Journal of Geology, Geography and Geoecology

Journal home page: geology-dnu.dp.ua

ISSN 2617-2909 (print)
ISSN 2617-2119 (online)

Journ. Geol. Geograph. Geology, 32(1), 079-088.

doi:10.15421/112309

Geoecological Analysis of Threats of Using Phosphogypsum in Construction of Roads

Olena V. Krainiuk[1], Yuriy V. Buts[2], Roman V. Ponomarenko[3], Vitalii V. Asotskyi[3], Vitaly V. Barbashyn[4], Andrii Y. Kalynovskyi[3]

[1]Kharkov National Automobile and Highway University, Kharkiv, Ukraine
[2]Sumy State Pedagogical University named after A.S. Makarenko
[3]National University of Civil Protection of Ukraine, Kharkiv, Ukraine, asotskiy@nuczu.edu.ua
[4]O.M. Beketov National University of Urban Economy in Kharkiv, Kharkiv, Ukraine

Received 27.05.2022;
Received in revised form 18.07.2022;
Accepted 23.07.2022

Abstract. The problem of recycling and storage of phosphogypsum is relevant for many countries of the world, as it is associated with environmental problems such as pollution of water bodies, soil and atmosphere. This study analyzes the possibility of using phosphogypsum for the construction of roads. The objective was a geoecological analysis of the danger of phosphogypsum stockpiles and a study of the possibility of using phosphogypsum in road construction to solve the problem of its accumulation in the environment. The chemical composition of phosphogypsum samples of the Sumyhimprom and Rivneazot companies was studied using the method of X-ray diffractometry. The content of heavy metals (HM) was analyzed using atomic absorption spectroscopy. An extremely high level of chromium was determined, accounting for more than 20-33 Maximum Concentration Values (MCV). The content of cuprum in the phosphogypsum samples of Rivneazot was 2 MCVs. The contents of other heavy metals did not exceed the MCVs, the synergistic effect should be taken into account. Migration of heavy metals is one of the main problems associated with phosphogypsum stockpiles. The increased acidity of phosphogypsum promotes the formation of soluble HM compounds. Depending on the solubility of toxicants, they accumulate in the ecosystem or migrate, dissolve, and enter plants. The traditional methods of storing phosphogypsum, both from an environmental and economic points of view, are less acceptable than the methods of its recycling and reuse in various sectors of the national economy. The paper theoretically substantiates that the reuse of accumulated phosphogypsum and the implementation of new technological solutions in road construction would reduce the level of technogenic loading that phosphogypsum imposes on the environment. Based on the analysis of the content of heavy metals and the development of concentration logarithmic diagrams, mobile forms of metals were studied and the harmful effect of metals leaching from phosphogypsum was considered. We determined the positions of toxic substances in the engineering road construction – environment. We recommended dividing hydroxides and hydroxocomplexes of heavy and toxic metals into three groups according to their solubility, having the ability to migrate in acidic, neutral and alkaline environments, respectively. Strict regulations are needed to protect soil cover in areas with acidic soils. We grouped soils on which it is not recommended to use engineered road structures with phosphohypsum due to increased migration of HMs into the ecosystem: sandy; soils rich in humus components, acidic soils (sod-podzolic) or in case of existing probability of an increase in soil acidity (unorganized ingress of industrial waste, acid rain, etc.); acidic soils salinized with chlorides; soils containing ammonia; soils containing sulfates.

Key words: phosphogypsum, dihydrate, hemihydrate, soil pollution, heavy metals, highway, industrial waste, construction.

Геоекологічний аналіз небезпеки використання фосфогіпсу при будівництві автомобільних доріг

О. В. Крайнюк[1], Ю. В. Буц[2], Р. В. Пономаренко[3], В.В. Асоцький[3], В.В. Барбашин[4], А.Я. Калиновський[3]

[1]Харківський національний автомобільно-дорожній університет, м. Харків, Україна,
[2]Сумський державний педагогічний університет імені А.С. Макаренка (Sumy State Pedagogical University named after A.S. Makarenko)
[3]Національний університет цивільного захисту України, м. Харків, Україна, asotskiy@nuczu.edu.ua
[4]Харківський національний педагогічний університет імені Г.С. Сковороди

