Scientific Essentials of Developing Geochemical Sorption Barriers against Lead Based on Aminoplastic-Ground Composite Materials

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Received November 10, 2014

Abstract—A procedure was developed to obtain a lead-protective sorption barrier based of sandy grounds modified with an uncatalyzed aminoplastic oligomer. The optimum component proportions in the ground composite were found in experiments. It was shown that the sorptive capacity of modified sandy ground considerably exceeded that of montmorillonite. The composite of this formulation is capable of adsorbing up to 500 mg of lead per 1 cm³ with loose packing with no compacting.

Keywords: ground composites, lead, sorption, protective barrier, montmorillonite

DOI: 10.3103/S0145875215020076

INTRODUCTION

Rapid urbanization and industrial development result in global transformations of the environment, including the growth of the amounts of solid wastes, liquid effluents, dusts, and gas leaks. In view of this, the problem of the storage of great amounts of toxic and poisonous substances in various facilities for burying the wastes is quite acute (Bartolomei et al., 2004; Informatsiya..., 2006; Problemy ekologii..., 1992).

In Russia, locally available grounds with low filtration coefficients are in common usage in constructing the storage facilities for waste burial. In the absence of ground as such, the current sanitary and building regulations (nos. 2.1.7.1038-01 and 2.01.28-85, respectively) require the formation of special coverings of ~10⁻⁵–10⁻⁸ cm/s. Nevertheless, it is evident that the improvement of protective barriers requires an integrated approach including not only the prevention of filtration but also the fixation of toxicants in an additional layer of a ground composite with a high sorptive capacity, i.e., with a double-layered protective shield (Fig. 1).

Attempts to transform ground to improve its sorptive capacity are made constantly. In view of this, studies on the optimization of compositions of bentonite–quartz mixtures deserve attention (Oblivantsev, 2007), especially the composite protective shields that are constructed on the basis of oxalate–alumosilicate gels (Buchatskii et al., 1976; Zaschita podzemnykh..., 1992; Sergeev, 2001). A number of reports on the sorption characteristics for heavy metals considered various modified and unmodified grounds (Bespamyatnov and Krotov, 1985; Brazhnik, 2007; Sergeev et al., 1999), natural (Gudushauri and Ugrekhilidze, 2006), sapropels, humic acids, and brown coals (Nguyen, 2006). However, many questions remain unanswered, including the secondary desorption of toxicants from a sorptive composite or ground.

A special field is formed of studies on the immobilization of heavy metals at burial sites, or so-called ecoconcreting (Knat’ko et al., 2001). However, the problems of ecoconcrete resistance against corrosive media and of the secondary mobilization of toxicants require additional studies.

A wall construction was presented recently in the United States for cleansing groundwaters against chromates, nitrates, and organochlorine compounds based on zero-valent metals (Evaluation..., 1998).

Fig. 1. The scheme of a double-layered protective shield.
This construction shows a limited sorptive capacity as well.

It is known that most industrial wastes are characterized by acid or subacid media that are favorable for the low-temperature polymerization of aminoplastics (Rodkina and Samarin, 2009). Hence, ground composites with an added non-catalyzed carbamide resin might be promising for preventing the secondary mobilization of toxicants. Our studies aimed at developing the optimum formulation for designing a double-layered protective shield consisting of the lower poorly-filtering layer (clay soil) and the upper sorptive layer of a ground composite with added non-catalyzed carbamide resin (Fig. 1).

To form a filtering sorptive layer, we examined the properties of ground composites that consist of sand of different grain sizes (1–2, 0.5–1, and 0.25–0.5 mm) and of uncatalyzed carbamide resin.

As a base for preparing the ground composites, sand (alQIII) collected from the depth of 2–10 m at the different grain sizes (1–2, 0.5–1, and 0.25–0.5 mm) were used (the data by Fomicheva), 724 m²/g specific surface, low-level cell, a cation exchange capacity of 1.26 mg-equiv/g, and numerous fine cavities to which some selvages of montmorillonite are associated. The density of mineral grains amounts to 2.65 g/cm³ and the hygroscopic moisture is 0.3% or less. The sand is not salinized: the solid residual of the aqueous extract amounts to 0.03%.

After the removal of autigenic films by a thrice-repeated treatment with 1.5% HCl, the sand fractions of 1–2 mm (coarse-grained), 0.5–1 mm (large-grained), and 0.25–0.5 mm (medium-grained) were separated using the sieving procedure.

The used M-3 carbamide resin is characterized by 1.184 g/cm³ density at 20°C, conventional viscosity of 4.5 (at 20 ± 0.5°C with a VZ-1 viscometer with a 5.4 mm nozzle diameter), and an 0.4% content of free formaldehyde.

