

# Lithosphere preservation in geoconstruction on the base of geoeochemical reactions

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**Abstract.** The paper deals with modern geosystem problems and suggests ways of solving them. The main aim of the study is to develop new methods of geosystem preservation on the base of geoeochemistry through geoeochemical reactions. Both theoretical, namely thermodynamic, method and experimental one are used in the research. Three new geoeochemical techniques such as energy economy, soil restoration and alternative technologies are introduced for natural resource preservation. Every technique is estimated with relation to negative changes of Gibb's free energy. These changes take place as a result of geoeochemical reactions and determine a level of geosystem preservation. Using the first technique it is possible to save energy, a few hundreds of kilojoules per mol, due to formation silicates, phosphates, etc. Other techniques of geosystem restoration are heavy metal ion detoxication and alternative technologies, e.g. lithosynthesis, for natural resource preservation. Geoeochemical techniques of lithosphere preservation can be useful for any geoconstruction technology like soil strengthening, highway and railway construction and other earthwork operations.

## 1 Introduction

Geosphere preservation in geoconstruction is paid great attention in the paper. Some solutions of lithosphere preservation have already been defined [1-6] and now one can introduce three new techniques of geosystem preservation in terms of new energy sources, protection of natural and technogenic environment against pollution and alternative technologies.

The first technique is based on internal energy use instead of any other kind of energy one in processes of productive environment preservation.

In the Table 1 the examples of internal energy conservation which some natural substances have are shown and in the Table 2 one can see the geoeochemical reactions of energy extraction when forming a stone and for heavy metal ion detoxication.

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**Table 1.** Conservation of natural and artificial mineral substance energy.

Substance	$\Delta H^{\circ}_{298}$ , KJ/mol
$Al_2O_3 \cdot 4SiO_2 \cdot 2H_2O$	-5764,6
$Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$	-4136,7
$H_3PO_4$	-1289,26
$SiO_2$	-909,9
$Al_2O_3 \cdot 2SiO_2$	-3311,4
$CaSO_4 \cdot 2H_2O$	-1810,2

**Table 2.** Examples of energy extraction through geocochemical reactions.

Reactions of clay with $H_3PO_4$	$\Delta H^{\circ}_{298}$ of reactions
$AlO_3 \cdot 2SiO_2 \cdot 2H_2O + 6H_3PO_4 \rightarrow 2(SiO_2 \cdot H_2O) + 2Al(H_2PO_4) + 3H_2O$	-282,77
$Al_2O_3 \cdot 4SiO_2 \cdot 2H_2O + 2H_3PO_4 + H_2O \rightarrow 2(SiO_2 \cdot H_2O) + 2[Al(OH)_2H_2PO_4]$	-292,49
$Al_2O_3 \cdot 4SiO_2 \cdot 2H_2O + 6H_3PO_4 \rightarrow 4(SiO_2 \cdot H_2O) + 2Al(H_2PO_4)$	-315,82
$AlO_3 \cdot 4SiO_2 \cdot 2H_2O + 2H_3PO_4 + 3H_2O \rightarrow 4(SiO_2 \cdot H_2O) + 2[Al(OH)_2H_2PO_4]$	-325,5

Detoxication of heavy metal ions is the second technique of internal energy use and geosphere preservation. In the Tables 3 and 4 thermodynamic calculations are presented. So, it is evident that, when detoxicating by means of mineral geoantidotes, systems' free energy negative changes are used and it is the main point of the second technique for geosphere preservation.