Анотація. Проблема утилізації та зберігання фосфогіпсу актуальна для багатьох країн світу, оскільки пов’язана з екологічними проблемами забруднення водойм, ґрунту та атмосфери. У даному дослідженні аналізується можливість безпечного використання фосфогіпсу для будівництва автомобільних доріг. Метою роботи є геоекологічний аналіз небезпеки відвалів фосфогіпсу та дослідження можливості використання фосфогіпсу у дорожньому будівництві задля вирішення проблеми його накопичення у довкіллі. Хімічний склад зразків фосфогіпсу ПАТ «Сумихімпром» та ПрАТ «Рівнеазот» вивчався з використанням методу рентгенографічної діфрактометрії. Вміст важких металів (ВМ) проаналізований за допомогою атомно-адсорбційної спектроскопії. Встановлено надзвичайно високий рівень хрому понад 20-33 гранично-допустимих концентрацій (ГДК). Вміст купруму у зразках фосфогіпсу ПрАТ «Рівнеазот» становить 2 ГДК. Вміст інших ВМ не перевищує ГДК, але слід пам'ятати про синергетичний вплив. Міграція ВМ є однією із головних проблем, що пов'язані з функціонуванням відвалів фосфогіпсу. Підвищена кислотність фосфогіпсу сприяє утворенню розчинних сполук ВМ. Залежно від розчинності токсикантів відбувається їх акумуляція та накопичення у екосистемі або їх міграція, розчинення, надходження у рослини. Визначено, що традиційні методи складування фосфогіпсу як з екологічної, так і економічної точки зору є менш прийнятні, ніж способи його утилізації та використання у різних галузях народного господарства. У роботі теоретично обґрунтовано, що утилізація вже накопиченого фосфогіпсу та реалізація нових технологічних рішень у дорожньому будівництві дозволить знизити рівень техногенного навантаження від фосфогіпсу на навколишнє природне середовище. На підставі аналізу вмісту ВМ та побудови концентраційно-логарифмічних діаграм досліджено рухливі форми металів та розглянуто шкідливий вплив ВМ, що вилуговуються з фосфогіпсу, а також визначено положення токсичних речовин у системі «інженерно-дорожня споруда – навколишнє природне середовище». Рекомендується розділяти за розчинністю гідроксиди та гідроксокомплекси важких та токсичних металів на три групи, що мають здатність до міграції відповідно у кислому, нейтральному та лужному середовищах. Необхідно пред'являти жорсткіші вимоги до охорони ґрунтового покриву в районах з кислими ґрунтами. Розроблено рекомендації щодо встановлення екологічно безпечних умов використання фосфогіпсу у будівельній індустрії. Згруповані ґрунти, на яких не рекомендується використовувати інженерно-дорожні споруди з фосфопіпсом через підвищену міграцію ВМ в екосистему: піщані; ґрунти, багаті гумусовими компонентами, кислі ґрунти (дерново-підзолисті) або при існуючій ймовірності підвищення кислотності ґрунту (неорганізоване потрапляння промстоків, випадання кислотних дощів та ін.); кислі ґрунти, засолені хлоридами; ґрунти, що містять аміак; ґрунти, що містять сульфати.

Ключові слова: фосфогіпс, дигідрат, напівгідрат, забруднення ґрунту, важкі метали, автомобільна дорога, відходи промисловості, будівництво

Introduction

Phosphogypsum (hydrate of calcium sulfate $CaSO_4 \cdot 2H_2O$) is a by-product of the production of extracted phosphoric acid, obtained from phosphate rocks by wet process of breakdown using sulfuric and phosphoric acids by dehydration technique. Production of one tonne of phosphoric acid leaves 5 tonnes of phosphogypsum.

Phosphogypsum is low-cost, but its recycling remains a problem due to admixtures it contains, including heavy metals, radionuclides and acid residues (Meskini, 2021).

Phosphogypsum is almost unusable by-product of the manufacturing of phosphate fertilizers that contains several valuable components: calcium sulfate and its hydrates, such chemical elements as Si, Fe, Ti, Mg, Al and Mn, and also a number of heavy metals (HMs). Phosphogypsum is commonly stored openly in stockpiles. Phosphogypsum is usually piled in open areas in the vicinity of enterprises, natural complexes and even settlements, occupying large territories. Transportation and storage of phosphogypsum in stockpiles are associated with additional exploitation costs. For instance, up to 10% of the production cost of phosphoric acid comprises transportation and storage expenses. Phosphogypsum accumulates at the estimated rate of 200 M T annually, while only 10-15% of it is used (Chernysh, 2021).

The amounts of phosphogypsum accumulated in stockpiles in Ukraine account for 50 M T (Armiansk, Sumy, Rivne and other cities).

Disposal and burying of the gypsum by-product causes serious ecological problems. Each year, about 100-280 M T of phosphogypsum are produced.

Chemically, phosphogypsum dihydrate is a gypsum dihydrate with admixtures of soluble (phosphoric and sulfuric, mono- and dicalcium phosphate, fluorine silicates, sodium and potassium salts) and insoluble (silica, phosphates) compounds. Phosphogypsum contains toxic admixtures (F, As, Sr, U, and other heavy metals). Having various amounts of admixtures, phosphogypsum changes its properties: in particular, linkage slows and binding properties solidify. Such changes in the physical-chemical specifics can be obstacles for its industrial use.

Taking into account poor water-solubility of some chemical compounds of phosphogypsum and insignificant concentration of other, better soluble, components of the road basis comprising compacted soil, sand and crushed stone, it is believed that its application would not be a source of environmental pollution. Nonetheless, there are data about high solubility of phosphogypsum samples. Therefore, according to the analysis (Soldatkin, 2019) of phosphogypsum samples from piles of the Balakovo branch of Apatit JSC, losses of sample weight after 140 days were 87.4% in the conditions of periodic water saturation.

The results of the experiment demonstrated that application of phosphogypsum in road construction can lead to destruction of roads in areas with high intensity of water exchange and also to sulfate pollutions of soils and groundwater.

At the same time, the results of a groundwater monitoring, conducted at the industrial site and stockpiles (Balakovo branch of Apatit JSC), revealed presence of a serious pollution of the groundwater by compounds deriving from the phosphogypsum stockpiles. Mineralization of groundwater in areas of phosphogypsum stockpiles reaches 90 g/dm^3 because of high concentrations of phosphates (up to 33.5 g/ dm^3) and sulfates (up to 8.99 g/dm^3). The concentrations of microcomponents were also significant: Mn – up to 83 mg/dm^3, Zn – up to 15 mg/dm^3, Cu – up to 16.8 mg/dm^3, Ni – 6.6 mg/dm^3, Cr – up to 6.4 mg/dm^3 (Soldatkin, 2018). High concentrations indicate quite high solubility of phosphogypsum.

Some authors note extremely high contents of an array of heavy metals in phosphogypsum, particularly Cd, Cr, Zn and As (Moussa, 2022).

There is also a practice of utilizing phosphogypsum in agriculture. However, this experience in Tunisia demonstrated that HMs present in phosphogypsum transform into soluble form and accumulate in plants, especially the root system (Ben Chabchoubi, 2021).

