

# Soling processes in technologies of civil engineering and environmental protection

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**Abstract.** The paper deals with soling technologies in civil engineering and environmental protection. The object of the interest is silica sol coating, which is formed when a concrete article gets hard in silica sol solution, as well as the sediments of silica sol soil detoxification. The main aim of the research is physical and chemical specificities of soling process. The methods of the study are electronic microscope scanning, x-ray analysis, derivatographic and chemical analysis. It has been found that in silica sol technology, layers of new phases are formed on the surface of cement concrete articles, e.g. calcium hydrates. The depth of the layers has been established. The nature of silica gel after heavy metal soil detoxification has been determined. The prospects of new sol-gel technologies are discussed.

## 1 Introduction

The paper deals with the topical issues of civil engineering and geosphere protection. The paper [1-6] presents new technologies of silica sol use for improvement of physical and mechanical properties of concrete by means of silica sol absorption and silica sol use in soil detoxification. Silica sol absorption technology (SAT) is used in hardening of cement concrete. The technology represents holding cement articles after 3 days of hardening in 3% sol solution for 24 hours. Portland cement, self-stressing cement and expanding cement were used for the research. According to the papers [7-12], table 1 shows the average level of improvement of physical and mechanical properties for articles made of various cements.

**Table 1.** Results of SAT-concrete.

Improvement of properties, $\Delta\%$ , class of concrete B30				
Compression strength, $+\Delta$	Bending strength, $+\Delta$	Water absorption, $-\Delta$	Abrasiveness. $-\Delta$	Frost resistance cycles, $+\Delta$
15-30	20-35	50-65	20-30	75-90

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More than that, silica sol solution can be used for soil detoxification against heavy metal ions. This article studies the reasons of concrete article properties improvement and soil detoxification.

## 2 Methods of analysis

To make an electron-microscope image of the silica gel sediments with heavy metal ions absorbed and layers on the concrete, we used the signals of secondary or reflected electrons (SE, RE) making it possible to obtain, respectively, a morphological or compositional contrast.

Determining the element composition of the samples is carried out by the method of electron probe microanalysis, which is based on comparing characteristic X-ray spectra of the analyzed sample and the standards of the known composition. The sensitivity of the method is ~ 0.1 wt. %.

Unanalyzed elements: H, Li.

X-ray phase analysis is based on collecting diffraction spectra of the reflection from the phase structures included in the sample and identifying them by catalogue. Amorphous component is not collected. Reflections with a big width of peaks may correspond to various isostructural phases with close parameters of the grid. The sensitivity of X-ray phase analysis is ~ 5 wt. % (provided the data of X-ray microanalyzer).

### 2.1 Equipment for the analysis

1. Scanning electron microscope (SEM) Vega 3SBH (Tescan);
2. Energy-dispersive X-ray microanalyzer (XRM) x-act Energy (Oxford Instruments);
3. Thermal spraying unit Q15R (Quortum technologies);
4. Diffractometer RIGAKU SmartLab3 (Rigaku);
5. Supporting equipment for sample preparation.

### 2.2 Analysis requirements

Scanning electron microscope: accelerating voltage - 30keV, WD=15mm, Probe current – 5·10-10A

X-ray microanalyzer: Voltage - 30keV, Probe current – 3·10-9A, Analysis time – 100 sec.

Diffractometer: Voltage – 40 kV, current – 30mA, monochromatic radiation CuK $\alpha$ , scanning speed – 2 gon/min, registration step – 0,01 degree, computerized registration of diffraction pattern. The processing and reading X-ray patterns was carried out in accordance with Rigaku programs using ASTM catalogue.

Sample preparation for sediments

XRM: representative powder sample was mechanically ground in the agate mortar. After that, it was put into the graphite slab with a bowl and then it was tamped. The graphite slab doesn't give background emission.

Diffractometer: the quantity of powder was ground in the agate mortar, then, was wet with alcohol, after that was put into the cuvette and was leveled with the cover-glass in the cuvette for the analysis.

Sample preparation for examining the concrete surface

For our research, we also used Scanning electron microscope (SEM) and X-ray microanalyzer (XRM) enabling to obtain the data about the morphology, element and phase composition around the cross-section of the samples towards the spread of the impregnating

composition. For this purpose, the cross-section in the central part was opened, and the samples were analyzed using the mentioned methods at the depth of 0,1,3,5,10,15,20 below the surface of the impregnation to obtain the comparative data about the layer-by-layer change in the materials.

The accuracy of the data obtained depends on the type of the opening of the sample which has a destroying effect on the sample. To minimize the damage, the opening was carried out using a specialized cutter (Buchler) by a thin diamond disc (0,3mm) at low rotation and minimum load and power. The cut sample was carefully blown over, was given a dry polish (without water) on a 10-micron abrasive, after that it was installed on the microscope board.