Lead was selected as a toxicant because this metal is toxic to living organisms at any concentration in terms of affecting normal vital activities.

**Characterization of the treated ground and materials.** To form the poorly-filtering layer in the experiments, kil clay (K₈s) collected from a section in the Bodrak River valley (Bakhchisarai district, Crimea) was used. The clay contained 95.8% of montmorillonite, 0.7% of andesine, 3.0% of calcite, and 0.4% of quartz. The fraction of ≤5 μm grain size containing ≥98% of montmorillonite was separated from the natural clay by decantation (the samples were prepared by E.N. Fomicheva). The structural formula of montmorillonite calculated by the data of the bulk chemical analysis:

\[
\text{H}_2\text{O}^-(\text{Na, Ca})_{0.54}(\text{Al}_{1.35}\text{Fe}^{3+}_{0.14}\text{Fe}^{2+}_{0.01}\text{Mg}_{0.51}\text{Ti}_{0.01})\text{(Si}_{13.97}\text{Al}_{0.03})\text{O}_{9.91}(\text{OH})_{2.19}
\]

allows one to consider the prepared sample among high-charged Al-montmorillonites according to Drits (sand, montmorillonite, and carbamide resin) were prepared by E.N. Fomicheva). The structural formula of montmorillonite calculated by the data of the bulk chemical analysis:

\[
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\]

after a three-repeated treatment with 1.5% HCl, the sand fractions of 1–2 mm (coarse-grained), 0.5–1 mm (large-grained), and 0.25–0.5 mm (medium-grained) were separated using the sieving procedure.

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The procedure of the experiments. To evaluate the efficiency of the double-layered protective shield, first, the sorptive capacity and peculiarities of the interactions with lead for each component of the system (sand, montmorillonite, and carbamide resin) were studied (Rodkina, 2004; Rodkina and Samarin, 2009) and second, the efficiency of the proposed ground complex (the sorption barrier) was examined.

The ground composites were prepared to provide the maximum infilling of the space between the sand grains by carbamide resin with no forced compaction of the samples. Therefore, the following volume proportions of sand and aminoplastic were used: 1 : 1 in view of the 0.52 coefficient of pore filling for a simple cubic cell; 1.5 : 1 according to the model of random close packing for spherical grains with 0.61 coefficient of filling; 2 : 1 according to the 0.68 filling coefficient of a body-centered cubic cell, and 3 : 1 according to the 0.47 filling coefficient of a face-centered cubic cell for medium-grained sand.

The prepared ground composites, with no preliminary packing, were placed into the filtering set (Fig. 2). The height and diameter of the sample amounted to 16 and 8 cm, respectively. The physical characteristics of the composites are given in Table 1.

A solution of lead nitrate with a 0.0992 N concentration and pH 2.0 was filtered through the samples. This value is equal to 333 times the maximum allowable concentration of lead for soil (30.0 mg/kg (Bespamyatnov and Krotov, 1985)) because this lead concentration (10 g/L) is reached at local areas of waste burial sites (Mikhailov, 2003).

The experiments were carried out at three different rates of filtration (10⁻⁶, 10⁻⁵, and 10⁻⁴ cm/s) and an I = 10 head gradient. The rates were determined using paper filters treated with 1 N NH₄Cl to prevent the
separation of formaldehyde and placed at the foot of the casing.

After finishing the experiment, the ground composites were treated by stage extraction using the procedures of Tessier (Tessier, 1979), The Standards, Measures, and Tests (BCR) of the European Union (Bruder–Hubscher et al., 2002), and GOST R 50686–94.

To evaluate the sorptive capacity of the double-layered protective shield, experiments on using montmorillonite as a low-permeability layer with a 3-cm thickness were performed. The filtration rate in these experiments amounted to about $8 \times 10^{-4}$ cm/s.

For a single analysis of the filtrate, an aliquot was taken of a volume that was equal to that of the resin in the given sample (here and below, the pore volume), in which the pH value and concentrations of lead and formaldehyde were determined. The concentration of Pb$^{2+}$ ions in the solution was determined by atomic absorption (PND F 14.1:2.21-95 environmental normative document developed by the KORTEK Co., Moscow) and by inversion voltammetry (PND F 14.1:2.:149, developed by the VOLTA Co., St. Petersburg). The Pb$^{2+}$ content in the samples was determined using x-ray fluorescence according to the M049-P/04 procedure by Spektron Co., St. Petersburg. The content of formaldehyde in the filtrate was determined with urotropine (Vorob’eva, 1998). The amount of lead on the filters was determined by Krupskii and Aleksandrova (GOST R 50686-94). The quantity of adsorbed lead as calculated by the difference of concentrations in the initial and equilibrium solutions and that determined by the analysis of the solid phase were different by 3% or less.