Despite those facts, phosphogypsum is used in construction, including road building. The incorporation of phosphogypsum in road construction is now becoming relevant because it can replace natural crushed stone. Expansion of the phosphogypsum use in road construction would solve the problem of phosphogypsum accumulation and reduce construction costs.

The use of phosphogypsum wastes in road construction would solve the problem of disposal and recycling of phosphogypsum by putting it to use as a local material for the construction of roadbed and bases (layers of crushed stone and sand on compacted soil) for roads; by replacing natural gypsum by cheap raw material for road building; decreasing costs of road constructions and extending periods between repairs through improvements of road properties. Roadways built using phosphogypsum are 30% cheaper than those laid traditionally. Moreover, due to the specifics of the material, combining monolithicity and light weight, phosphogypsum is irreplaceable on wetlands. It allows paving reliable and long-life roads. The construction is five times more firm (Kochetkov, 2019). However, that report had no information on phosphogypsum composition and its ecological safety.

Due to the broad range of chemical composition and, particularly concentrations of sulfates and rare-earth elements, phosphogypsum is not suitable for all constructions of roads, and therefore in most cases an expensive preparation is needed to adjust the material to sanitary norms.

In Ukraine, phosphate hemihydrate in road building has been used by the Sumy Oblast Department of Roads. Fresh phosphogypsum hemihydrate was applied as the main layer-forming material, as well as mixed with lime (7-30%) or cement (10-25%) for strengthening soil. The study of experimental plots of the roads, determining solidity of the constructions and testing the samples revealed that road coatings made of the indicated mixtures develop strong water- and frost-resistant properties. The coating has been in good condition for 4-5 years, and no signs of ruinations or deformations were noted. Based on the provided data, the Oblast Department of Roads recommends using calcium sulfate hemihydrate phosphogypsum for laying upper and lower layers of the road bases for the concrete and crushed-stone-based coatings (Soldatov, 2020). However, that study did not take into account the ecological aspect.

An integrated generalized study (Zavadskaya, 2020) analyzed the adhesive properties of phosphogypsum that are necessary for the creation of structures with a given firmness of road coating, economic and technological aspects of using this approach in road construction, but included no data on ecological side of this issue.

Phosphogypsum is most often discharged to superficial water objects (Bezsonnyi, 2021) without any known consequences or is dumped on open grounds, leading to serious environmental pollutions. There are reports demonstrating that recycling of phosphogypsum as a road construction material is safe and causes no pollution of groundwater and has no radiological impact (Amrani, 2020).

The authors (Calderón-Morales, 2021) studied the mechanical strength of phosphogypsum-containing concrete, including such characteristics as linkage, binding properties, long life (in cases of being permeated by chlorides, undergoing carbonization and being subject to sulfates and acids). In addition, the study provided the data on radioactivity of phosphogypsum and radium-226 and radon-222 contents in samples of phosphogypsum-containing construction materials.

The objective of the study

The objective of the study was geoecological analysis of the threats coming from phosphogypsum stockpiles and the study of the possibility of using phosphogypsum in road construction in order to solve the problem of its accumulation in the natural environment.

Accordingly, we solved the following tasks:

- Analysis and systematization of scientific studies of risks that phosphogypsum that is used in road construction poses to the geological environment;
- Analysis of technogenic loading in the process of phosphogypsum storage;
- Designing models of how phosphogypsum impacts the components of the natural environment;
- Analysis of migration of dangerous phosphogypsum components in the geological environment.

Materials and methods

The authors employed such methods of study as X-ray diffraction, atomic-adsorbtion spectroscopy, pH-metry and methods of theoretical analysis.

Results and analysis

Phosphogypsum may contain hazardous components (first of all heavy metal compounds), which are highly soluble, first of all in acidic environment (Table 1, 2). In such a case, they are introduced to the environment in mobile form and cause toxic impact on the ecosystem components: soil and groundwater. Furthermore, even workers in road construction are subject to impacts of the toxicants if phosphogypsum is being applied. Fluorides in phosphogypsum irritate the respiratory organs, can cause nose bleeding, and have toxic effects on the liver. Fluoride compounds can accumulate in the organism, affect the entire complex of the organs and systems, including cardiorespiratory, neuroendocrine, and bone-muscular (Shalina, 2009).

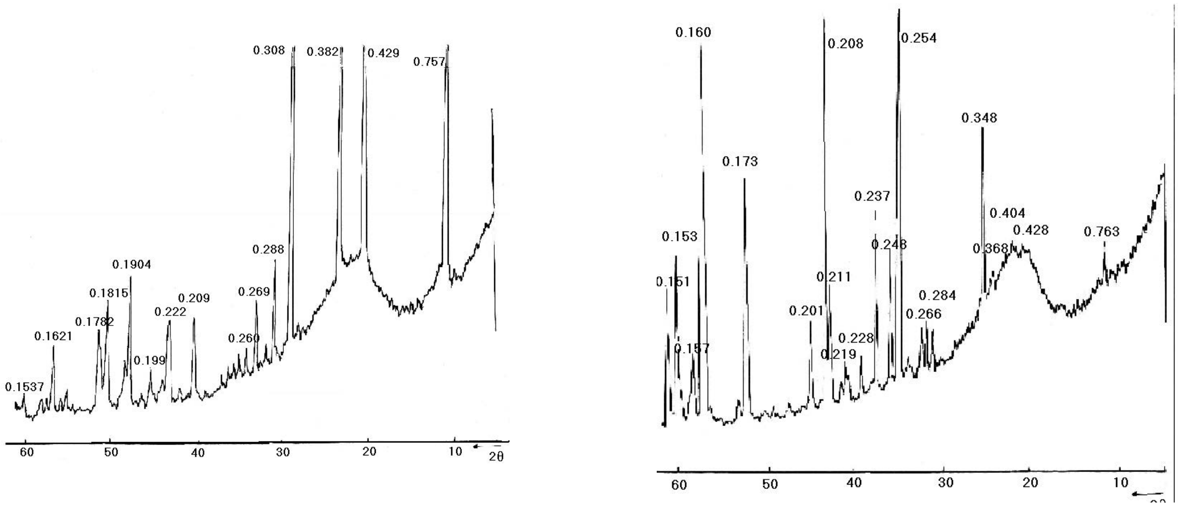
The study by Yanin (Yanin, 2007) has confirmed that one of the sources of fluoride contamination of agricultural soil is phosphogypsum.

