The trial of immobilization amphoteric metals cations in clay-cement hydroisolation barriers

Agata Stempkowska

Faculty of Mining and Geoengineering, AGH University of Science and Technology, Al. Mickiewicza 30, PL-30059 Cracow, Poland

Corresponding author: stemp@agh.edu.pl

Abstract. One of the main problem of degraded post-industrial areas, preventing their introduction into the secondary economic cycle, is pollution of soil and the impact of these pollution on groundwaters. With the new European Union directives, managers are encouraged to find sound solution for these problems. The process of interaction of contaminated areas is complicated, and the transport of pollutants from the danger place to the usable underground aquifers levels passes through a series of stages of varied mileages. The article presents the possibilities of using ground binders to reduce the emission of ions from soil. The tests have shown that in the case of amphoteric metals, it is possible to accumulate almost 100% of the contamination using clay-cement suspensions.

1. Introduction
The post-industrial ground materials are considered as a waste according to the Polish decree of 27 April 2001 [1]. These sediments can contain a variable amount of inorganic pollutants (heavy, transitions and amphoteric metals) and organic ones [2-6]. In general, this materials have insufficient mechanical properties for Civil Engineering applications, such as hydroisolation barriers [7,8]. The treatment of sediments using hydraulic binders and granular corrector could improve the mechanical and physical characteristics [9-12].

Many experimental works have shown the feasibility of waste materials in civil engineering and have been explored by several authors in many different fields such as for sub-base course and road construction, [13] for manufacture of aggregates for concrete mixtures and also for cement, [14] for brick, [15] and glass or glass–ceramic materials [16,17], and hydroisolation barriers production [18].

The environmental compatibility is an important issue and the waste reuse can contribute to the pollutant release in the environment, especially when concrete is demolished or comes in contact with water [19, 20].

Some of the harmful elements have the amphoteric properties, which mean that they can behave as both the acid and base. Transition metals produce the inorganic compounds that show the strongest amphoteric properties. This property is very common for the hydroxides of the metals with a medium electronegativity. The amphoteric property of the compound is related to the ability of each element to create the anions and cations in the aqueous solution. As an example, the chromium ion, \( \text{Cr}^{3+} \) in the strong acidic solution forms the salt, \( \text{CrCl}_3 \) (in the presence of abundance of chloride ions forms a complex ion). In the weak acidic and neutral solution chromium ion precipitates as little soluble
hydroxide Cr(OH)$_3$. In that form chromium hydroxide in the alkalic solution dissolve to create chromium ions [Cr(OH)$_4$]$^-$ and has a tendency to migrate to the environment [21-23].

The researches show that clay-cement hydroisolation barriers have a very good immobilization properties for the metal cations. Despite the successful inhibition there is the risk that amphoteric metals in the strong basic solution can form compounds easily dissolved in water. This publication explains the relation between very strong basic clay-cement hydrobarriers and possibility to release the harmful metal cations to the environment. The article also considers the possibility of the forming the silicate compounds in the reaction with sodium silicate (commonly known as a waterglass), that is addend to the clay-cement hydrobarriers to control the hydratation process [24-26].

2. Sample preparation

The various samples of clay-cement binders were prepared using as a base two different types of the mineral compounds, the first one was Koniecpol clay and the second one was Belchatów clay, and the third type of samples the waste ashes were used. In this preparation as a filler the medium mesh size sand was imputed. Samples contain also 1% wt of sodium silicate (waterglass) type R145 with Mk=2.5.

The standards for hydroisolation slurry preparation indicate the quantity of sodium silicate should not exceed 1% of composition because the higher values of that has a negative impact on the rheological properties. However for academic purposes and comparison study, the samples with high concentration of sodium silicate and the samples without it were tested.

Amount and type of the compounds in the samples are presented in the Table 1, as well as the pH values for that type of mixtures.

