Title: Calcium and magnesium in leachate waters of post-industrialized waste tips

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CALCIUM AND MAGNESIUM IN LEACHATE WATERS OF POST-INDUSTRIALIZED WASTE TIPS

WAPŃ I MAGNEZ W WODACH ODCIEKOWYCH SKŁADOWISK ODPADÓW PRZEMYSŁOWYCH

Abstract: The waste-tips of industrial wastes are essential source of water pollution both of surface and underground waters. Hydrosphere pollution is basically aftermath of forming of leachate waters with high concentration of toxic substances. Apart from typical toxic elements as cadmium, lead leachate may contain high concentration of other elements, Characteristics of leachate waters of landfills of coal mines were introduced in this paper. For purpose of studies three objects were selected. Obtained results revealed that leachate waters are characterized by high conductivity (maximal values ca 17 mS · cm^{-1}). They also have high concentrations of magnesium and calcium. In leachate waters calcium showed very high variance. The concentration of this ion varied from 240 to 872 mg/dm^3. High variation was also recorded in case of magnesium. The contents of this ion ranged from 109 to 702 mg/dm^3. Both these chemical elements can be considered as indicators of anthropogenic pollution of waters.

Keywords: calcium, magnesium, leachate, landfill, water pollution

The post-industrialized waste heaps are essential source of pollution of surface and underground waters in their vicinity. The hydrosphere pollution is mainly a result of origin of leachate waters, characterized by high concentrations of toxic substances. Apart from the substances considered as toxic ones as cadmium, lead, leachate waters may contain high contents of other chemical elements [1–4]. Amongst them there are also calcium and magnesium which can pose problem worldwide [5–7]. The concentrations of these common ions usually do not exceed 100 mg · dm^3 in underground waters in case of calcium and 30 mg · dm^3 of magnesium [8]. However, in surface waters lower concentrations of these ions are noted [9–11]. The ratio Ca^{2+}/Mg^{2+} in medium mineralized waters varies between 2 and 6 [12]. The completely different situation occurs in the surroundings of post-industrialized and communal wastes and in the areas

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of intensive agriculture. There are much higher concentrations of calcium and magnesium both in underground and surface waters [13, 14].

In the present paper results of studies on leachate waters of the three waste colliery waste tips were introduced.

Material and methods

For studies three colliery waste tips were selected. These are waste heap "Skalny" in Laziska and "Panewniki", "Murcki" in Katowice. They are characterized by concentrated sources of leachate waters output. Such outflows are created the most frequently when deposition of wastes lead to filling up river valleys or former open pit sand mine (Fig. 1, 2) [3, 15].