Phosphogypsum can also be in dust, thereby irritating the eyes, causing conjunctivitis. People working with phosphate-containing materials can experience astheno-vegetative syndrome, negative consequences for the nervous system, neuralgia, and diseases of the respiratory system. Road workers must wear individual protection when phosphogypsum is used.

The chemical compositions of the samples of phosphogypsum manufactured by PJSC Sumyhimprom and PRJSC Rivneazot were examined using the method of X-ray diffraction (Fig. 1, Table 1). We analyzed powdered phosphogypsum and phosphogypsum fragment.

The sample of PP (powdered phosphogypsum) has typical X-ray reflection for gypsums, measuring 0.757; 0.729; 0.308; 0.288; 0.269; 0.178 nm. The X-ray photos showed sulfohalite $Na_6[SO_4]_2(F,Cl)$, characteristic of X-ray reflections measuring 0.382; 0.280; 0.260; 0.190; 0.177 nm, and also jarosite – $KFe_3[SO_4]_2(OH)_6$ with peaks at 0.308; 0.222; 0.199; 0.182; 0.154 nm. There were also present fluorite CaF_2 (0.317; 0.190; 0.164 nm) and baryte $BaS0_4$ (0.308; 0.209; 0.127 nm).

The sample of PF (phosphogypsum fragments) was mainly composed of $CaSO_4$ grains and phosphates. There were reflections that are characteristic of this mineral group, measuring 0.348; 0.284; 0.270; 0.266; 0.262 nm, and also $Fe,Al_2[PO_4]_2(OH)_2$, peaking at 0.237; 0.228; 0.219 nm. We observed peaks that are characteristic for gypsum, measuring 0.763; 0.429; 0.307; 0.269 nm. There was possible presence of baryte, as indicated by strips measuring 0.384; 0.307; 0.208; 0.153; 0.127 nm.



a) PP – sample of powdered phosphogypsum

b) PF – sample of phosphogypsum fragment

Fig. 1. X-ray photograph of phophogypsum

Taking into account the mineralogical phase composition of the initial raw material and industrial phosphogypsum, we may quite confidently assume that in the conditions of such a complex of chemical components and factors, phosphogypsum promotes the development of sulfates, phosphates, carbonates and halides with complex composition and large share of anion isomorphism (Krainiuk, 2004). Furthermore, as demonstrated by the X-ray analysis of the samples, high concentrations of sulfates and chlorides, which together with the analyzed metals form well-soluble compounds (except $PbSO_4$), and thus can migrate in soil to large distances from phosphogypsum piles or phosphogypsum-strengthened soil. As they travel in soil, they are consumed by plants.

Concentration of HMs, analyzed using atomic-adsorbtion spectroscopy (Table 2). In the construction of roadways, phosphogypsum is most often used to stabilize soil by mixing soil and phosphogypsum or by laying a layer of phosphogypsum on soil. Therefore, we compared the contents of HMs with the MCVs. Similar comparisons have been carried out by other authors. For example, when phosphogypsum is used in agriculture, concentrations of its admixtures of toxic elements, including Cd, As, Hg, Pb (Korobka, 2016) are recommended to be compared with the MCVs in soil.

We determined extremely high level of chromium, measuring 20-33 MCVs. The cuprum concentration in the samples of Ltd Rivneazot phosphogypsum accounted for 2 MCVs. The concentrations of other HMs did not exceed the MCVs, but we should keep in mind the synergic effect.

Accumulation of HMs in soil poses a threat to human health through the trophic chain of soil-plant (animal)-human. When HMs accumulate in soil, the orientation and intensity of many biochemical reactions could be inhibited or altered. Heavy metals can disturb the soil's optimal dynamic balance between synthesis and breakdown of organic matter. Presence of excessive HM concentrations in soil moisture leads to degradation of soil coverage, partial dying of microbial community and decrease in erosion resistance of the upper humus horizon (Homyakov, 2017). Heavy metals were determined to have phytotoxicity in the following descending order: Cd, Ni, Cu, Zn, Cr, Pb. Toxicity of metal in pure form is lower than in polymetal (complex) contamination of soil.

When piled, phosphogypsum undergoes changes and transformations. There occur dehydration and processes of consolidation, decrease in phosphogypsum moisture. Because of wind and water erosion, infiltration, heavy toxic components migrate to soil, groundwater and air around the phosphogypsum stockpiles (Krainiuk, 2004).

The ability of phosphogypsum to be a source of contaminants manifests during physical water and wind erosions of stockpiles, chemical leaching by water currents and in the conditions of oxidizing conditions (Pérez-López, 2007). The concentrations of mobile forms of contaminants that can enter soil in form that is available to plants per 1 T of phosphogypsum were 700 g of Sr, 110 g of Fe, 55 g of Y, 30 g of Ce, 12 g of Cr, 11 g of Yi, 5 g of Zn, 4 g of Cu and Pb, 3 g of V and Cd, 2 g of As and Ni, 1 g of U (Pérez-López, 2010).