This type of sample preparation (dry polish without epoxy resin impregnation) makes it possible to preserve the original structure and composition of the samples, since the epoxy resin impregnation (or any other impregnating composition) of the samples with the developed surface leads to a considerable impoverishment of the overall picture. Using water medium in polishing may cause leaching, dissolution and modification of some components of the cement stone including new formations (hydroxide salts, hydrated silicates etc.)

To avoid unwanted effects related to recharging the non-conductive samples with electron beams, as well as to improve the contrast of X-ray images, a thin layer of Au (~200Å) was sputtered onto the samples using cathode sputtering unit JFC-1100 (JEOL). For SEM and XRM methods, we chose the zones of binder matrix (of the cement stone), the porous morphological structure of which determines the level and the specificities of the concrete sample impregnation.

As “indicator” of impregnation depth any element may be chosen with the concentration changing monotonously by the depth and different from the equilibrium one; or needle-shaped crystals of the new formations formed in the interaction of the impregnation composition and the cement stone.

### 3 Results and discussion

Tables 2-5 show the results of concrete articles. Tables 6-7 and Figure 1 present the results of sediments of silica gel with heavy metal ions.

**Table 2.** The data of layer-by-layer X-ray image of the Portland cement sample impregnated with 3% silica sol (% wt).

h,mm	CaO	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	MgO	SO <sub>3</sub>	Na(K)OH
0	57,1	27,0	9,0	2,1	1,6	2,5	0,7
1	59,9	25,3	6,9	3,0	2,0	1,9	1,0
2	61,9	24,2	5,5	3,3	1,8	2,2	1,1
3	63,3	23,8	4,7	3,2	2,0	2,2	0,8
5	64,5	23,5	4,0	3,1	1,8	2,3	0,8
>10*	<b>64,6</b>	<b>23,3</b>	<b>4,0</b>	<b>3,0</b>	<b>1,9</b>	<b>2,2</b>	<b>1,0</b>

\*The sample is not exposed to silica sol and its chemical composition is the same as the composition of the reference sample.

**Table 3.** The data of layer-by-layer X-ray image of the self-stressing cement sample impregnated with 3% silica sol (% wt).

h,mm	CaO	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	MgO	SO <sub>3</sub>
0	52,0	24,0	12,5	0,0	1,0	10,0
1	53,8	22,8	12,4	1,2	0,6	8,9
1,98	55,0	21,3	12,4	2,6	0,6	7,7

3	56,1	19,9	13,0	3,4	0,7	6,5
4,94	57,4	18,1	13,4	4,7	0,6	5,2
>10*	<b>57,5</b>	<b>18,0</b>	<b>13,0</b>	<b>5,0</b>	<b>1,0</b>	<b>5,0</b>

\*The sample is not exposed to silica sol and its chemical composition is the same as the composition of the reference sample

**Table 4.** The data of layer-by-layer X-ray image of the expanding cement sample impregnated with 3% silica sol (% wt).

h,mm	CaO	SiO2	Al2O3	Fe2O3	MgO	SO3	Na(K)OH
0	52,0	24,1	12,5	0,0	0,9	10,0	0,5
1	49,8	20,6	16,5	0,5	1,3	10,6	0,7
2	48,3	17,7	20,0	1,0	1,0	11,5	0,5
3	47,2	15,8	22,5	1,5	1,1	11,1	0,9
5	46,2	14,5	24,5	1,9	0,8	11,5	0,6
>10*	<b>46,0</b>	<b>14,0</b>	<b>25,0</b>	<b>2,0</b>	<b>1,0</b>	<b>11,5</b>	<b>0,5</b>

\*The sample is not exposed to silica sol and its chemical composition is the same as the composition of the reference sample

**Table 5.** Summary of the samples impregnated with 3% silica sol.

Sample	hre, mm	hxrmm, mm	hnf, mm	S/S0 %	n/f	Morphological types of n/f
Portland cement	1,5	3,5	5	33	+	CSH Tobermorite Ettringite
Self-stressing cement	2,0	4,0	7	37	+++	
Expanding cement	2,5	3,8	7	40	++++	

hre – depth of impregnation, determined by contrast in RE,

hxrmm – depth of impregnation determined by the change of chemical composition in the surface layer using X-ray microanalyzer,

hnf - maximum depth at which characteristic new formations were found using scanning electronic microscope,

S/S0 – the square occupied by micropores and microfractures (characterizes the level of permeability of the sample),

n/f – new formations represented by needle-like crystals and flakes and their density.

