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CONTAMINATED SITES 2018

BANSKÁ BYSTRICA, SLOVAK REPUBLIC, 8 – 10 OCTOBER 2018

The activity has been implemented within the framework of national project
***Information and providing advice on improving the quality of environment in Slovakia**.*
The project is cofinanced by Cohesion Fund of the EU under Operational programme Quality of Environment.

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SILICON-BASED APPROACH TO DETOXIFICATION AND PURIFICATION OF CONTAMINATED SITES

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The activity has been implemented within the framework of national project ***Information and providing advice on improving the quality of environment in Slovakia****. The project is cofinanced by Cohesion Fund of the EU under Operational programme Quality of Environment.*

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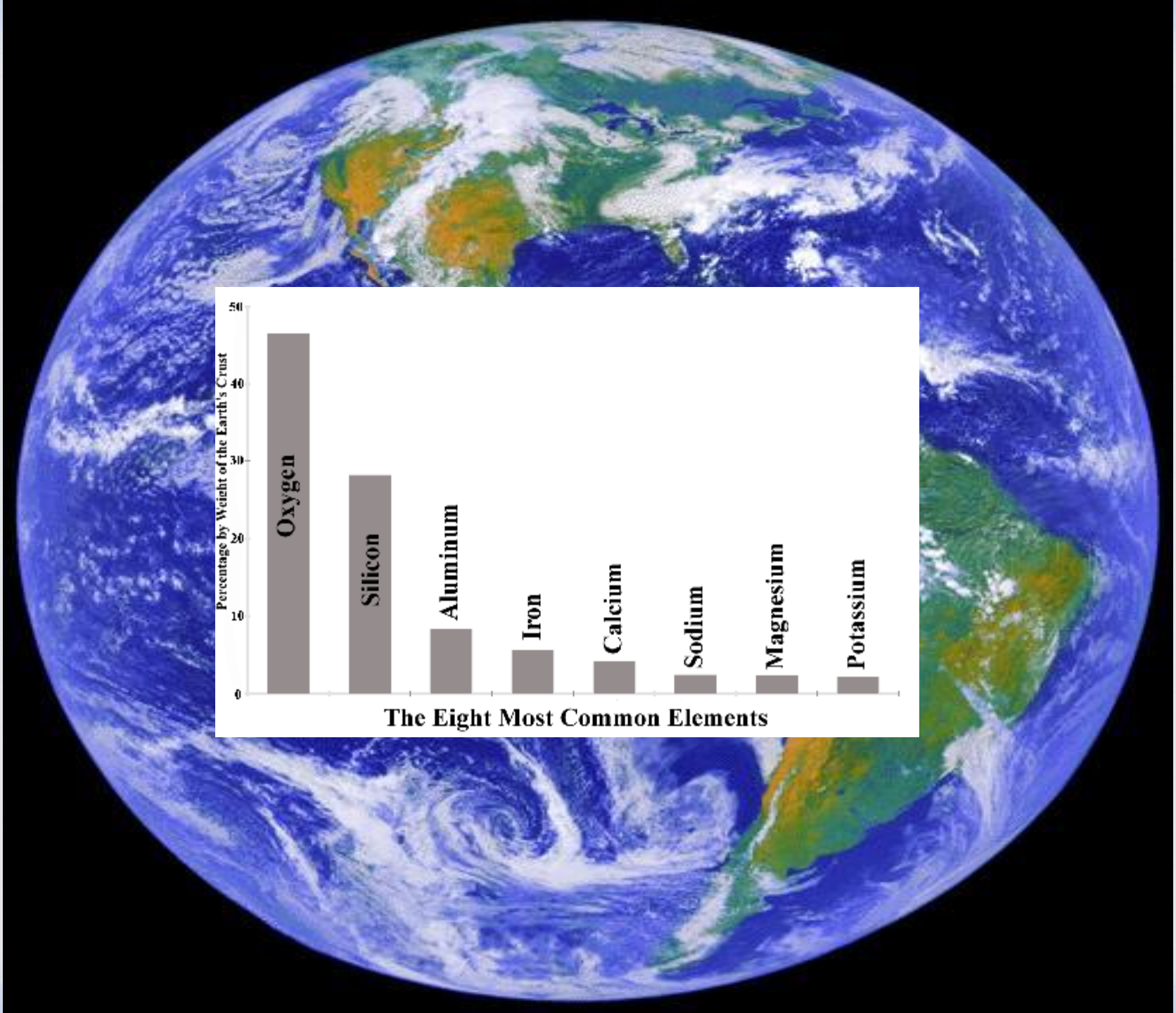
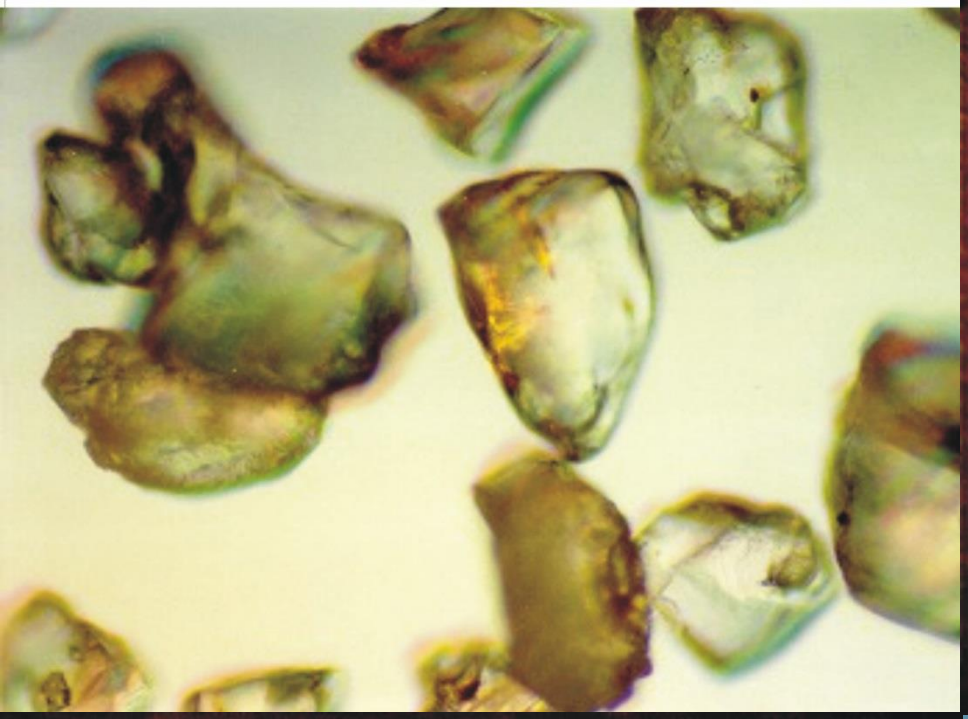
SLOVAK ENVIRONMENT AGENCY