When phosphogypsum is stored in open areas, contamination of the environment by components of the stockpiles occurs through atmospheric precipitations. Soil near stockpiles undergoes technogenic contamination by HMs, contained in phosphogypsum stockpiles (Chernysh, 2021).

Table 1. Chemical composition of phosphogypsum, %

Phosphogypsum	CaO	SiO_2	Fe_2O_3	Al_2O_3	MgO	SO_3	P_2O_5	F	Water (crystal.)	pH of water solution
PJSC Sumyhimprom										
PP	31	0.4	1.2	0.5	0.1	46	1.1	0.1	19	2.4
PF	31	0.5	1.8	0.5	0.1	41	1.5	0.1	19	4.9
PRJSC Rivneazot										
PP+PF	36	0.4	0.2	0.4	0.1	57	0.8	0.1	18	4.4

Migration of HMs is one of the main problems related to phosphogypsum stockpiles. Heightened acidity (pH<6) of phosphogypsum promotes the formation of soluble HM compounds. Depending on solubility of toxicants, they accumulate in the ecosystem or migrate, become solved and consumed by plants.

Having entered soil, HMs can form poorly soluble hydroxides, and also metals can form hydroxo-complexes with various amounts of hydroxide ions. We studied the range of sedimentation of hydroxides and regions of dominance of soluble hydroxocomplexes by developing concentration-logarithmic diagrams (CLD), as we have earlier discussed (Buts, 2018,

Table 2. Contents of some heavy metals in the samples of phosphogypsum C, mg/kg, %

Phosphogypsum samples	Cu	Zn	Cr	Pb	Ni	
PJSC Sumyhimprom						
MCV soil	3.0	23.0	0.1	30.0	4.0	
PP	1.6	21.7	3.3	13.0	2.2	
C_i/MCV_i	0.5	0.9	33.0	0.4	0.6	
PF	1.5	22.2	2.1	11.8	2.2	
C_i/MCV_i	0.5	1.0	21.0	0.4	0.6	
PRJSC Rivneazot						
PP+PF	6	20	2.0	9.8	1.6	
C_i/MCV_i	2	0.9	20	0.3	0.4	

2019, 2020, Krainiuk 2021) and provided methods of studying the possibility of the formation of poorly-soluble or mobile forms of some metals, e.g. Cu.

For example, we provide a principle of CLD structure of nickel (Fig. 3). For nickel compounds, we observed the following dependence (Fig. 2): in acidic and neutral environment, there dominate mobile forms of nickel compounds, however, when pH changes, for example even from 5.5 to 6.0, the amount of mobile forms of nickel decreases 10-fold from $lg[Ni^{2+}]=-1$ to $lg[Ni^{2+}]=-2$, i.e. the concentration of Cu^{2+} ions changes from 0.1 mol/L to 0.01 mol/L after pH is increased from 5.5 to 6.0. At pH>8, nickel compounds would be in insoluble form.

To predict the migration or accumulation of nickel compounds in soil environment, we developed a dependence of concentration of most probable ions $[Ni(OH)_n{}^{2-n}]$ on environmental pH and created a trend line (Fig. 3).

Dependence of soluble nickel compounds on pH can be described by the following pattern:

$$lg[Ni(OH)_n{}^{2-n}]= 0.0147 \cdot pH^3 - 0.1968 \cdot pH^2 - 1.1505 \cdot pH + 8.5013 \quad (1)$$

This dependence well correlates with the designed concentration-logarithmic diagram, as indicated by the significance of approximation of $R^2=0.99$

Thus, of all particles $[Ni(OH)_n{}^{2-n}]$, Ni^{2+} dominate in acidic and neutral environments. Their concentrations in soil solution are described by the equation (1) thst is relevant for pH>5. At pH<5, all nickel in the solution is in the form of Ni^{2+}. At pH=8–14, there form insoluble particles $[Ni(OH)_n{}^{2-n}]$, mainly $Ni(OH)_2$. Since the migration of nickel compounds becomes impossible, it accumulates.

Such prognostic models were designed for all heavy metals found in the phosphogypsum samples that were examined in this study, and also other HMs found by other authors (Chernysh, 2021, Moussa, 2022). The analysis of the developed diagrams allowed

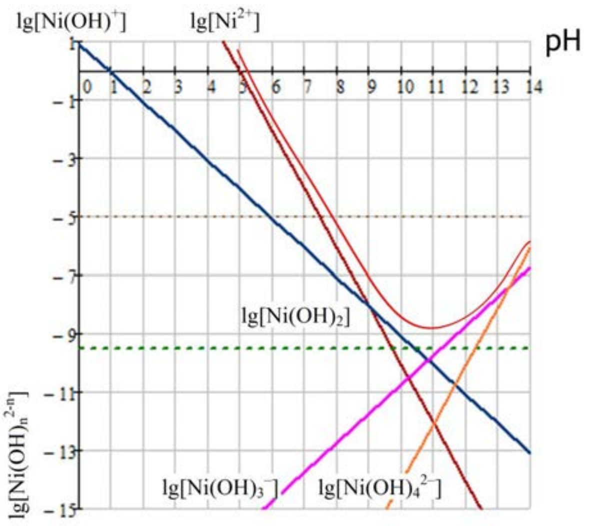


Fig. 2. Concentration-logarithmic diagram of formation of nickel hydroxo complexes

for the grouping of HMs according to their abilities to accumulate or form mobile forms and migrate.

