FIXATION OF Pb-CATIONS BY TWO DIFFERENT TYPES OF CLAYS FROM THE POLISH LOWLAND IN WARSAW'S SURROUNDINGS

Beata Łuczak-Wilamowska

Faculty of Geology, Warsaw University, Żwirki i Wigury 93, 02-089 Warszawa, Poland
Phone: +48 22 5540606, Fax: +48 22 5540001, e-mail: B.LuczakW@uw.edu.pl

Abstract
The ability of fixation of Pb-cations from water solutions by two types of clays occurring in surroundings of Warsaw – Neogene Poznań Series clay from Mszczonów and Quarternary varved clay from Zielonka – was studied in order to check the applicability of these soils in protection of the environment. The clays from Mszczonów are mainly composed of beidellite and illite. Carbonates are not present. The light laminae of the varved clay comprise quartz, carbonates and clay minerals (illite), and the dark laminae comprise illite, iron oxides and iron hydroxides. The varved clay contains about 6% $CaCO_3$. The specific surface area of the Poznań Series clays and the varved clay are equal to 250–350 and 41–93 m^2/g, respectively. However, both soils show similar value of fixation of Pb-cations. Therefore, the main factor controlling the immobilization is not the specific surface but the buffering capabilities of a soil. In the varved clay, the precipitation of Pb as heavily soluble hydroxides, takes place at the pH=6. The Poznań Series clays do not exhibit buffering capabilities, and fixation of Pb-cations takes place due to sorption. Its value decreases along with the decreasing pH. Both soils release the previously bound Pb only in subordinate amounts.

Introduction
Two types of clays occurring in Warsaw's surroundings were examined. The first type, the Poznań Series of clays occurs on the Polish Lowland and forms a large cover of palustrine sediments of Miocene-Pliocene on more than a half of the territory of Poland (1). In the outcrop in Mszczonów there occur clayey sediments of variegated colours: brown, brownish-grey, grey, black and blue, the latter one being markedly least common. These sediments form a uniform lithologic complex constituting a final part of the sedimentary cycle. Among them there occur lenses and streaks of sandy and dusty sediments, often water-saturated (2).
The clays of a second type were sedimented in the Warsaw stagnant-lake, which was formed in the transgression-stage of the Vistula-glaciation (North-Polish glaciation). The sediments comprise mainly clays (3, 4), and form stacked varves. The varve is composed of one light and one dark layer. The light layer gradually turns into an upper laying dark one, and the dark layer is distinctly separated from the overlying light layer of the next varve. It is supposed that each varve was formed as result of a single episode of discharge of material which subsequently underwent sedimentary fractionation (3).
Laboratory tests were carried out on samples: (i) of the Poznań Series clays: black, brown, and brownish-grey clays from Mszczonów; (ii) of the varved clays from Zielonka: light and dark layers. The tests involved determinations of the mineral composition, the specific surface (by methylene blue), the fixation of Pb-cations (by the batch method). The term 'fixation' is meant as decrease of Pb-concentration in water solution due to its interaction with a soil.

Mineral composition

The mineral composition of clays from Mszczonów was determined by thermal analysis (Table 1).

Table 1. Mineral composition and organic matter content of the Poznań Series clays from Mszczonów

Clay type	Clay minerals:	Beidellite	Illite	Kaolinite	Goethite	Quartz and others	Organic matter*
	wt %						
brown	78.8	53.6	13.4	11.8	6.2	14.6	0.4
brownish-grey	84.2	60.0	6.6	17.6	not detected	14.7	1.1
black	85.0	67.1	traces	17.9	not detected	7.5	7.5

*by the method of hydrogen peroxide

Variably coloured clays do not differ markedly in their mineral composition. Beidellite, a clay mineral belonging to the smectite group, is the main constituent, its content ranging up to 67 wt%. Other clay minerals present are kaolinite and illite. Roughly 15 wt% of the composition of the clays are attributed to quartz, iron minerals (goethite, rarely pyrite), carbonates (calcite and/or siderite concretions) and sulphates (gypsum). Only the black clay contains pronounced amounts of organic matter, 7.5 wt%. Dispersed calcium carbonate content does not exceed 1 wt%. Wiewióra, Wyrwicki (5) and Kłapyta, Żabiński (6) showed that beidellite present in the Poznań Series clays is Fe-rich and contains Ca^{2+} and Mg^{2+} as exchangeable cations.

The mineral composition of the varved clays from the Warsaw stagnant-lake was analysed by Myślińska (3, 4) and is given in Table 2.

