

# Investigation of post-industrial pollutions' immobilization in a hydraulic self-solidifying clay-cement binder

A Stempkowska<sup>1</sup>, Ł Wójcik<sup>2</sup>, P Izak<sup>2</sup>, M Staszewska<sup>1</sup> and J Mastalska-Popławska<sup>2</sup>

<sup>1</sup> Department of Mining and Geoengineering, AGH University of Science and Technology, al. Mickiewicza 30, 30-059 Krakow, Poland

<sup>2</sup> Department of Materials Science and Ceramics, AGH University of Science and Technology, al. Mickiewicza 30, 30-059 Krakow, Poland

stemp@agh.edu.pl

**Abstract.** Antifiltration barriers are used to secure deep excavations and flood embankments as well as to prevent the penetration of harmful substances into the ground and groundwater, also as part of the environmental protection system of waste landfills and production plants. The barriers are usually formed from a liquid suspension with binding properties which, after being pumped to the destination, passes into a solid with a fixed strength. One of the main problems of degraded post-industrial areas, preventing their introduction into the secondary economic cycle, is pollution of soil and the impact of pollution on groundwater. The interaction process of contaminated sites is complicated and the transport of pollutants from the place of danger to usable aquifers underground levels passes through a series of varied course. The article presents the possibilities of applications ground binder to reduce the emission of pollutant ions from soils in order to develop new mixtures of binders. The carried out research has shown that in the case of highly contaminated soils (eg Glasgow), almost 100% of heavy metals can be accumulated using clay-cement composites, and also significantly reduce the penetration of aromatic and aliphatic hydrocarbons. Some of the aliphatic hydrocarbons that allowed to enter to the penetrating solutions during measurements also did not exceed the standards.

## 1. Introduction

Soil contamination can be divided into two groups, one of them includes inorganic pollution, mainly heavy metals, and the other group constitutes of organic impurities, mostly in the form of petroleum-derived substances [1,2].

Decontamination of soils from heavy metals and petroleum substances is carried out by "*in situ*" methods (directly in contaminated areas) or "*off site*" methods (by moving contaminated soil into a place designed for this purpose), eg by using live microorganisms or by washing the soil with special solutions [3, 4, 5]. However, these processes, are long-term, often requiring additional work related to further processing of pollutants.

One of the method of immobilization of pollutants is a hydraulic self-solidifying mixture designated to locate environmentally hazardous post-industrial waste, prepared on the basis of a mineral binder with the addition of hazardous waste and stabilizing substances [4,5,6,7,8,9].



Due to their anti-filtration properties, such mixtures are also used to prevent the penetration of harmful substances into the ground and groundwater as part of the environmental protection system of waste landfills and production plants. These barriers are usually formed from a liquid suspension with binding properties which, after being pumped to the destination, passes into a solid with a fixed strength.

A characteristic feature of clay-cement binders is that in the entire bonding range they behave like viscoplastic fluids and there is not formed stiff crystalline structure, eg characteristic for concrete. Thanks to this combination of the sealing suspension with rock or soil (during excavation shaft works or other environmental works) does not harm their structure, and the fine-disperse clay fractions contained in the suspension ensure high tightness [10]. Changes of composition also allow modification of rheological and structural properties of clay-cement suspensions in a wide range.

In general the formation of the internal structure of the suspensions in the light of physicochemistry of colloids, can be explained as a specific aggregation of particles, as a result of intermolecular interactions. According to the DLVO theory [11], these interactions are the resultant of two phenomena:

- attraction - resulting from van der Waals forces ( $F_A$ ),
- repulsion - resulting from electrostatic and spatial effects ( $F_R$ ) (equation 1.):

$$F_{DLVO} = F_R + F_A \quad (1)$$

where:  $F_{DLVO}$  –force DLVO,  $F_R$  – repulsive electrostatic force,  $F_A$  – attractive force van der Waals.

As a result of these forces, spatial structures of the suspension spontaneously arise and their stiffness depends on the mutual ratio of these forces, which results from particles shape. The reversible internal structure of the suspension determines its rheological properties. The clay-cement slurries are a special case of a system in which the reversible processes associated with the thixotropic behavior of clay minerals overlap with the irreversible physico-chemical processes that accompanying the hydration process of cement. These processes, which include changes in the composition of the solution and the formation of solid reaction products, have a significant impact on the rheology of clay-cement slurries.