LEAD SORPTION BY GROUND COMPOSITES AND COMPONENTS OF A MULTILAYERED PROTECTIVE SHIELD

Previously, the authors proved in experiments that quartz sand that is cleaned of natural autigenic films adsorbed an insignificant amount of lead (Rodkina et al., 2009).

**Sorption of lead by montmorillonite.** With the increase of pH values of the contacting solution from 3.0 to 5.0, a considerable increase of the amount of adsorbed lead is seen: 19 mg/g at pH 3.0, 190 mg/g at pH 4.0, and 250 mg/g at pH 5.0 (Rodkina, 2004). The lead sorption at pH 3.0 and 4.0 is described adequately by the Langmuir isotherm, which indicates, on the one hand, uniform filling of adsorption sites of the surface of montmorillonite, and, on the other hand, a decrease of the distribution coefficient, viz., the ratio of the amount of an adsorbed substance and its content in the outer electrolyte with the infilling of the surface (Sposito, 1984). The isotherm is of a feebly-marked S-shape, which is characteristic for polylayer adsorption under which polynuclear associations of adsorbate are formed on the adsorbent surface (Sposito, 1984). The proportion of the nonspecific (volume) sorption of lead is almost independent of the metal concentration in the outer electrolyte (from $5.0 \times 10^{-3}$ to $2.4 \times 10^{-1}$ mg-equiv/mL), decreasing from 29 to 25% of the total amount of adsorbable lead with a pH increase from 3.0 to 5.0 in the filtering solution, yet increasing in quantity (from 5.5 mg/g at pH 3.0 to 44.5 mg/g at pH 5.0).

During lead desorption by the Tessier method, regardless of the pH value of sorption, the total quantity of extracted lead amounts to 90% or more (Rodkina, 2004).

**Sorption of lead with carbamide resin.** Under the interaction with Pb(NO$_3$)$_2$ solution, the polycondensation of carbamide resin is accompanied by the removal of lead from the contacting solution. In the course of direct potentiometric titration of a Pb(NO$_3$)$_2$ solution with the resin, the oligomer polycondensation takes place within the 2–5 pH range; in this case, all of the lead is adsorbed from the solution, even at pH 2.2 (52.66 mg Pb per g of resin). For back titration,

Table 1. The physical characteristics of the ground composites used in the experiments

<table>
<thead>
<tr>
<th>Composite formulation: resin/sand</th>
<th>Density, g/cm$^3$</th>
<th>Porosity, %</th>
<th>Moisture, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1/1</td>
<td>1.92</td>
<td>33</td>
<td>10</td>
</tr>
<tr>
<td>1/1.5</td>
<td>2.06</td>
<td>28</td>
<td>8</td>
</tr>
<tr>
<td>1/2</td>
<td>2.16</td>
<td>23</td>
<td>6</td>
</tr>
<tr>
<td>1/3</td>
<td>2.28</td>
<td>28</td>
<td>5</td>
</tr>
</tbody>
</table>
the resin polycondensation proceeds within the 8–5 pH range and the quantity of the adsorbed lead amounts to 61.3 mg/g. In this case, the complete immobilization of the metal is attained and lead is not extracted, even under much more rigid conditions of treatment, including Tamm’s reactant at pH 3.3 and a mixture of HF and HClO₄ (Tessier et al., 1979); with hydrogen peroxide, ammonium acetate, and nitric acid (Bruder-Hubscher et al., 2002); and with acetate–ammonium buffer at pH 4.8 (GOST P 50686-94). This is caused by the formation of the stable bond between lead ions and amide radicals, either immediately or by way of the CH₂ group (Fig. 3). This assumption is confirmed by the fact that the IR spectra of the polymer that was cured in the presence of lead cations show no reflex at 906 cm⁻¹ that conforms to the oscillations of the CONH group, which is characteristic of a pure polymer (Rodkina and Samarin, 2009).

**Sorption of lead with sand–aminoplastic composites.**

The sorptive capacity of all of the examined ground composites lies within the range from 50 to 594 mg/cm² of a sample and depends on the rate of filtration, the grain size of the sand, and the quality of the package of modified grounds.

The ground composites based of coarse-grained sand (Fig. 4) are characterized by the regular growth of the amount of adsorbed lead with an increase of the resin content in the composite and of the time of the composite interaction with the filtrate controlled by the filtration coefficient: from 50 mg/cm³ at 1 : 2 component ratio and \( K_f \sim 1 \times 10^{-4} \) cm/s to 166 mg/cm³ at 1 : 1 component ratio and \( K_f \sim 1 \times 10^{-6} \) cm/s.