Table 2. Mineral composition of varved clays from Zielonka (3, 4)

Layers	Main minerals	Subordinate minerals	Accessory minerals
Dark	clay minerals (hydromicas), iron oxides and hydroxides	quartz, carbonates, montmorillonite, kaolinite	feldspars (plagioclase), small amounts of glauconite and heavy minerals (garnet, hornblende, epidote, staurolite, kyanite, zircon, rutile, tourmaline)
Light	quartz, carbonates, clay minerals (mainly hydromicas)	iron oxides and hydroxides, montmorillonite, kaolinite	

Clay minerals (43–60 %), quartz and carbonates (up to 15–16 %) are the main components of the varved clays. Among clay minerals, illite prevails over chlorite, smectite and kaolinite. Quartz occurs in a fraction above 2 μm (3, 4). Light and dark layers contain the same minerals, however, their proportions are different (Table 2). The light layers contain more quartz and feldspars than the dark ones, due to the higher content of more coarse fractions. The dark layers have higher content of clay minerals and iron compounds. Moreover, light layers contain more carbonates (up to 6 %) as compared to the dark ones (up to 4 %).

Specific surface

Specific surface of the studied clays was determined by the method of sorption of methylene blue (7). This pigment is easily adsorbed by clay minerals from water solution. It is distributed both in interlayer and on the surface of grains. It is also absorbed by the organic matter. Specific surface of the clays from Zielonka is lower than that that one of the clays from Mszczonów. In varved clays, the light layers have values of specific surface about three times lower than the dark layers (Table 3). High values of specific surface of the Mszczonów clays are caused by the high content of clay minerals, especially smectite. The black clay records the highest value owing to the highest content of both clay minerals and organic matter. Apart from clay minerals, the light layers of the varved clays from Zielonka contain also coarse grains of dusty and sandy fraction. Dark layers are more fine-grained, contain more clay minerals, and therefore their specific surface is much higher. However, even the values of the specific surface of the black layers of the varved clays are lower than these ones of the Poznań Series clays. This is caused both by the content of clay minerals and by the nature of main clay mineral present in both types of clays. Contrary to beidellite, the interlayer space of illite (the main clay mineral present in black layers of varved clays) is closed for methylene blue. When considering specific surface, clays from Mszczonów can be classified as average mineral sorbents while the clays from Zielonka as poor mineral sorbents.

Table 3. Sorption capacity and specific surface of clays from Mszczonów and from Zielonka

Clay type		Sorption capacity of methylene blue (MBC) [g/100g soil]		Specific surface (S_t) [m^2/g]	
		direct measurement	measurement after 20 hours	direct measurement	measurement after 20 hours
Mszczonów	brown	10.52	12.06	220.36	252.61
	brownish-grey	15.40	16.34	322.40	342.23
	black	14.60	16.56	305.65	346.84
Zielonka	dark layers	4.23	4.44	88.55	92.89
	light layers	1.51	1.97	32.73	41.27

Fixation of Pb-cations by clays from Mszczonów and Zielonka

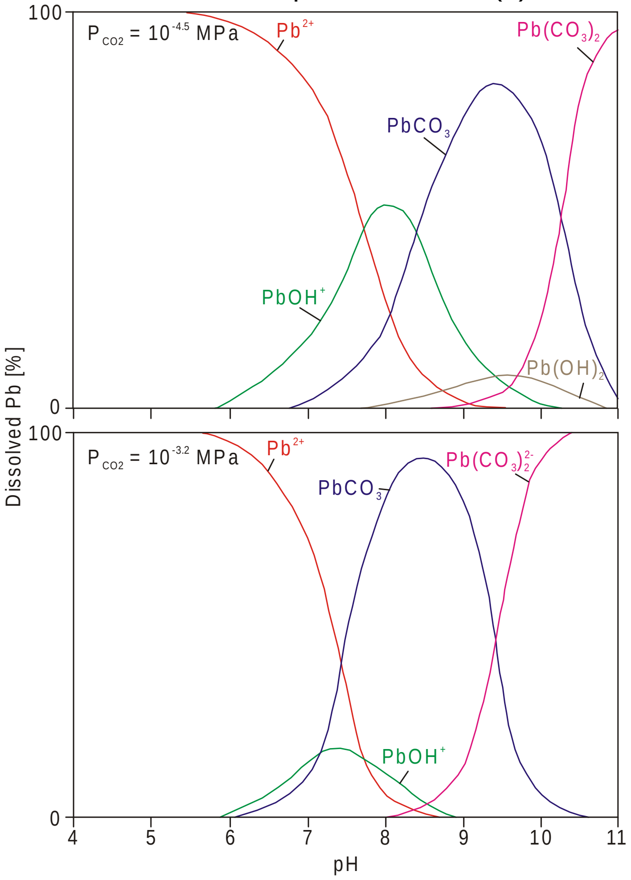
The value of fixation of Pb^{2+} cations from water solution of concentration 14.93 mg Pb/dm^3 was determined by the batch method (e.g. 8, 9). The solution was poured over dried clay samples in proportion 10 g $soil/dm^3$, and the suspension was shaken for 20 hours to ensure the equilibration of Pb-cations partitioning between the solid and the liquid. Then, the liquid and the solid were separated by centrifugation, and the Pb-concentration was measured in the liquid by AAS method. Distilled water was then poured over the treated soil, and the analytical procedure was repeated in order to determine the value of releasing the previously bound Pb by leaching. The maintenance of pH-value during the experiment is of great importance. Figure 1 shows the variation of the chemical form of Pb present in water solution along with the varying pH. Two series of tests were carried out: by spontaneously established pH (series A) and by pH fixed to about 6 using KOH (series B). Experiments showed that the ability to capture Pb-cations from solutions by black clay and by dark layers is very high and reaches 97 %. The amounts of Pb released from the analysed clays are low and do not exceed 1.7 %. However, the varved clay fixes Pb a little better, while the clay from Mszczonów releases slightly more Pb.