**Table 3.** Reactions of geosphere preservation on the base of alkali system.

Reactions	$\Delta H^{\circ}_{298}$ , KJ/mol	$\Delta H^{\circ}_{298}$ of detoxication, KJ/mol	$\Delta G^{\circ}_{298}$ , KJ/mol	$\Delta G^{\circ}_{298}$ of detoxication, KJ/mol
$AlO_3 \cdot 2SiO_2 + NaOH + 2H_2O = NaAlSi_2O_6 \cdot H_2O + 0,5(Al_2O_3 \cdot 3H_2O)$	-274,6	–	-275,45	–
$2(Al_2O_3 \cdot 2SiO_2) + 4NaOH + 4H_2O + Cd^{2+} = 2(NaAlSi_2O_6 \cdot H_2O) + Cd(OH)_2 + Al_2O_3 \cdot 3H_2O + 2Na^+$	-419,51	-144,9	-709,5	-434,05
$2(Al_2O_3 \cdot 2SiO_2) + 4NaOH + 4H_2O + Pb^{2+} = 2(NaAlSi_2O_6 \cdot H_2O) + Pb(OH)_2 + Al_2O_3 \cdot 3H_2O + 2Na^+$	-682,68	-408,5	-732,48	-457,03

**Table 4.** Reactions of geosphere preservation on the base of sulphates.

Reactions	$\Delta H^{\circ}_{298}$ , KJ/mol	$\Delta H^{\circ}_{298}$ of detoxication, KJ/mol	$\Delta G^{\circ}_{298}$ , KJ/mol	$\Delta G^{\circ}_{298}$ of detoxication, KJ/mol
$CaSO_4 \cdot 0,5H_2O + 1,5H_2O = CaSO_4 \cdot 2H_2O$	-18,0	–	-5,35	–
$2(CaSO_4 \cdot 0,5H_2O) + H_2O + Pb^{2+} = PbSO_4 + CaSO_4 \cdot 2H_2O + Ca^{2+}$	-58,12	-40,12	-29,42	-24,07
$2(CaSO_4 \cdot 0,5H_2O) + H_2O + Ba^{2+} = BaSO_4 + CaSO_4 \cdot 2H_2O + Ca^{2+}$	-71,86	-53,86	-42,40	-37,05

The third technique is a new alternative technology of lithosynthesis which is performed through lithoreactions. Lithoreactions are reactions in a mineral stone resulting from solution absorption by pores and capillaries, e.g. silica sol solution, and resulting in calcium silicate hydrate formation in a stone. This technology is an alternative to cement use. In the Table 5 the geochemical reactions of lithosynthesis which also use systems' internal energy are demonstrated.

**Table 5.** Lithosynthesis of calcium silicate hydrate formation with silica sol solution.

Reactions	$\Delta H^{\circ}_{298}$ KG/mol
$\text{Ca}(\text{OH})_2 + 2(\text{SiO}_2 \cdot \text{H}_2\text{O}) = \text{CaO} \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O} + \text{H}_2\text{O}$	-169,19
$2\text{CaO} \cdot \text{SiO}_2 \cdot 1,17\text{H}_2\text{O} + 2\text{SiO}_2 \cdot \text{H}_2\text{O} = 2\text{CaO} \cdot 3\text{SiO}_2 \cdot 2,5\text{H}_2\text{O} + 0,67\text{H}_2\text{O}$	-180,56
$6\text{Ca}^{2+} + 3(2\text{SiO}_2 \cdot 3\text{H}_2\text{O}) + 12\text{OH}^- = 6\text{CaO} \cdot 6\text{SiO}_2 \cdot \text{H}_2\text{O} + 14\text{H}_2\text{O}$	-287,89
$\text{Ca}^{2+} + 2(\text{SiO}_2 \cdot \text{H}_2\text{O}) + 2\text{OH}^- = \text{CaO} \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O} + \text{H}_2\text{O}$	-201,65

## 2 Methods

Experimental methods were applied as the base for artificial stone formation. Changes of internal energy were used for phosphate system hardening. At low temperatures (-15°C – -17°C) clay mixed with H3PO4 and some additives was hardened. Then it was tested for strength and compared with hardening at above-zero temperatures (+20°C – +22°C). For detoxication silica sol solution was used. Soils polluted by heavy metal ions, Pb(II), Cd(II) and others, to index of TC ≈ 1000 were saturated with 3-30% silica sol solution (where: TC – tolerable concentration of pollutants in soils, mg/kg; index of TC – number of TC to be detoxicated). After 1-7 days the aqueous extract was taken and investigated for heavy metal ion presence by means of selected electrodes.

