10.00	4.21	77.26

TABLE 6. Effectiveness of chloride reduction

Material	Chloride concentration [$mg \cdot dm^{-3}$]		pH		Conductivity [$mS \cdot cm^{-1}$]		Temperature [$^{\circ}C$]	
	initial	final	initial	final	initial	final	initial	final
Activated carbon	1529.13	758.69	10.27	10.85	3.68	4.62	20.6	15.1
	1529.13	957.23	10.25	10.41	3.71	4.10	20.8	14.9
Geza	1529.13	1269.21	8.28	7.23	4.59	4.63	20.5	15.2
	1529.13	1028.22	8.57	7.75	3.11	4.79	20.6	15.2
Zeolite	1529.13	1198.31	7.32	7.36	4.54	4.56	20.0	14.7
	1529.13	1191.22	6.73	7.13	4.00	4.66	20.0	15.1
Zero – valent iron	1529.13	1198.31	6.47	9.59	3.90	4.51	20.8	15.3
	1529.13	1035.22	8.48	9.68	3.58	4.54	20.2	15.4

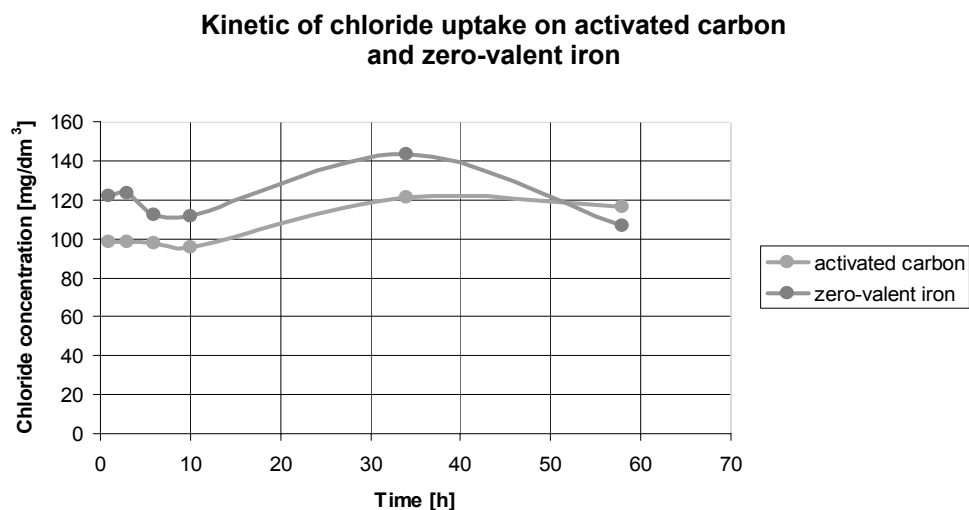


FIGURE 5. Kinetic of chloride uptake on activated carbon and zero-valent iron

Results of batch equilibrium tests for activated carbon and zero-valent iron are presented in Table 7 and 8, whereas Freundlich adsorption isotherms are shown in Figure 6. Both materials tested reduce chloride concentration but with low intensity. However, these materials are widely used as reactive materials fulfilling PRBs, and presumably they have ability to heavy metals and organic compounds retention, also in the vicinity of roads. Therefore, it is important to examine, whether this materials are suitable to

minimize the salt concentration in run-off water from roads.

In calculations Langmuir isotherms could not be used. Langmuir equation is intended for low concentrations of substances in solution. Presumably initial chloride concentrations exceeded the applicability of the Langmuir model. As in the previous case, Henry equation, also have not resulted in gratifying fitting: for activated carbon R^2 is 0.45 whereas parameter of Henry isotherm for zero-valent iron could not be es-

TABLE 7. Results of batch equilibrium tests for activated carbon (Michniak 2010)

Sample number	Conductivity [$\text{mS}\cdot\text{cm}^{-1}$]		Initial chloride concentration [$\text{mg}\cdot\text{dm}^{-3}$]	Equilibrium chloride concentration [$\text{mg}\cdot\text{dm}^{-3}$]
	Initial	Equilibrium		
1	652	674	150	143.23
2	696	719	170	159.54
3	736	845	190	180.81
4	817	874	210	190.74
5	1150	945	230	212.01
6	970	986	250	221.23

TABLE 8. Results of batch equilibrium tests for zero-valent iron (Michniak 2010)

Sample number	Conductivity [$\text{mS}\cdot\text{cm}^{-1}$]		Initial chloride concentration [$\text{mg}\cdot\text{dm}^{-3}$]	Equilibrium chloride concentration [$\text{mg}\cdot\text{dm}^{-3}$]
	initial	final		
1	560	563	150	146.61
2	598	609	170	163.37
3	721	722	190	183.65
4	754	763	210	204.21
5	875	771	230	222.64
6	990	1009	250	238.70