The cement hydration process is a complicated reaction, during which comes to the overlapping influence, reacting with water and forming the Portland clinker phases. This process is multi-stage, and individual clinker phases retain their specific reaction. Due to the above properties, clay-cement suspensions seem to be a good material for immobilization of inorganic as well as organic impurities.

The research involved a series of clay-cement mixtures with various composition, to determine the leaching of hazardous components bound in the structure of the clay -cement barrier. Immobilization was carried out with the participation of heavily contaminated soil containing hazardous ingredients eg heavy metals. The idea of the research was the possibility of both binding them in waterproofing barriers, as well as limitations of getting beyond the barrier.

## 2. Materials and methods

A landfill in Glasgow is post-industrial homogeneous contaminated soil. The provided samples were characterized by a very alkaline reaction and contained metal ions mainly Fe, but also Pb, Cr, Ni, Cu, Zn. However, the biggest ecological risk to the environmental to the Glasgow landfill is the content of hydrocarbons, especially aromatic ones, which have exceeded the applicable standards at least twice.

For the needs for the study, a series of mixtures with contaminated soil was prepared, the composition of which are presented in table 1. The content of soil in the samples is from 30-70%, the rest is a clay-cement binder with a cement content of 10 to 20%. For example, sample G 4.10 means Glasgow soil, binder 40% content of cement in a binder 10%. The mass of samples were similar and amounted to approx. 110-120 g

The samples were placed in pipes with a diameter of  $\phi=50$  and after concretion a distilled water flow was forced through them under pressure of 1 atm at a volume of 100 ml. The water permeability of concreted samples was on the level  $10^{-10}$  m/s.

The following research methods were used:

- determination of pH and sulphates concentration- multifunctional WTW inoLAB multi 9310 device equipped with suitable electrodes including ion-selective,
- determination concentration of metals in binders - XRF method (Olympus X-5000 analyzer)
- determination concentration of leached out metals concentration in the filtrates- ASA method (using Thermo Scientific iCE 3500)
- determination of hydrocarbons' concentration - IR method (FTIR spectrometer from BIO-Rad model FTS-165)

**Table 1.** Characteristics of pollutants in a soil sample from Glasgow.

Component	Concentration	Unit
Humidity	18	(%)
Arsenic, As	3.5	(mg/kg)
Boron, B	0.38	(mg/kg)
Cadmium, Cd	<0.50	(mg/kg)
Chromium, Cr	26	(mg/kg)
Copper, Cu	27	(mg/kg)
Iron, Fe	23000	(mg/kg)
Lead, Pb	72	(mg/kg)
Mercury, Hg	<0.25	(mg/kg)
Nickel, Ni	40	(mg/kg)
Zinc, Zn	65	(mg/kg)
Soluble sulphates	0.090	(%)
pH	8.6	-
Aliphatic hydrocarbons (C5-C44)	45	(mg/kg)
Aromatic hydrocarbons (C5-C44)	840	(mg/kg)

The measuring system set-up forcing filtration is shown in figure 1. The hydraulic gradient was generated by compressed air with stabilized pressure. The filtrate was subjected to analytical tests. The total content of soluble (salinity), pH and potential Eh as well as concentrations of Na, Fe, Pb, Cr, Ni, Cu metals (selection determined by the composition of primary samples), and the concentration of aliphatic and aromatic hydrocarbons were also determined. Additionally, the filtration coefficients were determined and the scale of pollutants spread migration the year was calculated.



**Figure 1.** Filtration system.

### 3. Results and discussion

Compositions of mixtures' series containing contaminated soil from Glasgow with clay-cement binder are shown in table 2 and pH values of the filtrate are presented in table 3.

**Table 2.** The masses of individual components in mixtures.

Sample	Weight of sample, (g)	Mass of contaminated soil, (g)	Contribution of binder, (% wt)
<b>G-4.10</b>	110.2	66.1	40
<b>G-4.15</b>	122.4	73.4	40
<b>G-4.20</b>	117.6	70.6	40
<b>G-5.10</b>	111.2	55.6	50
<b>G-5.15</b>	112.3	56.2	50
<b>G-5.20</b>	126.7	63.4	50
<b>G-6.10</b>	119.8	47.9	60
<b>G-6.15</b>	112.6	45.0	60
<b>G-6.20</b>	105.3	42.1	60
<b>G-7.10</b>	112.3	33.7	70
<b>G-7.15</b>	119.1	35.7	70
<b>G-7.20</b>	107.0	32.1	70
<b>G-8.10</b>	109.5	21.9	80
<b>G-8.15</b>	115.4	23.1	80
<b>G-8.20</b>	119.2	23.8	80