| Sample | Weight [g] | Sodium silicate [g] | Cement [g] | Soil [g] | pH   |
|--------|------------|---------------------|------------|----------|------|
| P25.50.0 | 106.3      | 0                   | 53.2       | 53.2     | 13.03|
| P25.50.1 | 109.2      | 1.09                | 54.6       | 54.6     | 13.29|
| P25.50.2 | 105.6      | 2.11                | 52.8       | 52.8     | 13.44|
| P25.60.0 | 106.5      | 0                   | 63.9       | 42.6     | 13.27|
| P25.60.1 | 102.8      | 1.03                | 61.7       | 41.1     | 13.48|
| P25.60.2 | 108.1      | 2.16                | 64.9       | 43.2     | 13.48|
| P25.70.0 | 105.6      | 0                   | 73.9       | 31.7     | 13.37|
| P25.70.1 | 100.3      | 2.01                | 70.2       | 30.1     | 13.54|
| P25.70.2 | 109.2      | 2.18                | 76.4       | 32.8     | 13.25|
| K.50.0  | 107.0      | 0                   | 53.5       | 53.5     | 13.25|
| K.50.1  | 103.1      | 1.03                | 51.5       | 51.5     | 13.34|
| K.50.2  | 105.4      | 2.11                | 52.7       | 52.7     | 13.34|
| K.60.0  | 108.5      | 0                   | 65.1       | 43.4     | 13.15|
| K.60.1  | 109.2      | 1.09                | 65.5       | 43.7     | 13.58|
| K.60.2  | 106.7      | 2.13                | 64.0       | 42.7     | 13.43|
| K.70.0  | 108.0      | 0                   | 75.6       | 32.4     | 13.48|
| K.70.1  | 106.1      | 1.06                | 74.3       | 31.8     | 13.37|
| K.70.2  | 101.8      | 2.04                | 71.3       | 30.5     | 13.54|
| B.50.0  | 107.6      | 0                   | 53.8       | 53.8     | 13.43|
| B.50.1  | 102.3      | 1.02                | 51.2       | 51.2     | 13.25|
| B.50.2  | 105.1      | 2.10                | 52.6       | 52.5     | 13.34|
| B.60.0  | 104.3      | 0                   | 62.6       | 41.7     | 13.15|
| B.60.1  | 108.2      | 1.08                | 64.9       | 43.3     | 13.23|
| B.60.2  | 105.6      | 2.11                | 63.4       | 42.2     | 13.58|
| B.70.0  | 107.5      | 0                   | 75.3       | 32.2     | 13.25|
| B.70.1  | 106.3      | 1.06                | 74.4       | 31.9     | 13.15|
| B.70.2  | 102.8      | 2.06                | 71.9       | 30.8     | 13.23|
The slurry mixes were spiked with various amphoteric hydroxides of metals that are considered as a harmful after Minister of Environment act „Standards for soil and earth quality” published in 2001. For the purposes of this research, there elements were chosen: Lead II, Zinc (II) and Chromium (III). The standards for the those elements contents are show in Table 2.

The hydroxides of those elements were added to the slurry mixes in the quantity exceed twice the standards for its concentration in the soil, with the parameters as follows:

- Lead – 2000 mg/kg
- Zinc – 40 mg/kg
- Chromium – 1600 mg/kg

On account of slurry high pH factor, the hydroxides started dissolve and created aqua soluble complex ions such as: \([\text{Cr(OH)}_4]^-\), \([\text{Zn(OH)}_4]^{2-}\), \([\text{Pb(OH)}_4]^{2-}\). In this state investigated compounds should be successfully inhibited in clay-cement slurry.

| No. | Pollution | Grupa A | Grupa B | Grupa C |
|-----|-----------|---------|---------|---------|
|     | Depth [m] |         |         |         |
| 0-0.03 |         | 0-3-15 | >15     | 0-2     | 2-15    |
| Water infiltration [m/s] |
| up to | below | up to | below | up to | below |
| \(1\times10^{-7}\) | \(1\times10^{-7}\) | \(1\times10^{-7}\) | \(1\times10^{-7}\) |
| 1 | Chromium | 50 | 150 | 150 | 190 | 150 | 380 | 500 | 150 | 800 |
| 2 | Zinc | 1 | 4 | 5 | 6 | 4 | 10 | 15 | 6 | 20 |
| 3 | Lead | 50 | 100 | 100 | 200 | 100 | 200 | 600 | 200 | 1000 |

The samples were saturated with distilled water and extraction was allowed to occur for 48h. In the next step, the samples were filtered under the pressure of 1atm to obtain 100ml of extract. The filtration system has been shown on Figure 1.
3. Results
The physical and chemical characteristics of effluents are presented in Table 3 and 4 and concentration of metals cations are show the Figures 1-3. The trace amounts of the metal ions were observed in the samples. The percentage of the leaching of this ions to the soil is very low, therefore it is not significant for the study of cement-clay slurry as the hydroisolation barriers.