Table 4. Ability to capture and subsequent release of Pb-cations in clays from Mszczonów and from Zielonka

Clay type		Series A				Series B			
		Initial concentration Pb 14.95 ppm				Initial concentration Pb 14.76 ppm			
		Capturing		Releasing		Capturing		Releasing	
		pH	%	pH	%	pH	%	pH	%
Mszczonów	brown	2.7	32.02	5.3	1.37	5.8	63.35	5.4	0.60
	brownish-grey	2.7	38.28	5.4	1.64	5.8	77.94	5.4	0.90
	black	3.1	54.76	5.5	1.26	6.9	98.15	5.6	0.59
Zielonka	dark layers	5.3	96.85	5.5	0.51	5.8	97.72	5.7	0.16
	light layers	5.6	80.23	5.6	0.97	5.9	89.01	5.6	0.33

It is worth to stress that at fixed pH the value of capturing Pb-cations by varved clays is higher in spite of lower specific surface. Various processes may contribute to this phenomenon. As sorption mainly occurs on mineral surfaces, fixation of Pb should be positively correlated with the specific surface of a soil. The correlation does not exist in this case; one should, therefore, consider another process. The Zielonka clays are relatively rich in carbonates, and iron oxides and hydroxides. Precipitation of Pb-hydroxide and carbonate

Figure 1. Chemical forms of Pb occurring in water solution as a function of pH and P_{CO2} at the temperature 25 °C (9)



occurs just by pH near to 6, a value similar to that one was established spontaneously during the series A experiments. Therefore, the processes of precipitation and co-precipitation are likely responsible for fixation of Pb by the clays from Zielonka. This could be supported by the fact that the dark and light layers, having similar $CaCO_3$ contents, fix similar amounts of Pb in spite of a pronounced difference in contents of clay minerals, especially at pH close to 6 (Table 4). These facts imply that varved clays have buffering capabilities contributing to enhancement of fixation properties of these clays. Such properties of varved clays may be utilized in designing and constructing of linings of landfills in the case of a risk of generation of acid leachates. Due to an interaction with varved clays, an acid reaction of leachates would be minimized what in turn would result in an enhancement of fixation of heavy metals present in leachates. However, the interaction of acid solutions with mineral material rich in carbonates would result in their leaching, and therefore would cause changes in the structure and the strength of mineral lining of landfill. The more intense fixation of Pb cations by the clays from Zielonka may also be stimulated by the affinity of Pb to illite (10) which is the main clay mineral of this soil. The fixation of Pb in the clays from Mszczonów mainly occurs due to the sorption by beidellite. These clays do not contain carbonates and the processes of precipitation, if any, could be attributed only to the iron and manganese hydroxides.

Conclusions

1. Analysed samples of the Poznań Series clays have specific surface 250–350 m^2/g which is characteristic for fairly good mineral sorbents. Specific surface of the varved clays is much lower, 41–93 m^2/g. Nevertheless, this difference is not crucial for the value of fixation of Pb-cations from a solution.
2. Higher value of fixation of Pb-cations is shown by the varved clays, independently of the pH value of solutions. Due to the carbonate content these clays have buffering capabilities causing an increase of pH up to 6, favoring precipitation of slow-dissolving Pb-hydroxide.
3. The Poznań Series clays do not have such buffering capabilities and sorption is the main process responsible for fixation of Pb.
4. The experiments showed that the buffering capabilities of a soil are the most important factor controlling the fixation of Pb-cations from solutions. The presence and type of clay minerals is less important.
5. Similarly, releasing of Pb is lesser in soils having buffering capabilities – clays from Zielonka release only up to 1 % of previously bound cations.

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