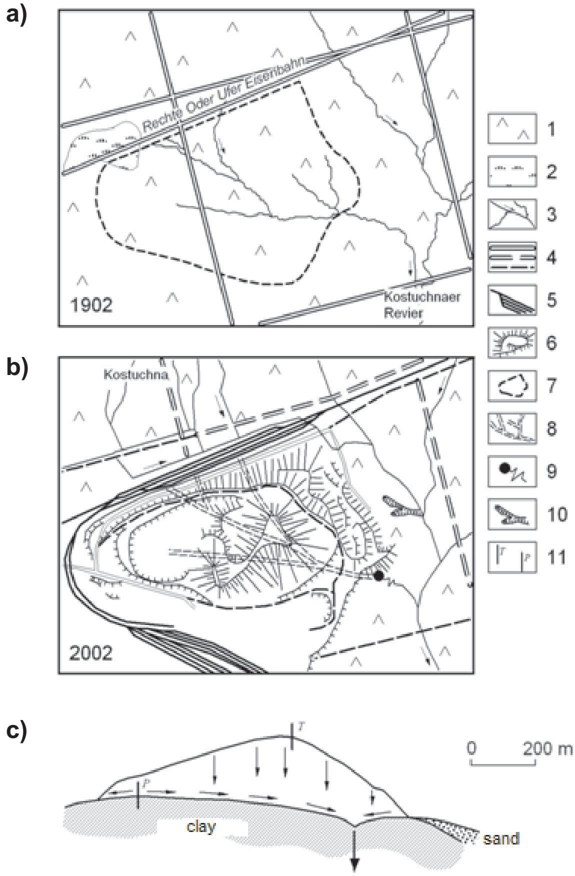

Fig. 1. The scheme of waters migration within of the landfill "Kostuchna" [12]: a) – Situation in 1902, b) – Situation in 2002, c) – horizontal section of the waste tip (1 – forest, 2 – meadows, 3 – water courses, 4 – roads, 5 – railways, 6 – margins of the landfill, 7 – the borders of contemporary of landfill on the map from 1992, 8 – drainage system of buried river valleys, 9 – outflow of leachate waters, 10 – erosion cut, 11 – watersheds: T – topographic, P – underground)

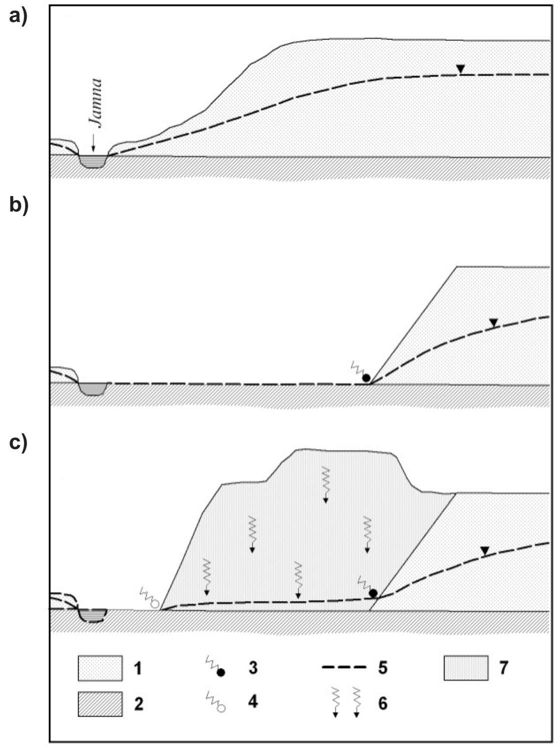

Fig. 2. The changes in relief and water conditions within the waste tip "Panewniki" [14]: a) – Initial state 1950, b) – state during the sand exploitation 1970, c) – present state 2010 (1 – sands and gravel, 2 – boulder clay, 3 – outflow of underground water, 4 – leachate, 5 – level of underground water, 6 – infiltration of precipitation water, 7 – barren rocks)

Hydrographic mapping aiming at estimation of changes in water relations of the areas of the waste tips were performed according to the methodical assumptions by [16]. The measurement of pH, temperature and conductivity were done directly by means of gauge Multi-Line P-4. The determinations of selected ions were conducted according to PN-ISO 6058:1999 as well as PN-ISO 6059:1999. For statistical analyses series of data collected in the years 2002–2009 (minimal number of observations = 12) were used. The measurements of flow intensity were performed by RBC flume for water discharge measurement by Eijkelkamp company.

Samples of rocks for analyses were collected in the sites of outflows of leachate waters. These were pieces of Carbon rocks with the incrustations of minerals on their surface. Additionally, evaporates on hydrophytes stems were taken for analyses. The incrustations were prepared and analyzed by microscope (SEM) Philips XL 30 ESEM/TMP with analytic countershaft EDS (EDAX Sapphire). Within micro-areas of examined preparations photographs in BSE mode (*Back-Scattered Electron*) were taken. The composition of chemical elements and identification of minerals were based on spectral analysis EDS (*Electron Dispersive Scanning*).

To test the significance of differences the non-parametric equivalent of the one-way analysis of variance of Kruskal-Wallis was applied, while to test for multiple comparisons – the Conover test was used. All the data were presented using box-and-whiskers plots (Fig. 3). When compared with the significance of the median differences of the variables, such as the physical or chemical parameters of the water from different objects, these differences were indicated by appropriate small letters (a, b, c) placed at the top of the figure. Different letters indicate that the values differ significantly at $p < 0.05$.