Background parameters: Salinity 6.06 mg/l, pH 6.99

**Table 3.** The value of pH , potential Eh, sodium concentration in filtrates of series with contaminated soils.

Sample	Participation of contaminated soil, (% wt)	pH	Salinity (mg/l)	Eh (mV)	c <sub>Na</sub> (mg/l)
G 4.10	60	10.03	106.5	22	5.47
G 4.15	60	10.29	138.0	45	5.21
G 4.20	60	10.44	170.8	35	5,36
G 5.10	50	10.27	115.4	-12	4.07
G 5.15	50	10.48	163.6	13	4.46
G 5.20	50	10.48	166.1	-24	5.36
G 6.10	40	10.37	138.1	-22	4.39
G 6.15	40	10.54	185.1	7	4.98
G 6.20	40	10.25	113.2	34	4.42
G 7.10	30	10.43	155.7	15	3.60
G 7.15	30	10.25	114.2	-23	3.10
G 7.20	30	10.34	139.4	-16	3.44
G 8.10	20	10.15	100.4	10	2.37
G 8.15	20	10.23	114.3	8	2.29
G 8.20	20	10.58	217.0	13	3.11

The pH values of the filtrates in all cases was above 10 which exceeds the standard [maximum allowable/permisible value 6.5-9] [12] and also indicates the presence of a large amount of alkalies. The average salinity was about 140 mg/l and no changes in leaching depending on the composition of the samples was observed. The value of salinity is in consistence with the Regulation from 2014 [12] which determines the acceptable quantity at the level of 1000 mg/l. The migration of ions depends on the type of binder's structure and filtration coefficient.

Large positive or negative Eh values or oxidation-reduction potential, indicate an unstable chemical system, where large positive values mean above 590 mV, and in the case of negative values below -150 mV. Pure water in equilibrium with oxygen has oxidizing properties. The Eh potential in all analyzed cases is weakly reducing. Under natural conditions, the Eh potential changes in the oxidizing direction, which in the case of barriers may affect the surrounding soils [13].

In primary samples alkaline metals were not determined, but since pH value was high, the sodium concentration was taken into consideration (table 3). It is the fastest migrating element, actually a not subject to sorption. Its concentration in the filtrate depends in proportion to the content of contaminated soil the filtrate is determined in proportion to the value of the soil contaminated, however, in all cases it is in the permisible concentrations (800 mg/l) [12]. But if the sodium cations are not compensated by the anions of acidic residues (low salinity, the presence of insoluble compounds), this results in the formation of active OH<sup>-</sup> groups. Such a system causes a potential corrosive effect and reducing the character of Eh.

The concentration of nickel, copper and chromium in the soil are at the limit of the requirements of the standard (Ni, Cu) and lead concentration is exceed them (Pb). The permisible iron content is not specified. However, these concentrations have been referred to the most restrictive conditions, or for permeable soils, in the case of impermeable soils, the concentrations in the entire range meet the standards.

The concentration of selected metals was tested before and after the filtration process (limit of detection was  $0.2 \cdot 10^{-4}$  mg/l). In the case of Ni, Zn, Pb, Fe, the cation content in the filtrate is below the sensitivity of the diagnostic devices. For content of Cu and Cr, a minor migration to the solution was observed [14].

After the filtration process, it was observed that the content of selected metals cations is almost in 100% accumulated in the binders, it means that they are stable and insoluble in water. Therefore, there

is no risk of these harmful cations passing into soils and groundwater. The leaching of transition and heavy metals from the tested binders is also much lower than the limit values (the sum should not be higher than 14.0 mg/l). Therefore, there are no threats to the migration of harmful cations to soil and groundwater.