In neutral environment, most metals (Al, Cr, Zn, Cu, Fe(II), Co, Ni) form poorly soluble compounds (hydroxides), which is related to low migration ability and accumulation of elements in soil. However, a change in acidity can promote solubility of hydroxides and formation of soluble hydroxicomplexes (Fig. 4).

Some metals are mobile in neutral environment (Fe(II), Cd, Mg, Mn).

In acidic soil (4.5<pH<5.8), which could be sod-podzolized, podzolized and solodized soils, almost all HMs, except Fe(II), form well soluble hydroxicomplexes that are able to migrate.

Increase in alkalinity stops migrations of Cd, Co, Fe(II), Fe(III), Mn, Ni. In such conditions, Mg compounds are able to migrate, as well as Al, Cr, Cd, but in smaller amounts.

According to the results of the study, the authors developed recommendations of determining the ecologically safe conditions of using phosphogypsum

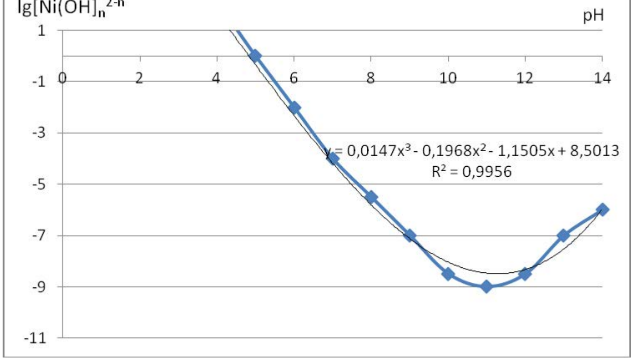


Fig. 3. Dependence of the formation of particles [Ni(OH)n 2-n] on pH of soil environment

for the construction according to the properties of soil. The recommendations we put forward are relevant for all roadways that contain phosphogypsum, which in turn contains HMs and toxic compounds that can migrate into soil, groundwater and air, especially when a road is being ruined. The recommendations we propose are based on different abilities of HMs and toxic elements to migrate in various environments.

The use of wastes for the construction of roads is regulated by a number of normative documents (DSTU B.C 2.7-1-93 DSU «Construction materials. Common phosphogypsum. Technical conditions», DSTU B B.2.7-82:2010 «Gypsum binder compounds. Technical conditions»). However, those documents classify the stockpiles according to granulometry, density, origin, moisture, solubility, etc. The contents of calcium sulfate, water, phosphates and fluorides are regulated. Unfortunately, the concentrations of HMs in phosphogypsum is not identified. The chemical composition of stockpiles, ecological purity, sanitary-hygienic properties are not taken into account.

Therefore, ecological expertise is recommended, as well as sanitary-hygienic evaluation of whether the industrial wastes could be reclaimed as construction materials.

Ecological expertise of any construction project of roadways should take into account the following requirements:

- migration of compounds to the natural environment must be lower according to the MCVs for all environments (soil, water, air);

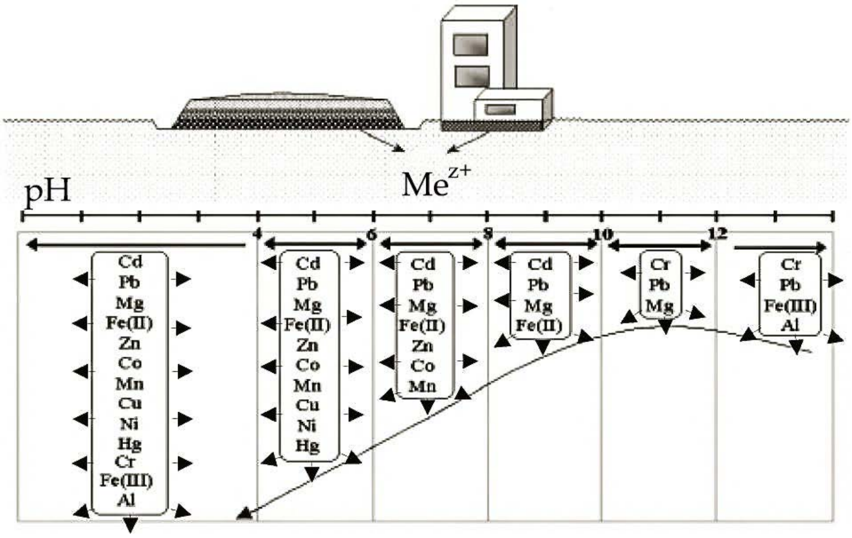


Fig. 4. Migration of heavy metal compounds into the environment during the ruination of roads and road-transport structures (developed by the authors)

- roadways that contain industrial wastes must not have toxic and allergic effects;
- radioactivity of a roadway must be at an allowable level;
- exploitation conditions of a roadway that contains industrial wastes must be analyzed;

The suggested recommendations are for materials used in making road bases and coatings, and also roadway infrastructure. Industrial wastes could also be blast furnace slag, chemical industry wastes, ash slag, phosphogypsum, galvanic sludge, etc, which release chromium, lead, nickel, cadmium, ferrum, cobalt, cuprum, aluminium, manganese, hydrargyrum, zink, barium, arsenic, fluorine, etc compounds into the environment (Krainiuk, 2004).

The authors' suggestions contain data that are necessary for the ecological expertise of materials utilized in road building and could be used by manufacturers of road-construction materials so as to take into account the geoecological assessment of a project.

The purpose of sanitary-chemical studies is determining the chemical composition of wastes and possibility of migration of HMs from constructed objects to the environment, and also predicting possible negative impact of HMs on it and humans.

