Application of Demolition Products of Buildings and Structures to Ensure Reduction of Concentration of Heavy Metal Ions in Man-Made Soils at Construction Facilities

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Abstract. The article considers the problem of soil contamination in St. Petersburg with heavy metals. It has been shown that the degree of contamination is such that soils lose their ability to self-clean and can be attributed to technologically modified soils. Geochemical barriers are required to reduce the concentration of heavy metals. Based on the principle of A.I. Perelman, it is shown that the most promising wastes of the construction industry for use in geochemical barriers are silicate-containing wastes from demolition of buildings and structures. Capacity of heavy concrete and aerated concrete in relation to some heavy metals is determined in the work. The absence of selectivity of wastes to various heavy metals is shown. The formula for calculation of the life of the geochemical barrier taking into account its size, capacity and amount of contamination coming with melted and rain drains is proposed. The life of the geochemical barrier is calculated to prevent the migration of iron ions in the form of a railway embankment, which amounted to 47 years, provided that granite crushed stone is completely replaced by heavy concrete.

1. Introduction

The relevance of the work is related to the need to carry out construction and economic activities taking into account the increase in the "level of environmental safety and conservation of natural systems" (the state program of the Russian Federation "Environmental Protection" for 2012 - 2020 years). Heavy metals to pollution of construction and economic facilities. In 80% of cases, in Russian cities there are exceedances of their permissible concentrations in soils. Therefore, the search for construction facilities and their wastes, the use of which will lead to the detoxification of heavy metal ions, is relevant for construction and economic activities.

The active anthropogenic effect on the lithosphere in large cities and urban agglomerations forms deposits called man-made soils. Soils on the territory of cities can be attributed to technogenically changed soils of natural occurrence (GOST 25100-2011), since they were subjected to anthropogenic influence at the place of occurrence. Pollution of man-made soils of St. Petersburg today is one of the geochemical problems of the city, since according to Rospotrebnadzor (State report "On the state of sanitary and epidemiological well-being of the population in the Russian Federation in 2018") more than 3 times the average Russian level of soil pollution with chemicals in the Primorsky Territory (40.4% of samples), Novgorod region (28.6%), St. Petersburg (26.9%), Murmansk region (23.4%), Kirov region (21.3%), Chelyabinsk region (20.5%), Trans-Baikal Territory (20.1%), Sverdlovsk Region (20.0%). Thus, St. Petersburg is one of the five regions with the highest level of soil pollution with chemicals. In terms of cadmium content, Petersburg is in third place in Russia (after North Ossetia and the Sverdlovsk region).
According to the Russian Geocological Center (RGEC) in St. Petersburg, their content in man-made soil almost everywhere exceeds the MPC, in places - several dozen times (Table 1).

| Elements | Total samples including tests | < MPC % | 1-2 MPC % | 2-5 MPC % | > 5 MPC % |
|----------|-------------------------------|---------|-----------|-----------|-----------|
| Total in St. Petersburg | | | | | |
| Lead | 885 | 876 | 99 | 9 | 1 | - | - | - | - |
| Zinc | 885 | 266 | 30 | 207 | 23 | 255 | 29 | 157 | 18 |
| Cadmium | 885 | 442 | 50 | 164 | 19 | 153 | 17 | 126 | 14 |
| Arsenic | 885 | 343 | 39 | 220 | 24 | 166 | 19 | 156 | 18 |
| Including: Recreational areas | | | | | |
| Lead | 79 | 79 | 100 | - | - | - | - | - | - |
| Zinc | 79 | 5 | 6 | 22 | 28 | 37 | 47 | 15 | 19 |
| Cadmium | 79 | 59 | 75 | 11 | 14 | 9 | 11 | - | - |
| Arsenic | 79 | 19 | 24 | 33 | 42 | 14 | 18 | 13 | 16 |
| Residential zones | | | | | |
| Lead | 288 | 288 | 100 | - | - | - | - | - | - |
| Zinc | 288 | 122 | 42 | 80 | 28 | 70 | 24 | 16 | 6 |
| Cadmium | 288 | 162 | 56 | 79 | 27 | 34 | 12 | 13 | 5 |
| Arsenic | 288 | 121 | 42 | 98 | 34 | 43 | 15 | 26 | 9 |
| Industrial zones | | | | | |
| Lead | 200 | 193 | 97 | 4 | 2 | 3 | 1 | - | - |
| Zinc | 200 | 15 | 7 | 29 | 14 | 77 | 39 | 79 | 40 |
| Cadmium | 200 | 36 | 18 | 29 | 15 | 61 | 30 | 74 | 37 |
| Arsenic | 200 | 26 | 13 | 44 | 22 | 58 | 29 | 72 | 36 |