**Table 4.** Copper concentration before and after filtration.

Sample	$c_{Cu}$ before filtration, (mg/kg)	$c_{Cu}$ in filtrate, (mg/l)	$c_{Cu}$ after filtration, (mg/kg)	Accumulation of contaminations in the mixture, (%)
<b>G 4.10</b>	18	0.0026	17.9974	99.985
<b>G 4.15</b>	16	0.0022	15.9978	99.986
<b>G 4.20</b>	19	0.0056	18.9944	99.970
<b>G 5.10</b>	15	0.0037	14.9963	99.975
<b>G 5.15</b>	13	0.0054	12.9946	99.958
<b>G 5.20</b>	13	0.0026	12.9974	99.980
<b>G 6.10</b>	11	0.0045	10.9955	99.959
<b>G 6.15</b>	11	0.0023	10.9977	99.979
<b>G 6.20</b>	10	0.0031	9.9969	99.969
<b>G 7.10</b>	9	0.0045	8.9955	99.950
<b>G 7.15</b>	9	0.0012	8.9988	99.986
<b>G 7.20</b>	8	0.0070	7.9930	99.912
<b>G 8.10</b>	5	0.0027	4.9973	99.946
<b>G 8.15</b>	5	bs	-	100
<b>G 8.20</b>	5	0.0016	4.9984	99.968

bs - below sensitivity

**Table 5.** Chromium concentration before and after filtration.

Sample	$c_{Cr}$ before filtration, (mg/kg)	$c_{Cr}$ in filtrate, (mg/l)	$c_{Cr}$ after filtration, (mg/kg)	Accumulation of contaminations in the mixture, (%)
<b>G 4.10</b>	16	0.0327	15.9673	99.795
<b>G 4.15</b>	16	0.0276	15.9724	99.827
<b>G 4.20</b>	15	0.0270	14.9730	99.820
<b>G 5.10</b>	13	0.0324	12.9676	99.750
<b>G 5.15</b>	12	0.0341	11.9659	99.715
<b>G 5.20</b>	12	0.0160	11.9840	99.866
<b>G 6.10</b>	10	0.0290	9.9710	99.710
<b>G 6.15</b>	10	0.0120	9.9880	99.880
<b>G 6.20</b>	11	0.0287	10.9713	99.740
<b>G 7.10</b>	8	0.0233	7.9767	99.708
<b>G 7.15</b>	7	0.0247	6.9753	99.647
<b>G 7.20</b>	8	0.0233	7.9767	99.708
<b>G 8.10</b>	5	0.0333	4.9667	99.334
<b>G 8.15</b>	4	0.0322	3.9678	99.195
<b>G 8.20</b>	4	0.0286	3.9714	99.285

#### 4. Hydrocarbons

Concentrations of aliphatic and aromatic hydrocarbons were determined in binders before and after the process of forced filtration. The results are shown in tables 6 and 7.

**Table 6.** The concentration of aliphatic hydrocarbons before and after the filtration process.

Sample	Concentration of aliphatic hydrocarbons before filtration, (mg/kg)	Concentration of aliphatic hydrocarbons in filtrate, (mg/l)	Concentration of aliphatic hydrocarbons after filtration, (mg/kg)	Accumulation of contaminations in the mixture, (%)
G 4.10	27.78	5.415	22.365	80.507
G 4.15	28.12	5.180	22.940	81.579
G 4.20	25.87	4.670	21.200	81.948
G 5.10	22.76	3.169	19.591	86.076
G 5.15	23.29	4.470	18.820	80.911
G 5.20	21.17	4.903	16.267	76.840
G 6.10	18.09	5.010	13.080	72.305
G 6.15	18.20	3.698	14.502	79.681
G 6.20	17.61	3.475	14.195	80.607
G 7.10	14.59	3.326	11.264	77.203
G 7.15	14.45	3.321	11.129	77.017
G 7.20	13.02	2.159	10.861	83.417
G 8.10	9.91	2.514	7.396	74.631
G 8.15	9.34	2.403	6.937	74.272
G 8.20	8.87	3.930	4.940	55.693

**Table 7.** The concentration of aromatic hydrocarbons before and after the filtration process.

Sample	Concentration of aromatic hydrocarbons before filtration, (mg/kg)	Concentration of aromatic hydrocarbons in filtrate, (mg/l)	Content of aromatic hydrocarbons after filtration, (mg/kg)	Accumulation of contaminations in the mixture, (%)
G 4.10	504	bs	unchanged	100
G 4.15	567	bs	unchanged	100
G 4.20	487	bs	unchanged	100
G 5.10	420	bs	unchanged	100
G 5.15	421	bs	unchanged	100
G 5.20	399	bs	unchanged	100
G 6.10	336	bs	unchanged	100
G 6.15	376	bs	unchanged	100
G 6.20	319	bs	unchanged	100
G 7.10	252	bs	unchanged	100
G 7.15	290	bs	unchanged	100
G 7.20	234	bs	unchanged	100
G 8.10	168	bs	unchanged	100
G 8.15	155	bs	unchanged	100
G 8.20	187	bs	unchanged	100

\* LOD/limit of detection is at approx. 0.017 mg/l

bs - below sensitivity

The total concentration of aromatic hydrocarbons in the binders greatly exceeds the permissible standards (15 mg/l), even for deeply located soils. In typical waterproofing barriers, there should be no more than 50% of contaminated soil for a depth of injection below 2 m. On the other hand, aliphatic hydrocarbons in filtrates meet the requirements of the standard for impermeable soils (15 mg/l).