Industrial wastes are recommended to be used in road construction on soils that accumulate HMs and toxic elements (according to the road zoning of Ukraine), in particular:

- on alkaline soils (meadow-chernozem solonetz, crusty, columnar solonchak soils on forest loam) with pH=10.2-10.5;
- on neutral soils that are favorable for the conversion of most metals (Al, Cr, Zn, Cu, Fe(II), Co, Ni) into poorly soluble forms;

- on soils rich in clayey components;
- on alkaline soils rich in ferrum and aluminium hydroxides, if lead is present in engineered road structures;
- on soils with oxidizing regime in cases of formation of poorly soluble sulfides (in broad pH range).

It is not recommended to be used on soils with increased migration of HMs into the natural environment:

- on sandy soils;
- on soils rich in humus components that form well soluble complex compounds with HMs;
- on acidic soils (sod-podzolized, podzolized and solodized), when all metals but Fe(II) convert into soluble compounds;
- on neutral soils, in presence of Mn compounds in wastes;
- on acidic soils, salinized by chlorides, where HMs transform into well soluble chlorides (meadow-chernozem, solonetz, solonchak soils, river valleys);
- on neutral and alkaline soils that contain chlorides, when using Cd, Pb, Fe(II) –containing wastes in road building;
- on ammonia-containing soils;
- on soils that contain sulfate ions
- on any soils that contain Cd, Pb compounds that are well soluble in broad pH range;
- on soils, acidity of which can increase as a result of unorganized ingress of industrial waste water discharges, acid rains, etc, which promotes solution of hydroxides and conversion of metals into soluble hydroxo complexes.

Conclusions

1. X-ray analysis revealed that the sample of powdered phosphogypsum contained crystallized gypsum, minerals of sulphohalite, jarosite, fluorite and baryte groups. The sample of phosphogypsum fragment included mostly calcium sulfate and secondary phosphates. All the discovered components have irritating effects, first of all for the respiratory and eyesight organs.

2. We determined that from both the ecological and economic standpoints, the traditional methods of phosphogypsum storage are less acceptable than ways of its reuse in various spheres of economy Currently, there are known various ways of recycling phosphogypsum, reported from all around the world: construction sphere, chemical industry, agriculture and biotechnologies of environmental protection. Most popular is its use in construction, whereas the greatest economic effect is achieved in agriculture. Nonetheless, phosphogypsum could be effective in road construction, from both economic and ecological perspectives, taking into account its chemical composition and characteristics of soils.

3. We have theoretically confirmed that combining the orientations of recycling of already accumulated phosphogypsum and implementation of new technological solutions in road construction would allow reducing the level of loading that technogenic phosphogypsum imposes on the environment.

4. Based on the analysis of HM content and structure of concentration-logarithmic diagrams, we studied the mobile forms. We recommend dividing hydroxides and hydroxo-complexes of heavy and toxic metals into three groups that are able to migrate in acidic, neutral and alkaline environments, respectively. More rigid requirements must be put forward for the protection of soil cover in areas with acidic soils.

5. We developed recommendations regarding ecologically safe conditions of using phosphogypsum in the construction. We grouped soils on which we not recommend using engineered road construction with industrial wastes due to increased migration of HMs into the ecosystem: sandy soils; soils rich in humus components, acidic soils (sod-podzolized) in the conditions of existing possibility of increase in soil acidity (unorganized ingress of industrial waste water, acid rains, etc); acidic soils that are salinized with chlorides; soils that contain ammonia; and sulfate-containing soils.

In the future, we are planning to perform a detailed study of composition of soils near roads constructed using phosphogypsum.

References

Amrani, M., Taha, Y., Kchikach, A., Benzaazoua, M., Hakkou, R. (2020). Phosphogypsum recycling: New horizons for a more sustainable road material application. *Journal of Building Engineering,* 30, 101267. DOI 10.1016/j.jobe.2020.101267

Ben Chabchoubi, I., Bouguerra, S., Ksibi, M., Hentati, O. (2021). Health risk assessment of heavy metals exposure via consumption of crops grown in phosphogypsum-contaminated soils. *Environmental Geochemistry and Health, 43*(5), 1953-1981.

Bezsonnyi, V., Ponomarenko, R., Tretyakov, O., Asotsky, V., Kalynovskyi, A. (2021). Regarding the choice of composite indicators of ecological safety of water in the basin of the Siversky Donets. *Journal of Geology, Geography and Geoecology*, 30(4), 622-631. https://doi.org/https://doi.org/10.15421/112157

Buts Y., Asotskyi V., Kraynyuk O., Ponomarenko R., Kovalev P. (2019). Dynamics of migration property of some heavy metals in soils in Kharkiv region under the influence of the pyrogenic factor

Формування *Journ. Geol. Geograph. Geoecology*, 28(3), 409-416. DOI 10.15421/111938

Buts, Y., Asotskyi, V., Kraynyuk, O., Ponomarenko, R. (2018). Influence of technogenic loading of pyrogenic origin on the geochemical migration of heavy metal. *Journ. Geol. Geograph. Geoecology*, 27(1), 43-50. DOI 10.15421/111829

Buts, Y., Kraynyuk, O., Asotskyi, V., Ponomarenko, R., Kalynovskyi, A. (2020). Geoecological analysis of the impact of anthropogenic factors on outbreak of emergencies and their prediction. *Journal of Geology, Geography and Geoecology*, 29(1), 40-48. DOI 10.15421/112004.

Calderón-Morales, B. R., García-Martínez, A., Pineda, P., García-Tenório, R. (2021). Valorization of phosphogypsum in cement-based materials: Limits and potential in eco-efficient construction. *Journal of Building Engineering*, 44, 102506. DOI 10.1016/j.jobe.2021.102506

Chernysh, Y., Yakhnenko, O., Chubur, V., Roubík, H. (2021). Phosphogypsum recycling: a review of environmental issues, current trends, and prospects. Applied Sciences, 11(4), 1575.