Table 3. The concentration of the selected metal cations in the effluents, determined by ASA method.

| Sample | Pb^{2+} [mg/l] | Zn^{2+} [mg/l] | Cr^{3+} [mg/l] |
|--------|----------------|----------------|----------------|
| P25.50.0 | 0.083          | 0.0033         | 0.433          |
| P25.50.1 | 0.071          | 0.0027         | 0.333          |
| P25.50.2 | 0.071          | 0.0076         | 0.322          |
| P25.60.0 | 0.073          | 0.0029         | 0.286          |
| P25.60.1 | 0.068          | 0.0012         | 0.296          |
| P25.60.2 | 0.067          | 0.0087         | 0.222          |
| P25.70.0 | 0.047          | 0.0031         | 0.271          |
| P25.70.1 | 0.038          | 0.0045         | 0.231          |
| P25.70.2 | 0.053          | 0.0012         | 0.246          |
| K.50.0  | 0.135          | 0.0045         | 0.377          |
| K.50.1  | 0.081          | 0.0023         | 0.361          |
| K.50.2  | 0.083          | 0.0031         | 0.343          |
| K.60.0  | 0.085          | 0.0022         | 0.327          |
| K.60.1  | 0.056          | 0.0056         | 0.276          |
| K.60.2  | 0.066          | 0.0037         | 0.273          |
| K.70.0  | 0.082          | 0.0045         | 0.254          |
Table 2. Amphoteric metals leaching test, from samples with 25% ash content.

| Sample | Pb^2+ | Zn^2+ | Cr^3+ |
|--------|-------|-------|-------|
| P5-50.0| 0.45  | 0.35  | 0.30  |
| P5-50.1| 0.40  | 0.30  | 0.25  |
| P5-50.2| 0.35  | 0.25  | 0.20  |
| P5-50.0| 0.40  | 0.30  | 0.25  |
| P5-50.1| 0.35  | 0.25  | 0.20  |
| P5-50.2| 0.30  | 0.20  | 0.15  |

Figures below (2-4) show the relationship between cation charge and concentrations of elements in effluent after washing. The higher concentration value of chromium ions be caused by different ions migration mechanism.

The maximum concentration is 0.45 mg/L which is considered as trace quality.

Figure 2. Amphoteric metals leaching test, from samples with 25% ash content.

Figure 3. Amphoteric metals leaching test, from samples based on Koniecpol clay.
Figure 4. Amphoteric metals leaching test, from samples based on Belchatów clay.

The results show negative dependence between cations leaching and the compositions of slurry mixtures samples. The data show no relation between ions migrations and the percentage of sodium silicate in the composition of binder. The observation was made that the type of materials (like clays or ashes) used in binder’s composition should not affect the accumulation of harmful elements.

3.1. Quality precipitation of silicates of the selected amphoteric metal cations.

The experiment was carried to confirm the prediction about the possibility that certain amphoteric metal cations may precipitate as insoluble and stable salts in strong alkaline solution. To each solution of soluble salts of the selected metal cations, the sodium silicate was addend, to observe if the precipitate will form. The experiment was conducted in the following conditions:

- the concentration of 20% of the following salts PbNO3, ZnCl2 and CrCl3
- the sodium silicate Mk = 2.5
- reagents in the proportion 1:1

To accelerate the rate of reaction the samples were put in the laboratory drier at 80 degree Celsius. All samples formed the insoluble precipitant as follows:

- monohydrate lead II silicate PbO·SiO2·H2O (white crystals)
- monohydrate zinc II silicate ZnO·SiO2·H2O (blue opalescent gelatinous precipitate)
- monohydrate chromium III silicate Cr2O3·SiO2·H2O (pale green crystals)

Additional validation of creating unsoluble chemical bonds were obtained by SEM images with EDS analysis (figure 5-7). The EDS analysis shows that transition metals content is significantly increased, while the contents of impurity elements (Zn, Cr, Pb). These metals are immobilized in cement phases (long tiny crystals).

Figure 5. SEM and EDS analysis of sample with 25% ash content.
Figure 6. SEM and EDS analysis of sample based on Koniecpol clay.

Figure 7. SEM and EDS analysis of sample based on Belchatów clay.

4. Conclusions

1. The cement-clay barriers have very good properties to retain the metal cations, as well as amphoteric metal cations, in their structure. The amphoteric metals in the strong alkaline solution undergo complex reactions and may create soluble compounds.

2. The trace amount of the metal cations were observed in the effluents, which can suggest that they do not dissociate from cement-clay binders, especially in the case of zinc.

3. The use of the sodium silicate as the additive in the cement-clay binders, improves retention of the harmful metal cations. The silicates form with lead, chromium and zinc.