The filtrate samples were extracted with tetrachlorethylene and after separation of the phases in the solution, the contents of particular compounds were determined by FTIR spectroscopy. No aromatic hydrocarbons were found in the filtrates (below the limit of detection). Aliphatic hydrocarbons only slightly leached out but still meet the requirements of the standard (permissible concentration of 15 mg/kg). Accumulation of these substances was stated in the binder.

**Table 8.** The sum of pollutants passing to migrating solutions.

Sample	Concentration of aliphatic hydrocarbons in filtrate, (mg/l)	Concentration of heavy metals in filtrate, (mg/l)	The sum of pollutants, (mg/l)
<b>G-4.10</b>	5.415	0.038	5.453
<b>G-4.15</b>	5.180	0.033	5.213
<b>G-4.20</b>	4.670	0.036	4.706
<b>G-5.10</b>	3.169	0.039	3.208
<b>G-5.15</b>	4.470	0.043	4.513
<b>G-5.20</b>	4.903	0.022	4.925
<b>G-6.10</b>	5.010	0.037	5.047
<b>G-6.15</b>	3.698	0.017	3.715
<b>G-6.20</b>	3.475	0.035	3.510
<b>G-7.10</b>	3.326	0.031	3.357
<b>G-7.15</b>	3.321	0.029	3.350
<b>G-7.20</b>	2.159	0.033	2.192
<b>G-8.10</b>	2.514	0.039	2.553
<b>G-8.15</b>	2.403	0.036	2.439
<b>G-8.20</b>	3.930	0.033	3.963

The filtration coefficient was determined according to the Darcy law from the formula below (equation 2) [15]:

$$k = Q / F \cdot I \quad (2)$$

where  $k$ - the filtration coefficient, (m/s),  $Q$  – quantity of water (m<sup>3</sup>/s),  $F$  – section area (m<sup>2</sup>),  $I$ - hydraulic gradient.

The filtration coefficients of the tested binders and phenomena possible migration of pollutants' during the year are presented in table 9. Filtration time was measured by using system shown on figure 1.

**Table 9.** Determination of the filtration coefficient and possible migration of pollutant during the year.

Sample	Filtration time (s)	Filtration coefficient (m/s)	Migration (m)	Comments
<b>G-4.10</b>	485710	$7.13 \cdot 10^{-10}$	0.023	-
<b>G-4.15</b>	512800	$5.90 \cdot 10^{-10}$	0.019	-
<b>G-4.20</b>	598750	$5.65 \cdot 10^{-10}$	0.018	-
<b>G-5.10</b>	98760	$4.00 \cdot 10^{-10}$	0.013	-
<b>G-5.15</b>	90140	$3.20 \cdot 10^{-09}$	0.101	-
<b>G-5.20</b>	89980	$4.07 \cdot 10^{-09}$	0.128	-
<b>G-6.10</b>	9780	$3.67 \cdot 10^{-08}$	1.160	-
<b>G-6.15</b>	142500	$2.72 \cdot 10^{-09}$	0.086	-
<b>G-6.20</b>	139840	$2.83 \cdot 10^{-09}$	0.090	-
<b>G-7.10</b>	4260	$9.08 \cdot 10^{-08}$	2.860	-
<b>G-7.15</b>	5487	$6.65 \cdot 10^{-08}$	2.100	-
<b>G-7.20</b>	6240	$7.05 \cdot 10^{-08}$	2.220	-
<b>G-8.10</b>	3480	$1.97 \cdot 10^{-07}$	<b>6.210</b>	The possibility of unsealing the barrier
<b>G-8.15</b>	3870	$1.58 \cdot 10^{-07}$	<b>4.980</b>	The possibility of unsealing the barrier
<b>G-8.20</b>	4100	$1.46 \cdot 10^{-07}$	<b>4,600</b>	The possibility of unsealing the barrier

Investigations have shown that the values of the filtration coefficient are strongly dependent on the content of contaminated soil and the amount of cement.