Chernysh, Y., Yakhnenko, O., Chubur, V., Roubík, H. (2021). Phosphogypsum recycling: a review of environmental issues, current trends, and prospects. *Applied Sciences*, 11(4), 1575.

Homyakov, D. M., Zhukova, A. D. (2017). Sistemyi ekologicheskogo menedzhmenta promyishlennyih proizvodstv i pochvenno-ekologicheskiy monitoring impaktnyih zon. [Environmental management systems for industrial production and soil-ecological monitoring of impact zones] Comprehensive assessment of the state of soils. (2), 4-6. (in Russian).

Kochetkov A.V., Shchegoleva N.V., Korotkovskiy S.A., Talalai V.V., Vasilyev Yu.E., Shashkov I.G. (2019). Ustroystvo sloev transportnyih sooruzheniy iz fosfogipsa polugidrata (othoda-pobochnogo produkta proizvodstva azotno-fosfornyih udobreniy). [The device layers and transport facilities of hemihydrate phosphogypsum (waste byproduct of the production of nitrogen-phosphorus fertilizers)] *Russian Journal of Transport Engineering*, 1(6). (in Russian). DOI: 10.15862/18SATS119

Korobka A.N., Orlenko S.Yu., Timofeev M.N. (2016). Teoriya i praktika primeneniya fosfogipsa neytralizovannogo v risovodstve: metodicheskie rekomendatsii [Theory and practice of using neutralized phosphogypsum in rice growing: guidelines]. 40. (in Russian).

Krainiuk, E. V. (2004). Stroitelstvo avtomobilnyih dorog pri bezopasnom ispolzovanii fosfogipsa i zoloshlakov TES [Construction of roads with safe use of phosphogypsum and ash slag from thermal power plants] avtoref. dis. kand. tehnich. nauk. Kharkiv. 180. (in Russian).

Krainiuk, O., Buts, Y., Ponomarenko, R., Asotskyi, V., Kovalev, P. (2021). The geoecological analysis performed for the geochemical composition of ash and slag waste obtained at Zmiiv thermal power plant. *Journal of Geology, Geography and Geoecology*, 30(2), 298-305. DOI 10.15421/112126

Medvedev, I. F., Derevyagin, S. S. (2017). Tyazhelyie metallyi v ekosistemah [Heavy metals in ecosystems]. Saratov: Rakurs. 178. (in Russian).

Meskini, S., Samdi, A., Ejjaouani, H., Remmal, T. (2021). Valorization of phosphogypsum as a road material: Stabilizing effect of fly ash and lime additives on strength and durability. *Journal of Cleaner Production*, 323, P.129161. DOI 10.1016/j.jclepro.2021.129161

Moussa, K. B., Eturki, S., Van Poucke, R., Bodé, S., De Grave, J., Van Ranst, E., Moussa, M. (2022). Evaluating the adsorptive capacity of three Tunisian clays deposits for several potentially toxic metals in phosphogypsum waste. *Arabian Journal of Geosciences*, 15(9), 1-12.

Pérez-Lopez R., Nieto J. M., López-Coto I., Aguado J. L., Bolívar J. P., Santisteban M. (2010). Dynamics of contaminants in phosphogypsum of the fertilizer industry of Huelva (SW Spain): from phosphate rock ore to the environment. *Applied Geochemistry.* V.25, 5, 705-715.

Perez-Lopez R., Alvarez-Valero A. M., Nieto J. M. (2007). Changes in mobility of toxic elements during the production of phosphoric acid in the fertilizer industry of Huelva (SW Spain) and environmental impact of phosphogypsum wastes. *Journal of hazardous materials*, V.48, 3, 745-750.

Shalina T. I., Vasileva L. S. (2009). Obschie voprosyi toksicheskogo deystviya ftora [General issues of the toxic effect of fluorine] *Siberian Medical Journal*, 5, 5-11. (in Russian).

Soldatkin, S., Hohlov, A. E. (2018). K voprosu o vozmozhnosti ispolzovaniya fosfogipsa v dorozhnom stroitelstve [On the question of the possibility of using phosphogypsum in road construction] *Subsoil of the Volga and Caspian regions*, 93, 73-76. (in Russian).

Soldatkin, S., Hohlov, A. E. (2019). Problemyi ispolzovaniya fosfogipsa v dorozhnom stroitelstve [Problems of using phosphogypsum in road construction] *Subsoil of the Volga and Caspian regions*, 97, 58-60. (in Russian).

Soldatov, A. A., Yashin, S. O., Yashin, A. O. (2020). Opyit ispolzovaniya fosfogipsa v dorozhnom stroitelstve

[Experience in the use of phosphogypsum in road construction] *Scientific and practical research*, 7-3, 51-53. (in Russian).

Yanin E.P. (2007). Ftor v okruzhayuschey srede (rasprostranennost, povedenie, tehnogennoe zagryaznenie) [Fluorine in the environment (occurence, behavior, industrial pollution)] *Environmental assessment*. 4, 2-98. (in Russian).

Zavadskaya, L. V., Kryazhikov, I. A. (2020). Vozmozhnost ispolzovaniya fosfogipsa v sovremennoy dorozhno-stroitelnoy otrasli [The possibility of using phosphogypsum in the modern road construction industry]. *Youth and systemic modernization of the country*, 288-292. (in Russian).

Zhu Pu S., Huo Z., W. (2021). Evaluation of engineering properties and environmental effect of recycled gypsum stabilized soil in geotechnical engineering: A comprehensive review. *Resources, Conservation and Recycling*, 174, P.105780. DOI 10.1016/j.resconrec.2021.105780