2. Material and methods
The basis of technological solutions using the products of demolition of buildings and structures in geochemical barriers may be the principle of A.I. Perelman, who, considering geochemical barriers, argued that if one of the reagents is present in an amount insufficient for the implementation of all possible reactions, then only those reactions are carried out that are characterized by maximum chemical affinity [1-4]. Based on this principle, it can be argued that in order to reduce the negative effect of heavy metal ions on man-made soils, it is necessary to introduce substances into the man-made geo-environment that would ensure the most negative change in Gibbs energy during the reaction with the pollutant [5-8].

The capacity of silicate-containing waste is estimated by the ability of a unit mass of waste to bind (neutralize) a unit mass of a pollutant (for example, heavy metal ions).

The atomic absorption method was used in determining the waste capacity with respect to heavy metal ions. Control of the degree of purification of the sample from heavy metal ions was carried out on an atomic absorption spectrometer (AAC) from Perkin Elmer (USA) model PE-305. It is designed to determine the concentration by absorption by pairs of a monochromatic light element whose wavelength corresponds to the center of the absorption line. AAS Re-305 allows you to determine more than 30 elements in the conditions of analytical and workshop production laboratories for solving the problems of ecology, agrochemistry, biology, medicine, geology, metallurgy, chemistry, scientific research. Stabilized emitters - hollow cathode lamps are used as light source in AAS. Such a light source produces narrow and bright spectral lines of determined elements with stable intensity. To isolate spectral lines, a monochromator, a rotating diffraction grating and a photoelectric photomultiplier are used in the PE-
305. The hollow cathode lamp is usually designed for one element, it indicates the analytical wavelength and discharge current, which during analysis should not exceed the maximum value. The gas burners have a slotted structure which increases the length of the absorption layer and thereby increases the sensitivity of the element determination. The burner is equipped with a solution sprayer with a spray rate controller, which is 8... 10 ml/min. The spray rate is selected to increase the sensitivity of the device. In AAS, the flame of a combustible gas mixture of acetylene-air was used.

Technical data:
Detection limits - 10-6... 10-7% (mass)
The expressiveness of the definition is 5... 10 s
Reproducibility - 0.5... 2%
Wavelength setting error - ±0.5 nm

Table 2. Shows detection limits and wavelengths for the analysed metals.

| Metal     | Wavelength, nm | Manganese | Iron   | Nickel | Chrome |
|-----------|----------------|-----------|--------|--------|--------|
| Detection limit, mg/l | 0.01 | 0.03 | 0.04 | 0.05 |

At the end of the adjustment, the absorption of a series of calibration solutions of the determined metal is measured, which are prepared from standard solutions (GSO series) and calibration graphs of absorption dependence on concentration are plotted (Fig.2.1). The analysed solution is then measured and the metal concentration in the filtrate is determined from the calibration schedule.

The quantitative characteristic of the man-made geochemical barrier is the gradient of the barrier, which is calculated using the formula 1:

$$G = \frac{m_1 - m_2}{L}$$  

where: $m_1$ – numerical expression of contamination index in migratory flow (e.g. concentration of heavy metal ions in groundwater) to barrier; $m_2$ - numerical expression of contamination index in migratory flow (e.g. concentration of heavy metal ions in groundwater) after barrier. $L$ – barrier power (width).

Another quantitative characteristic of geochemical barriers is the contrast of barrier S, determined by formula 2:

$$S = \frac{m_1}{m_2}$$

The life of the geochemical barrier, taking into account the supply of pollutants with rainwater and meltwater, can be calculated according to the formula 3:

$$T = \frac{aV\rho}{10\cdot h_s\cdot \Psi_{f}F \cdot C_{i,T} + 10\cdot h_r\cdot \Psi_{t}F \cdot C_{i,R}}$$