For lithosynthesis an artificial stone like foam concrete with density 400-600 kg/m<sup>3</sup> was used. After 28 days of hardening foam concrete absorbed 3% silica sol solution and then its technical properties were examined.

## 3 Results and discussion

In the Tables 6, 7, 8 the results of the experiments are given. Based on the results listed in the Table 6 one can established that it is possible to obtain an artificial stone in geoconstruction:

1. at low temperatures;
2. through the reaction between clay and H3PO4.

**Table 6.** The properties of clay system when hardening at low temperatures (-15°C – -17°C).

Mix, %	H <sub>3</sub> PO <sub>4</sub> /mix	Strength, MPa 28 days of hardening	
		-15°C – -17°C	+20°C – +22°C
Clay – 20 Sand – 80 Additive, FeO, – 15 above clay and sand	0,21	60-80	65-75

**Table 7.** Analysis of the aqueous extract from the polluted soil of the system and its mix with silica sol after 1-3 days.

Heavy metal ions in the polluted soil	Index of TC	Analysis by means of qualitative reactions when mixing with silica sol
Cu(II)	≈1000	not found
Fe(III)	≈1000	not found
Ni(II)	≈1000	not found
Pb(II)	≈1000	not found
Cd(II)	≈1000	not found

**Table 8.** Improvement of foam concrete properties when applying sol absorption technology.

Density of foam concrete, kg/m <sup>3</sup>	Change of foam concrete properties, %; after 28 days			
	Compressive strength, +Δ%	Hardness, +Δ%	Cold resistance, cycles, +Δ%	Water absorption, -Δ%
400	10-15	≈30	10-25	65-35
500	10-15	≈40	10-25	60-30
600	15-20	≈50	10-25	60-30

Such a result can be explained according to the proceedings [7-14]. So, it is an example of systems' internal energy use for preservation of construction geosystems. The Table 7 illustrates detoxication processes by means of silica sol as a mineral geoantidote. It should be noted that silica sol is the purest substance for lithosphere and the best one for soil purification. As an aside, it is worth mentioning that silica sol forms coloured sediments with heavy metal ions. They are coloured because of reactions between SiO<sub>2</sub>·nH<sub>2</sub>O and heavy metal ions. Sediment colours can identify the reactions listed in the Table 9.

**Table 9.** Qualitative express method of heavy metal ion pollution identification.

Soil polluted by heavy metal ions (aqueous extract)	Sediment colours according to silica sol reaction
Cu(II)	turquoise
Fe(III)	rust
Ni(II)	light green
Pb(II)	white
Cd(II)	white

The Table 8 indicates quality improvement of the construction system by means of silica sol absorption. Its main property is water absorption decrease and it acts like the systems described in the papers [15-22].

## 4 Conclusions

1. Three techniques of lithosphere preservation are introduced, namely: energy economy, soil restoration and alternative technologies. The base of the first technique is internal energy use. The main point of the second one is reactions of detoxication which are accompanied by negative changes of Gibb's energy and formation of very low solubility product substances. The third technique is a new one as well, it being presented such technologies as lithoreactions and lithosynthesis.
2. When using the technique of energy preservation by means of geochemical reactions one can save hundreds of kilojoules per mol. The reactions with H<sub>3</sub>PO<sub>4</sub> were performed as an example and one can conclude that it is possible to use natural products in these reactions in order to obtain an artificial stone.

3. In the technique of lithosphere restoration mineral geoantidotes such as silicates, phosphates and others can be applied, one of the best mineral geoantidote being silica sol. In the technique of alternative technologies lithosynthesis shows good results. It uses absorption technologies which are based on pollution absorption capacity, i.e. silica sol is absorbed by pores and capillaries of a mineral stone and as a result calcium silicate hydrates are formed. Applying this technique one can increase technical and geocoprotective properties of geosystems.

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