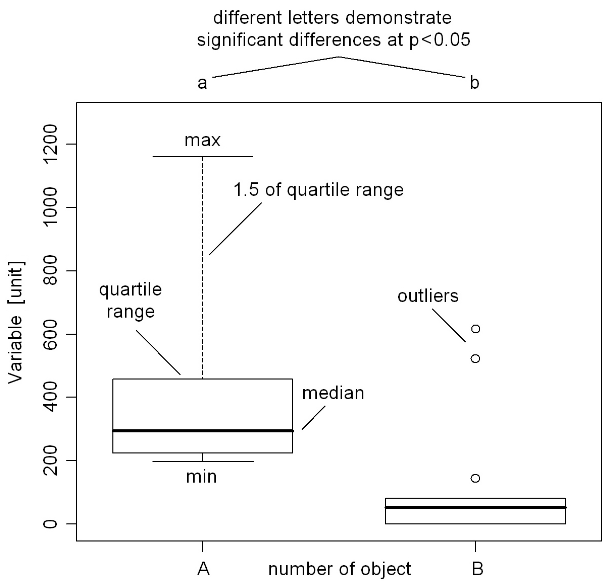

Fig. 3. Scheme of data presentation on box-whisker plots

Results and discussion

The efficiency of discharge of leachate waters is very diversified. The highest efficiency was noted in Panewniki II leachate (1.8–5 $dm^3 \cdot s^{-1}$). Lower values were observed in Skalny (0.5–1.5 $dm^3 \cdot s^{-1}$) and Kostuchna (0.2–0.6 $dm^3 \cdot s^{-1}$) leachates.

The waters of the investigated leachates are typified by high electrical conductivity (Fig. 4). The lowest value of conductivity amongst the studied objects was noted in waters of "Kostuchna". The mean value of conductivity amounted to 5.9 $mS \cdot cm^{-1}$ (from 5.4 to 6.8 $mS \cdot cm^{-1}$). Definitely higher values were measured for waste tip "Panewniki". The conductivity of this object varied between 7.2 to 8.3 $mS \cdot cm^{-1}$ in the case leachate I and respectively: from 7.9 to 10.6 $mS \cdot cm^{-1}$. The maximal values of conductivity (17.9 $mS \cdot cm^{-1}$) were observed in the waste heap "Skalny". In the same time the highest hesitations of this parameter were the highest from 12.1 to 17.9. Such

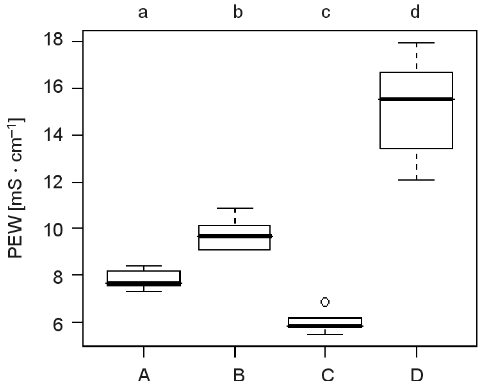

Fig. 4. Conductivity of leachate waters (A – leachate "Panewniki I", B – leachate "Panewniki II", C – leachate "Kostuchna", D – leachate "Skalny"; different letters mean that values are significant at $p < 0.05$)

high mS · cm^{-1} value of conductivity and high variability may be a consequence of processes of reclamation of the object.

During reclamation for purposes of fire extinguishing (it was thermically active object) mixtures of various dusts and other wastes, which caused mineralization of leachates, were used. It was observed that values of conductivity are comparable with those noted by [1, 3] in leachate waters of other colliery waste tips.The leachate waters are characterized by acid pH (Fig. 5). The leachate of waste tip Panewniki I and II as well as Kostuchna demonstrate slightly acid pH. It is mainly repercussion of pyrites decay (FeS_2) and origin of sulphuric acid. The waters of waste-tip "Skalny" are typified by slightly alkaline pH. It is a result of land reclamation of this object. During this process material which show buffer activity about acid substances were used. The pH of leachate waters of all studied waste-tips is very stable. The lowest coefficient variance (C_v – 1.8 %) was observed in leachate Kostuchna. The highest value (C_v – 7.8 %) in leachate Panewniki II.