Percentage by Weight of the Earth's Crust
50
40
30
20
10
0
Oxygen
Silicon
Aluminum
Iron
Calcium
Sodium
Magnesium
Potassium
The Eight Most Common Elements

Silicon content in the Earth's crust

Earth's crust	% SiO_2
Deep Earth's crust	53.1
Continental Earth's	59.1 – 64.8
Soils	
Clay soils	40 – 70
Sandy soils	90 - 98



RELATIVE MOBILITY OF ELEMENTS UNDER WEATHERING

(BY POLYNOV) 风化作用下的元素流动性

Energetic carry out: 易风化 Cl, Br, I, S

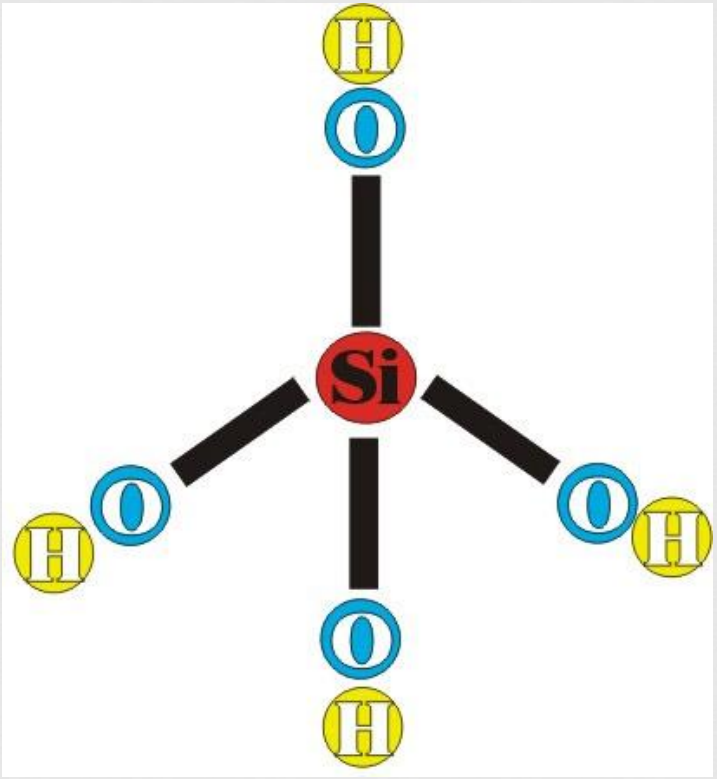
Lightly carry out: 弱风化 Ca, Na, K, Mg

Mobility: 移动性 Si, P, Mn

Weak mobility: 弱移动性 Fe, Al, Ti

Unmobility: 稳定性 SiO_2 (quartz)

Monosilicic acid



Monosilicic acid impacts heavy metal behavior through

1) formation of insoluble silicates;

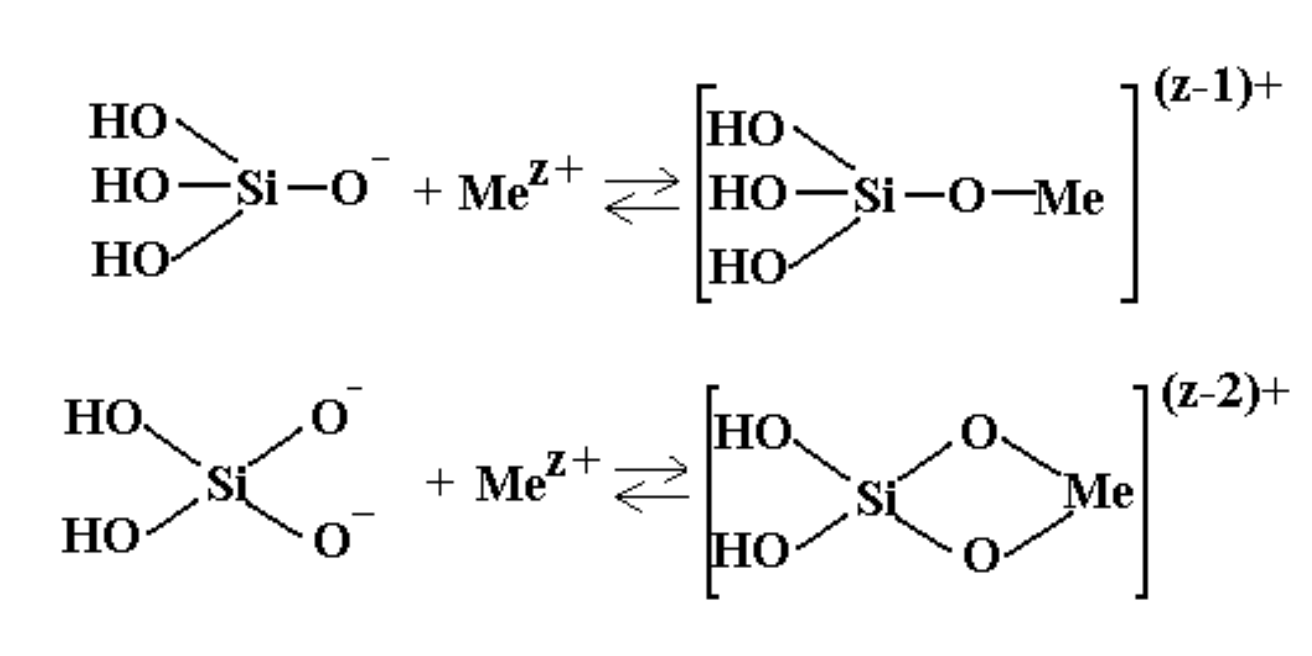
2) formation of water soluble complexes;

3) providing new area for HM sorption on solid materials.

Formation of heavy metal silicates

	logKo
$Pb^{2+} + H_4SiO_4 = PbSiO_3\downarrow + 2H^+ + H_2O$	5,94
$2Pb^{2+} + H_4SiO_4 = Pb_2SiO_4\downarrow + 4H^+ + H_2O$	18,45
$2Zn^{2+} + H_4SiO_4 = ZnSiO_4\downarrow + 4H^+$	13.15
$H_4SiO_4 + 2\ Cd(OH)_2 = Cd_2(SiO_4)\downarrow + 4\ H_2O$	
$H_4SiO_4 + Cd^{2+} = CdSiO_3\downarrow + H_2O + H^+$	
$A1_20_3.2Si0_2 + CdCI_2 + H_2O = CdOAl_2O_32SiO_2\downarrow + 2HC1$	

Formation of water soluble complexes



Where Me is any heavy metal (Schindler et. al., 1976) .