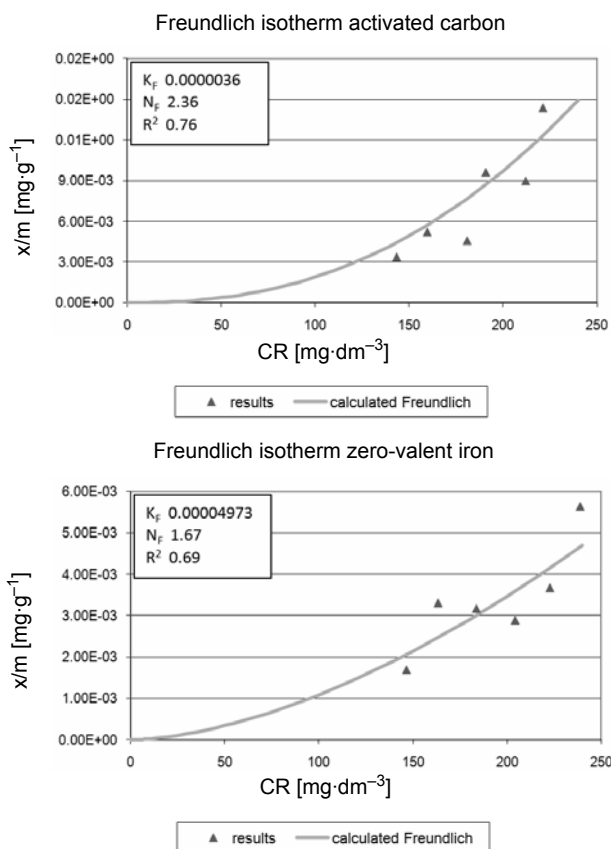


FIGURE 6. Freundlich isotherm (Michniak 2010)

tablished because is dedicate for linear relationship. In test results interpretation the Freundlich equation was used. This model in comparison to mentioned models, accurately describes chloride reten-

tion mechanism on the surface of tested materials. However, it is important to seek a better models for describe this retention processes.

CONCLUSIONS

The development of road infrastructure is closely linked to the level of environmental pollution in Poland. It is therefore of great importance to develop technology, which use can reduce the concentration of contaminants generated of road by transportation facilities, particularly in the most ecologically valuable areas. The application of (multilayer) Permeable Reactive Barriers filled with reactive materials promises the achievement of good results. However, chosen reactive materials should be able to reduce a wide range of contaminants with various physicochemical properties.

Results of conducted investigations showed that chloride concentration in snow samples is considerably varied even on the same sampling sites. These 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.

Basic and effective studies applied in determining the suitability of reactive materials for the retention of pollutants are batch tests. On the basis of these tests, it can be concluded, that activated carbon and zero-valent iron seem to be the best materials (activated carbon, zeolite, zero-valent iron, geza rock) for the reduction of chlorides. They are commonly used in PRBs as reactive materials causing reduction of several types of contaminants e.g. heavy metals and organic compounds. Therefore, it is reasonable to conduct further studies demonstrating the applicability of these materials as fillers PRBs in the vicinity of roads.

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Streszczenie: *Zastosowanie Przepuszczalnych Barrier Reaktywnych przy drogach do usuwania jonów chlorkowych.* Do poważniejszych źródeł zanieczyszczenia środowiska gruntowo-wodnego należą wody spływowe z dróg, które są mieszaniną substancji szkodliwych, złożoną m.in. z metali ciężkich, związków stosowanych do odładzania, związków organicznych i zawieszin. Powszechnie stosowaną substancją do odładzania nawierzchni jest negatywnie oddziaływujący na środowisko chlorek sodu. W przypadku nieprawidłowego zabezpieczenia środowiska gruntowo-wodnego wzdłuż dróg zanieczyszczenia mogą migrować do wód gruntowych, powodując zagrożenie dla źródeł wody pitnej. Jedną z metod zapobiegania tym zjawiskom jest wymuszony przepływ zanieczyszczeń przez materiały

reaktywne wypełniające przepuszczalną barierę reaktywną (PRB). Celem badań jest zbadanie przydatności wybranych materiałów reaktywnych do zmniejszenia stężenia chlorków w wodach spływowych z dróg. W artykule przedstawiono analizę czterech materiałów reaktywnych pod kątem usuwania chlorków. Wyniki badań wskazują na to, że materiały, które są najpowszechniej wbudowywane w PRBs – węgiel aktywny i żelazo elementarne, usuwają największą ilość tych zanieczyszczeń. Ponadto, w ramach badań, zbadano skład chemiczny próbek śniegu pobranych wzdłuż dróg w Warszawie.

Słowa kluczowe: Przepuszczalne Bariery Reaktywne, materiały reaktywne, oczyszczanie, zanieczyszczenia, środki do odładzania.

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