For the ground composites based on medium-grained sand (Fig. 5), all the examined formulations are also characterized by the growth of the amount of adsorbed lead with the increase of the time of the composite interaction with the filtrate: from 351 mg/cm³ at \( K_f \sim 1 \times 10^{-4} \) cm/s to 496 mg/cm³ at \( K_f \sim 1 \times 10^{-6} \) cm/s, i.e., 2.5- to 3.5-fold as high as the lead sorption by composites of other formulations. However, the maximum of the sorptive capacity belongs to the composites of 1 : 1.5 resin–sand ratio.

A similar view is also seen for the composites based on large-grained sand (Fig. 6). The maximum of lead sorption conforms to 1 : 1.5 and 1 : 2 resin–sand ratios (from 253 to 314 mg/cm³), with a slight trend to an increase (for ~ 10%) in more permeable samples of \( K_f \sim 1 \times 10^{-4} \) cm/s. This is caused by the formation of large (to 1 cm) resin aggregates covered with polymer film; hence, the further curing of resin in the central part of an aggregate proceeds owing to the diffusion of hydrogen ions through the surface film with no participation of lead ions.

Thus, the best material to form a sorption barrier against lead is the ground composite based on medium-grained sand at a 1 : 1.5 resin–sand ratio. Just the proportion of the components as such is favorable for uniform polymerization of the resin over the entire volume of the sand composite. This resulted in the appearance of quite large (to 2 cm in diameter) vitreous aggregates of sand cemented by polymerized aminoplastic, which is confirmed by binocular microscopy. In this case, the lower the rate of filtration is, the larger the aggregates are, which is caused by the increase of the time of interaction. Any variations in the resin content result in a decrease of the sorptive capacity of the composites.

The stage extraction of lead from the samples of composites after the filtration of lead nitrate solutions showed the complete immobilization of the metal, as in the experiments on pure resin. One must also note...
that the treatment of the filters with 1 N ammonium chloride is an effective way to remove formaldehyde from the filtrate.

In general, the results of the analyses of all of the ground composites show that a decrease of the sand grain size in the composites should allow one to decrease the amount of resin; in this case, the sorptive capacity of modified grounds tends to increase. This might be caused by the higher wettability of medium-grained compared to large- and coarse-grained sands; respectively, the lead filtration as well proceeds more uniformly over the ground volume.

**Sorption of lead by a double-layered barrier.** The additional sorption of the metal on montmorillonite (~3 cm height and 8 cm diameter of the mineral layer in the filtration set; 13 cm height and 8 cm diameter of the composite layer) resulted in an increase of the amount of adsorbed lead by 30–40 mg/cm³ (by 10% or less) compared to individual samples of composites. This is caused by the buffering effect of montmorillonite during its interaction with an acid solution and by its sorptive capacity (Table 2). Respectively, the secondary contamination of the environment under long-term filtration owing to lead desorption from montmorillonite is also moderate.

Thus, carbamide resins may be recommended for use in environmental protection purposes in the following ways:

1. to produce reactive (immobilizing and sorptive) ground composites in multilayered protective systems;
2. to form low-filtering shields of high sorptive capacity based on clay grounds mixed with a carbamide resin;
3. for emergency containment of contaminated permeable soils by injection of a carbamide resin that is poorly-catalyzed, e.g., by an ammonium chloride solution at a concentration that causes an increase in the resin viscosity up to the non-escaping level during incomplete curing of the resin.

**CONCLUSIONS**

1. Based on the experimental data, a fundamentally new double-layered structure for a protective shield is proposed. The structure includes a low-permeability layer of small thickness that controls the rate of filtration and a relatively permeable sorptive layer (i.e., the sorptive barrier). As a barrier as such, a ground composite on carbamide–sand formulation is recommended.

<table>
<thead>
<tr>
<th>Conditions of the experiment</th>
<th>Resin–sand ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1 : 2</td>
</tr>
<tr>
<td>grain size of sand, mm</td>
<td>0.25–0.5</td>
</tr>
<tr>
<td>Pb concentration, mg/cm³</td>
<td>41.94</td>
</tr>
</tbody>
</table>

**Fig. 5.** The quantity of lead adsorbed by ground composites based on medium-grained sand at different filtration rates. The figures over the diagrams are the resin–sand ratios.

**Fig. 6.** The quantity of lead adsorbed by ground composites based on large-grained sand at different filtration rates. The figures over the diagrams are the resin–sand ratios.
2. The optimum formulation of a ground composite that is able to noticeably improve the efficiency of a protective shield within the combination of common-used techniques was obtained (1: 1.5 resin—sand ratio; 10⁻⁶ cm/s filtration rate; and medium-grained sand).

3. Carbamide resin is an efficient modifier when developing artificial sorptive barriers based on filtering ground composites owing to high sorptive capacity and the complete immobilizing effect for lead.

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Translated by A. Rylova