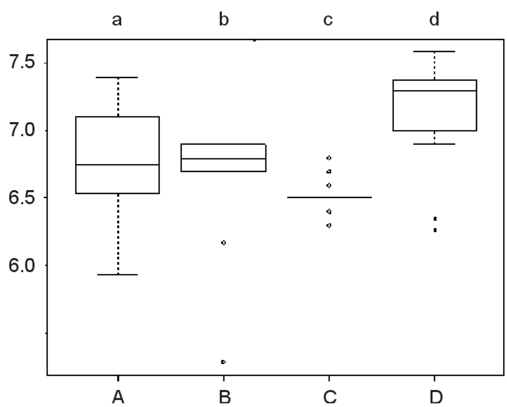

Fig. 5. Water reaction (pH) of leachate (A – leachate "Panewniki I", B – leachate "Panewniki II", C – leachate "Kostuchna", D – leachate "Skalny"; different letters mean that values are significant at $p < 0.05$)

As a result of lixiviation increase of contents of particular ions may occur. The source of calcium and magnesium are Carbon rocks deposited on the waste tip. In the case of Skalny object they contain, on the average, from 0.02 to 0.44 mg/100 g Ca and from 0.06 to 1.09 mg/100 g Mg. They are transported to leachate because of lixiviation. In leachate waters concentration of calcium was very diversified (Fig. 6). The concentrations of ion ranged from 240 to 872 mg · dm^{-3}.

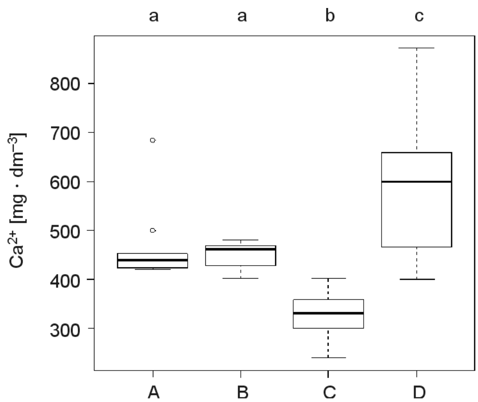

Fig. 6. Concentrations of calcium (Ca^{2+}) in leachate waters (A – leachate "Panewniki I", B – leachate "Panewniki II", C – leachate "Kostuchna", D – leachate "Skalny"; different letters mean that values are significant at $p < 0.05$)

Maximal concentrations were distinctly lower than those measured in other waste tips. For example, calcium in waters of the tip Czerwionka-Leszczyny was estimated at more than 2200 mg · dm^{-3} [1]. Also higher contents more than 3000 mg · dm^{-3} are noted in leachates from "young" communal waste tips [14]. There were no statistically significant differences in calcium concentrations in the leachates from the same waste tip – Panewniki. But such differences were noted in case of waters of two other leachates (Fig. 6). The greatest amplitude – 472 mg · dm^{-3} was recorded in the leachate of Skalny waste tip. Such a great variation was caused by reclamation processes of the waste tip which were mentioned above.

High variation of concentration concerned magnesium either (Fig. 7). The contents of this ion varied between 109 to 702 mg · dm^{-3}. The highest concentrations were recorded in "Skalny" tip. Similarly as in case of calcium the maximal values were considerably lower than those noted in communal waste heaps, where contents can reach 1500 mg · dm^{-3}. However, they can be compared with contents observed in other leachate waters of colliery waste tips [1]. Like in case of magnesium concentrations, no statistically significant differences in magnesium concentrations in the waters of the same leachate – Panewniki were observed. However, there were such differences in the waters of two other leachates (Fig. 6). Besides, in case of Skalny waste tip the greatest amplitude in magnesium concentrations (386 mg · dm^{-3}) was noted. The measured concentrations of calcium and magnesium are several times higher than those observed in waters of sources in this area [17].