The data of XRM and SEM in RE shows that 90% of the impregnation composition (silica sol particles) is concentrated in pre-surface layer, where the highest density of new formations is observed.

With increasing the depth, the density and the size of the new formations, represented by sol particles and crystalline hydrates, reduces.

Table 6 shows the data obtained by averaging the results of XRM for 20 particles of each sample.

**Table 6.** Data of X-ray microanalyzer (% wt).

№	N	O	Na	Mg	Si	Cl	K	Fe	Cu	Pb	C
1,2	-	53.4	0.7	0.5	46.9	-	-	-	-	-	4
3	-	52.3	0.3	-	45.4	-	-	-	1.9	-	2
4	-	53.9	0.1	-	42.3	-	-	-	0.1	3.7	2
5	-	52.5	-	-	46.0	0.2	-	1.1	0.1	-	2

1,2 – control, SiO<sub>2</sub>·nH<sub>2</sub>O;

3 – sediment with Cu(II);

4 – sediment with Pb(II);

5 – sediment with Fe(III).

Table 7 shows the difference between control  $\text{SiO}_2 \cdot n\text{H}_2\text{O}$  and Cu(II) and Pb(II).

**Table 7.** Derivatogram calculation.

Systems	Mass, mol, ion	Water loss according to derivatogram, %
Silica Sol-Ca(II)	40	25,02
Silica Sol-Cu(II)	63,5	9,0
Silica Sol-Pb(II)	207,	9,89

The sediments with heavy metal ions are characterized by a very high degree of condensation. All sediments are roentgen amorphous.

The works on concrete article surface modification and heavy metal ion soil detoxification unite the mechanisms of reactions  $\text{SiO}_2 \cdot n\text{H}_2\text{O}$  studied by Russian school of academician V.B. Aleskovsky [14-22]. In accordance with these works, it can be assumed that the processes of  $\text{SiO}_2 \cdot n\text{H}_2\text{O}$  interaction are controlled by the value of solubility product, SP, at the initial act of interaction represented by sorption. Each substance formed has its own composition and represents an individual compound, in so doing, solubility product for polysilicic salts is small and in the works of V.B. Aleskovsky it is called sorbability product.

**Table 8.** Sorbability product and solubility products of hydroxides of polysilicic acids.

Metal ions	Polysilicic salts		Hydroxides	
	Sorb.product	C, mol/l	Sorb.product	C, mol/l
Ca(II)	$10^{-9}$	$7 \cdot 10^{-5}$	$5,5 \cdot 10^{-6}$	$1,1 \cdot 10^{-2}$
Mg(II)	$4 \cdot 10^{-12}$	$2 \cdot 10^{-6}$	$1,8 \cdot 10^{-11}$	$1,65 \cdot 10^{-3}$
Al(III)	$10^{-60}$	$10^{-12}$	$10^{-32}$	$5 \cdot 10^{-9}$
Cd(II)	$4 \cdot 10^{-14}$	$10^{-7}$	$2 \cdot 10^{-14}$	$1,8 \cdot 10^{-5}$
Zn(II)	$10^{-17}$	$7 \cdot 10^{-9}$	$7,1 \cdot 10^{-18}$	$1,2 \cdot 10^{-6}$

In accordance with Table 8, the salts of polysilicic acids, as a rule, have lower values than hydroxides (columns 3 and 5) or in certain cases close to Cu(II).

The obtained data in this article, thermodynamic calculations made by us before [1-6], the data of Table 8 illustrate the potential of hydrated silicates and polysilicates responsible for the improvement of material properties in SAT-technologies. They increase the durability of the materials of civil engineering; in detoxification technologies they form low-soluble compounds of heavy metal ions, which is detoxification.

In accordance with the data obtained, it is possible to outline the prospects of silica sol use in civil engineering and environmental protection:

- production and use of modified  $\text{SiO}_2 \cdot n\text{H}_2\text{O}$  both by cation and by anion. It will improve concrete physical-mechanical properties and durability, since increasing complexity of phases increases the level of their durability accompanied by the increase of internal energy of the system;

- production of modified  $\text{SiO}_2 \cdot n\text{H}_2\text{O}$  aggregate for concretes which may affect contact properties and improve spiral properties, e.g. bending strength;

- expanding the possibility to use mineral technogenic raw materials by pre-treating their surface in order to detoxify and modify it.

## 4 Conclusions

1. The study examines the depth and the composition of the surface of the articles made of concretes of various cements, hardening in sol absorption technology. The article shows the formation of new phases as hydrated silicates which may improve the material properties.
2. The research shows that heavy metal ions form chemical compounds, mainly silicates, in silica sol soil detoxification technologies.
3. The article outlines the prospects of soling technology use in civil engineering and environmental protection from pollution.

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