4. The higher quantities of sodium silicate added to the cement-clay binders will probably retain the migration of metal cations, however the quantity of sodium silicate use as an additive to the cement-clay binders is restricted by decay the reological properties of those binders.

References

[1] Prawo ochrony środowiska (Dz.U. Nr 62, poz. 627)
http://prawo.sejm.gov.pl/isap.nsf/DocDetails.xsp?id=WDU20010620627

[2] Andersen S, Ødegård S and Seip H M 1994 Ecol. Eng. 3 pp 245-253

[3] Malviya R and Chaudhary R J 2006 J. Mater. Cycles Waste 8 pp78-87

[4] Seip H M, Pawalowski L and Sullivan T 1994 Ecol. Eng. 3 pp 205-206

[5] Wuana R A, Okieimen F E. 2011, ISRN Ecol. Article ID 402647, http://dx.doi.org/10.5402/2011/402647

[6] Chibuike G U, Obiora S C 2014 Applied and Environmental Soil Science Article ID 752708, http://dx.doi.org/10.1155/2014/752708
[7] Wang L K, Hung Y-T, Shammas N K 2010 Handbook of Advanced Industrial and Hazardous Wastes Treatment, CRC Press
[8] Spence W P, Kultermann E 2017 Construction Materials, Methods and Techniques, CENGAGE Learning
[9] Wójcik Ł, Izak P, Mastalska-Popławska J, Gajek M, 2015 J.Phys. Conference Series, 790, , pp 1–7
[10] Stempkowska A, Wójcik Ł, Izak P, 2011, Materiały Ceramiczne = Ceramic Materials / Polskie Towarzystwo Ceramiczne, Kraków, 6, pp. 278–282
[11] Wójcik Ł, Izak P, Kuś R, 2009, Materiały Ceramiczne = Ceramic Materials / Polskie Towarzystwo Ceramiczne, Kraków, 61, pp 27-30
[12] Izak P, Wójcik Ł, Słowikowski D, 2015 Materiały Ceramiczne = Ceramic Materials / Polskie Towarzystwo Ceramiczne, Kraków, 67, pp 158-163
[13] Kasmi A, Abriak N E, Benzerzou M et al. 2017, J. Mater. Cycles Waste Manag. 19, https://doi.org/10.1007/s10163-016-0529-5
[14] Dalton J L, Gardner K H, Seager T P, Weimer M I, Spear J C M, Magee B J 2004 Resour. Conserv. Recycl. 41 pp 227–241
[15] Collivignarelli M C, Abbà A, Sortini S. et al. 2017 J. Mater. Cycles Waste Manag. 19 p 1374 https://doi.org/10.1007/s10163-016-0523
[16] Andreola F, Barbieri L, Corradi A, Lancellotti I, Manfredini T, 2001, J. Mater. Sci. 36 pp 4869–4873
[17] Monteiro R C C, Figueiredo C F, Alendouro M S, Ferro M C, Davim E J R, Fernandes M H V 2008 Waste Manag. 28 pp 1119–1125 doi: 10.1016/j.wasman.2007.05.004
[18] Stempkowska A, Wójcik Ł, Izak P, Staszewska M, Mastalska-Popławska J 2018 IOP Conf. Ser.: Mater. Sci. Eng. 427 p 1
[19] Tang P, Florea M V A, Spiesz P, Brouwers H J H 2015 Construct Build Mater. 83 pp 77–94. doi: 10.1016/j.conbuildmat.2015.02.033
[20] Boghetich G, Liberti L, Notarnicola M, Palma M, Petruzzielli D 2005 Waste Manag. Res. 23 pp 57–61 doi: 10.1177/0734242X05050101
[21] Stempkowska A, Izak P, Mastalska-Popławska J 2017 Gospodarka Surowcami Mineralnymi = Mineral Resources Management 33 pp 139–149
[22] Lafhaj Z, Samara M, Agostini F, Boucard L, Skoczylas F, Depelsenaire G 2007 Constr. Build Mater. 148 pp 606–612
[23] Varshney S, Jain P, Srivastava S J 2017 Mater. Cycles Waste Manag. https://doi.org/10.1007/s10163-016-0539-3
[24] Zhang H, He P J, Shao L M. et al. 2008 J. Mater. Cycles Waste Manag. https://doi.org/10.1007/s10163-007-0191
[25] Wang D, Liu D, Tao L et al. 2017 J. Mater. Cycles Waste Manag. https://doi.org/10.1007/s10163-016-0508-x
[26] Bashir M J K, Aziz H A, Yusoff M S, 2011 J. Hazard. Mater. 186 pp 92–102