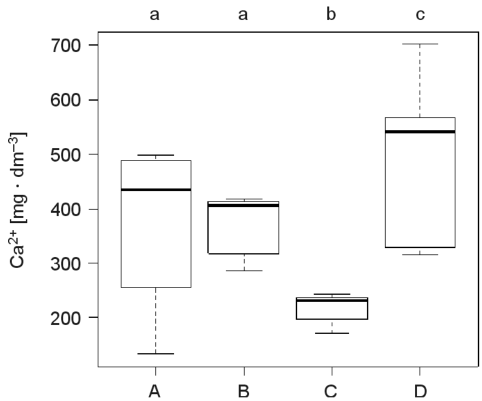

Fig. 7. Concentrations of magnesium (Mg^{2+}) in leachate waters (A – leachate "Panewniki I", B – leachate "Panewniki II", C – leachate "Kostuchna", D – leachate "Skalny"; different letters mean that values are significant at $p < 0.05$)

Leachate waters of colliery waste tips tend to sediment of carbonate compounds. They were confirmed during scanning (SEM) of bottom deposits collected nearby outflow sites. The most common evaporates were carbonate sulphur and magnesium sulphur. Forming of these rocks is an aftermath of high contents of sulphures in leachate waters. The maximal concentrations of this ion in the examined waters exceeded 5000 $mg \cdot dm^{-3}$. These bottom deposits are visible even at macroscale because they are sediment on stems of plants immersed in leachate waters. The comparison of contents of calcium and magnesium in leachates with waters from springs [17] unequivocally showed that deposition of post-coal mine wastes lead to increase of concentration of these ions. Thus, calcium and magnesium may be considered as good indicators of anthropogenic pollution of waters.

Conclusions

The conducted research demonstrated that mining waste exposed to atmospheric factors undergo of lixiviation processes. As a result leachate waters of landfills of coal mines are characterized by:

– high conductivity;
– they have high calcium and magnesium concentrations;
– they are prone to precipitate carbonate compounds.

Therefore, mining wastes landfills can be treated as permanent source of hydrosphere pollution. It concern both underground and surface waters. In turn, calcium and magnesium can be regarded as indicators of mining water pollution.

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WAPŃ I MAGNEZ W WODACH ODCIEKOWYCH SKŁADOWISK ODPADÓW PRZEMYSŁOWYCH

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Abstrakt: Składowiska odpadów przemysłowych są istotnym ogniskiem zanieczyszczenia wód powierzchniowych i podziemnych rejonu składowisk. Zanieczyszczenie hydrosfery jest głównie następstwem powstawania wód odciekowych o dużych koncentracjach substancji toksycznych. Oprócz substancji uznanych za typowo toksyczne, takich jak kadm oraz ołów, wody odciekowe mogą zawierać wysokie stężenia innych pierwiastków. W artykule przedstawiono wyniki badań stężenia wapnia i magnezu w wodach odciekowych składowisk odpadów górnictwa węglowego. Wykazano, że wody odciekowe charakteryzuje wysoka przewodność elektrolityczna (do 17 $mS \cdot cm^{-1}$) będąca następstwem ługowania zdeponowanych odpadów. Bardzo duże są również stężenia wapnia i magnezu. W wodach odciekowych wapń wykazywał bardzo duże zróżnicowanie. Stężenia tego jonu wahały się w szerokim zakresie od 240 do 872 mg/dm^{-3}. Duża zmienność stężeń dotyczyła również magnezu. Stężenia tego jonu zmieniały się w zakresie od 109 do 702 mg/dm^{-3}. Składowiska odpadów stanowią trwałe ognisko zanieczyszczenia wód powierzchniowych i podziemnych. Zarówno wapń i magnez można uznać za dobre indykatory antropogennego zanieczyszczenia wód.

Słowa kluczowe: wapń, magnez, wody odciekowe, składowiska odpadów, zanieczyszczenie wód