## 5. Conclusions

- The pH values of the filtrates do not meet the standards, because in all cases it was above the maximum allowable limit which also indicates the presence of alkalies.
- The systems initially are chemically unstable, the Eh potential in all cases is weakly reducing, but it will change with time in the oxidizing direction. In the case of barriers, this is an adverse (corrosive) impact on surrounding soils.
- The Na content is in the permissible concentrations (800 mg/l), but the cations are not compensated by anions (low salinity, the presence of insoluble compounds) which results in the formation of active OH<sup>-</sup> groups, and hence the potential corrosive effect and reducing the character of Eh. The amount of leached out sodium depends on the primary composition of the sample.
- Concentrations of heavy metal cations do not exceed standards, and even remain on the limit of determination.
- In bulk of the binders about 80% of all aliphatic hydrocarbons stay accumulated, approx. 20% are leached out. However, they are still below the permissible standard requirement (15 mg/kg).
- The content of aromatic hydrocarbons in filtrates is below the limit of detection. Accumulation capacity of the binder in all cases very high. There are no threats caused by the possible migration of aromatic hydrocarbons to groundwater and soils.
- Migration of pollutants strongly depends on the filtration coefficient and the initial concentrations of the tested substances. In extremely unfavorable conditions, the spread of analyzed pollutants it could be as high as 6m per year.

## Summary

- Generally the tested binders show a very good level of immobilization of dangerous substances in the soil, mixtures with soil contaminated from Glasgow can be used in barriers, under several conditions:
- The percentage of soil should not be higher than 50% due to environmental standards the injection should be at a depth below 2m depth according to Regulation from 2014 [12].
- The problem may be strong the sodium's migration through barrier, however, its filtration coefficient of  $10^{-10}$  m/s significantly limits it. The permeability of the binder usually increases if it is dried (additional monitoring).

Research conducted on heavily contaminated ground from the Glasgow landfill site does not limit the use of clay-cement binders to protect other landfills. However, due to their individual character, testing should always be carried out.

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## References

- [1] Kaczyńska G, Borowik A and Wyszowska J 2015 *Water Air Soil Pollut.* **226** pp 372
- [2] Rakowska J, Radwan K, Ślosorz Z, Pietraszak E, Łudzik M and Suchorab P 2012 *Usuwanie substancji ropopochodnych z dróg i gruntów* (Państwowy Instytut Badawczy: Józefów)
- [3] Cebula J and Rajca M 2014 *Oczyszczanie gleb i gruntów* (Wydawnictwo Politechniki Śląskiej: Gliwice)
- [4] Liu L, Li W, Song W and Guo M 2018 *Sci. Total Environ.* **633** pp 206-19
- [5] Wuana RA and Okieimen FE, 2011 *ISRN Ecology* **402647**
- [6] Radziemska M 2018 *Catena* **163** pp 123-9
- [7] Ou J, Li H, Yan Z, Zhou Y, Bai L, Zhang Ch, Wang X and Chen G 2018 *Sci. Rep.* **8** **4618**
- [8] Maiviya R and Chaudhary R 2006 *J. Mater. Cycles Waste Manag.* **8** pp 78 - 87
- [9] Kuś R, Janik G, Izak P, Wójcik Ł and Słowikowski D *Patent* PL 216864 B1
- [10] Izak P 2015 *Reologia w ceramice* (Kraków: Wydawnictwa AGH)
- [11] Sonntag H 1982 *Koloidy* (Warszawa: Państwowe Wydawnictwo Naukowe)
- [12] Rozporządzenie Ministra Środowiska z dnia 18 listopada 2014 r. w sprawie warunków, jakie należy spełnić przy wprowadzaniu ścieków do wód lub do ziemi, oraz w sprawie substancji szczególnie szkodliwych dla środowiska wodnego
- [13] Merkel B and Sperling B 1998 *Hydrogeochemische Stoffsysteme II* Kommissionsvertrieb Wirtschafts- und Verlagsgesellschaft Gas und Wasser GmbH.: Bonn)
- [14] Król A 2007 *Przemysł Chemiczny* **10** pp 971- 3
- [15] Kulma R 1995 *Podstawy obliczeń filtracji wód podziemnych* (Kraków Wydawnictwo AGH)