where:
- $a$ – capacity of silicate-containing waste (g/kg);
- $V$ – volume of silicate-containing waste (m$^3$);
- $\rho$ – the bulk density of silikatsoderzhashchyi withdrawal, kg/m$^3$;
- $F$ – is the total area of the geochemical barrier (m$^2$);
- $C_{i,T}$ – concentration of ith pollutant in rainwater (g/m$^3$);
- $C_{i,R}$ - concentration of the ith pollutant in melted waters (g/m$^3$);
- $h_s$ – sediment layer (mm), during the warm season;
- $h_r$ – layer of precipitation, (mm), during the cold period of the year;
- $\Psi_{f}$, $\Psi_{t}$ – is the total rainwater and meltwater runoff rate.
3. Results of the study
Thermodynamic analysis of the substances constituting the main phase of building wastes and reactions of their interaction with heavy metal ions showed that silicate-containing wastes (for example, heavy concrete, gas concrete) show the maximum chemical affinity estimated by the Gibbs energy value (Table 3).

Table 3. Assessment of chemical affinity of silicate-containing wastes by example of interaction with cadmium and iron ions.

| Possible reactions of interaction of the main phase of withdrawal | ΔG°298, kJ/mol | Chemical affinity |
|---------------------------------------------------------------|----------------|------------------|
| 3CaO·SiO2·H2O + 2H2O → 2CaO·SiO2·H2O + Ca(OH)2 | -39,30 | + |
| 3CaO·SiO2 + 2H2O + Cd2+ → CdO·SiO2·H2O + 2Ca(OH)2 + Ca2+ | -57,39 | + |
| 2(3CaO·SiO2) + 4H2O + Cd2+ → CdO·SiO2·2H2O + SiO2·2H2O + 6Ca2+ | -370,43 | - |
| CaO·SiO2·H2O + Cd2+ → CdO·SiO2·H2O + Ca2+ | -30,47 | + |
| CaO·SiO2·H2O + Cd2+ + H2O → Cd(OH)2 + SiO2·H2O + Ca2+ | -18,18 | + |
| CaO·SiO2·H2O + CdCl2 → CdO·SiO2·H2O + CaCl2 | -26,41 | + |
| 2CaO·SiO2·H2O + CdCl2 + H2O → CdO·SiO2·H2O + Ca(OH)2 + CdCl2 | -43,30 | + |
| 2(2CaO·SiO2·H2O) + CdCl2 + H2O → CdO·SiO2·H2O + CdCl2 | -296,82 | + |
| CaO·SiO2·H2O + 2Ca(OH)2 + CaCl2 | -595,23 | + |
| 2(2CaO·SiO2·H2O) + 3CdCl2 + 2H2O → CdO·SiO2·H2O + CaCl2 | -71,52 | + |
| CaO·SiO2·H2O + 2Cd(OH)2 + 3CaCl2 | -71,52 | + |
| 3CaO·SiO2 + 2H2O + Fe3+ → FeO·SiO2 + 2Ca(OH)2 + Ca2+ | -374,69 | - |
| 2(3CaO·SiO2) + 4H2O + Fe3+ → FeO·SiO2·2H2O + SiO2·2H2O + FeCl2 | -298,66 | + |
| 2(2CaO·SiO2·H2O) + FeCl2 + H2O → FeO·SiO2·H2O + FeCl2 | -654,25 | + |
| CaO·SiO2·H2O + 2Fe(OH)2 + 3CaCl2 | -654,25 | + |

Thus, silicate-containing construction waste can be the basis for the development of technological solutions to reduce pollution of man-made soils.

At the Department of Engineering Chemistry and Natural Science of PGUPS, the capacities of some silicate-containing waste were determined (Table 4).

Table 4. Dynamic capacity of silicate demolition products, mg/g.

| Filtration rate, m/h | gas concrete | Mn2+ | Fe3+ | Ni2+ | Cu2+ | Cd2+ | Cr3+ |
|---------------------|--------------|------|------|------|------|------|------|
| 3                   |              | 2,05 | 2,32 | 1,90 | 2,06 | 2,12 | 2,12 |
| 6                   |              | 1,98 | 2,10 | 1,85 | 2,01 | 1,98 | 2,04 |
| concrete of high specific weight |              | 0,78 | 0,45 | 0,98 | 0,60 | 0,79 | 0,98 |
| 3                   |              | 0,60 | 0,35 | 0,95 | 0,45 | 0,52 | 0,75 |
Preventive decisions to protect man-made soils from contamination with heavy metal ions are primarily related to the creation of geochemical barriers to the migration of heavy metal ions. Transport and metallurgical enterprises are the main sources of heavy metal ions entering man-made soils. In this case, in the places of possible ingress of heavy metals determined on the basis of monitoring of man-made soils for the content of heavy metal ions in man-made soils, it is necessary to build a geochemical barrier containing silicate-containing construction waste. Examples of such solutions are various geoeco-protective embankments along highways and railway tracks [9-15].

When creating geochemical barriers, it is necessary to take into account the presence of several types of heavy metal ions in man-made soil. It was determined that the capacity of silicate-containing wastes with several types of heavy metal ions at the same time was reduced approximately in proportion to the number of types of heavy metals (Table 5).

| Metal     | for each of the metals separately, g/kg | for each of the metals, in the presence of the other two, g/kg |
|-----------|----------------------------------------|----------------------------------------------------------|
| Mn$^{2+}$ | 0.60                                   | 0.20                                                     |
| Fe$^{3+}$ | 0.35                                   | 0.15                                                     |
| Cr$^{3+}$ | 0.75                                   | 0.31                                                     |

When creating a geochemical barrier per 1 km of railway embankment to protect surface effluents from iron ions using heavy concrete in the body of the railway bed, the life of the geochemical barrier was calculated.

It is known that the average area exposed to pollution per 1 km of construction length of the railway track is 9.25 ha or 9.25·104 m$^2$. Since the average annual rainfall for the North-Western region of the Russian Federation is 500 mm per year, it can be considered that on average per year the following amount of precipitation is allocated from the surface of the railway track 1 km long:

$$V = 0.5 \cdot 9.25 \cdot 10^4 = 46250 \text{ m}^3 \approx 50000 \text{ m}^3$$

Under the condition of concentration of iron ions in the surface runoff from the railway bed is up to 300 mg/m$^3$, the total amount of iron withdrawn from the surface of 1 km of the railway bed is:

$$m = 50000 \cdot 300 \approx 15000000 \text{ mg/year} \approx 15 \text{ kg/year}$$

Considering that the capacity of heavy concrete on iron ions is 0.35 g/kg, we obtain that 2·10$^6$ kg of material (approximate weight of heavy concrete on 1 km of track) are capable of absorbing 7·10$^5$ g or 700 kg of iron ions.

Then, the term of the "operation" of the geochemical barrier can be calculated according to formula 4.

$$T = \frac{M}{m}$$  \hspace{1cm} (4)

$M$ – weight of iron ions, which can be absorbed by 2·10$^6$ kg of heavy concrete (700 kg)

$M$ – total amount of iron ions discharged from the surface of 1 km of railway bed per year (15 kg/year)

$$T = \frac{M}{m} = \frac{700}{15} = 47 \text{ (year)}$$

It should be borne in mind that during the period of operation of the geochemical barrier, it will be contaminated with suspended substances and film oil products, which will significantly reduce its service life, as well as it should be taken into account that this calculation is carried out under the condition of 100% use of heavy concrete as a ballast material. With a decrease in the share of heavy concrete use, the life of the geochemical barrier will accordingly decrease. The actual service life can be established only based on the results of long-term (at least 5 years) observations of the concentration of iron ions in the surface runoff from the section of the railway track. It should also be borne in mind that the timing of the replacement of railway rubble depends on the load stress of the track.
Liquidation technological solutions for protection of man-made soils from contamination with ions of heavy metals can be implemented by application of ground silicate-containing wastes directly into man-made-changed soil.

Thus, to reduce the concentration of heavy metal ions in man-made soils of construction facilities, it is possible to use the creation of geochemical barriers based on the use of silicate-containing construction waste. In this case, agricultural equipment intended for the application of solid mineral fertilizers can be used.

4. Conclusions
1. Due to the large pollution of technologically modified soils in the territory of large cities, it is necessary to create geochemical barriers.
2. Using the principle of A.I. Perelman, it is shown that the most promising wastes on the basis of which geochemical barriers can be created are silicate-containing demolition products of buildings and structures.
3. Solid mineral silicate-containing wastes from the demolition of buildings and structures have a capacity in relation to heavy metal ions.
4. A formula is proposed for calculating the life of the geochemical barrier taking into account its size and the amount of pollution coming from melted and rain drains.
5. It is shown that wastes from demolition of buildings and structures do not have selective sorption in relation to different ions of heavy metals.
6. It is calculated that when creating a geochemical barrier from heavy concrete in the railway embankment to prevent the migration of iron ions with surface runoff, provided that granite crushed stone is completely replaced with heavy concrete, the service life reaches 47 years.

5. References
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