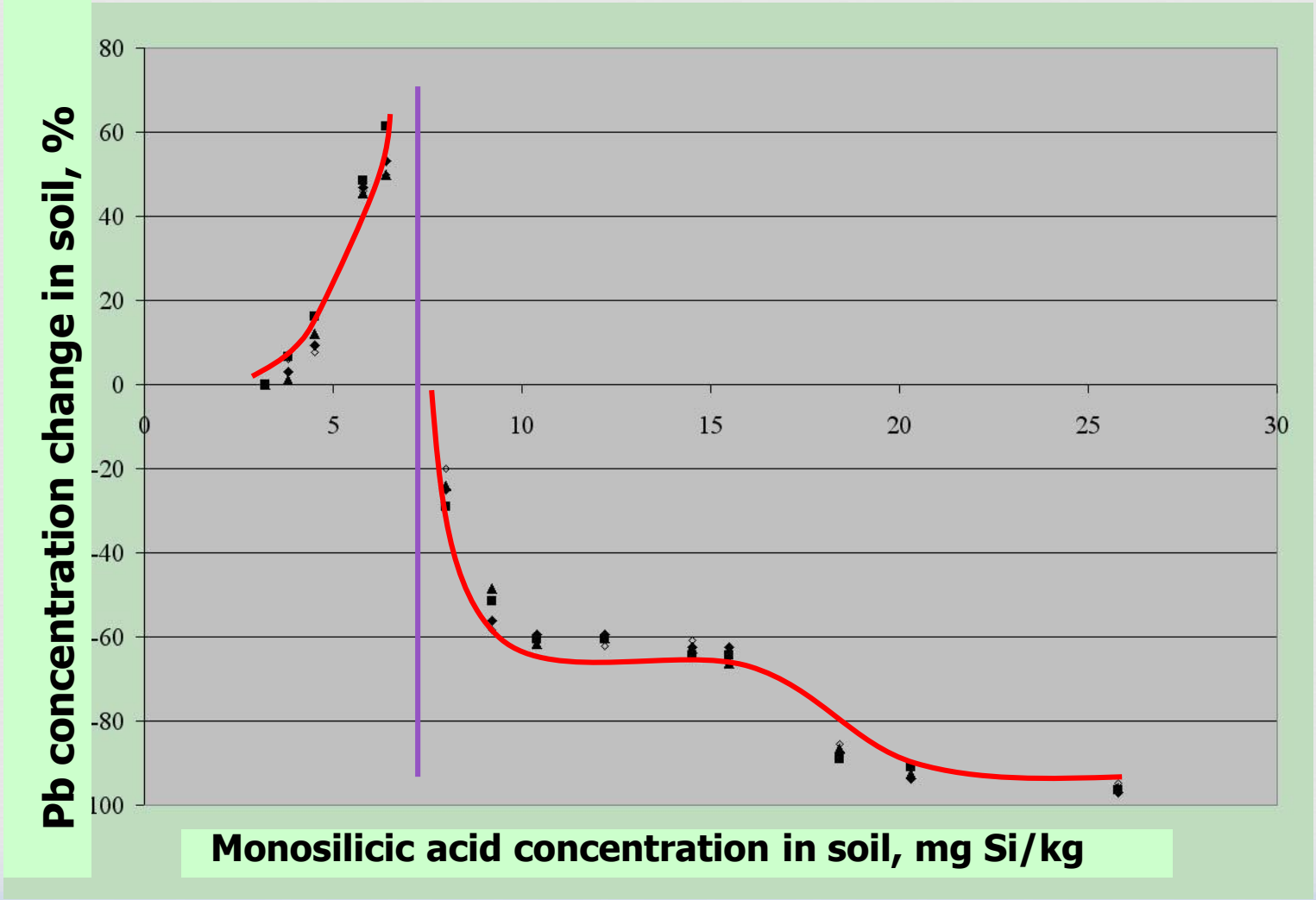
Effect of monosilicic acid on heavy metal mobility

1. Increasing mobility of heavy metals.
2. Decreasing mobility of heavy metals.

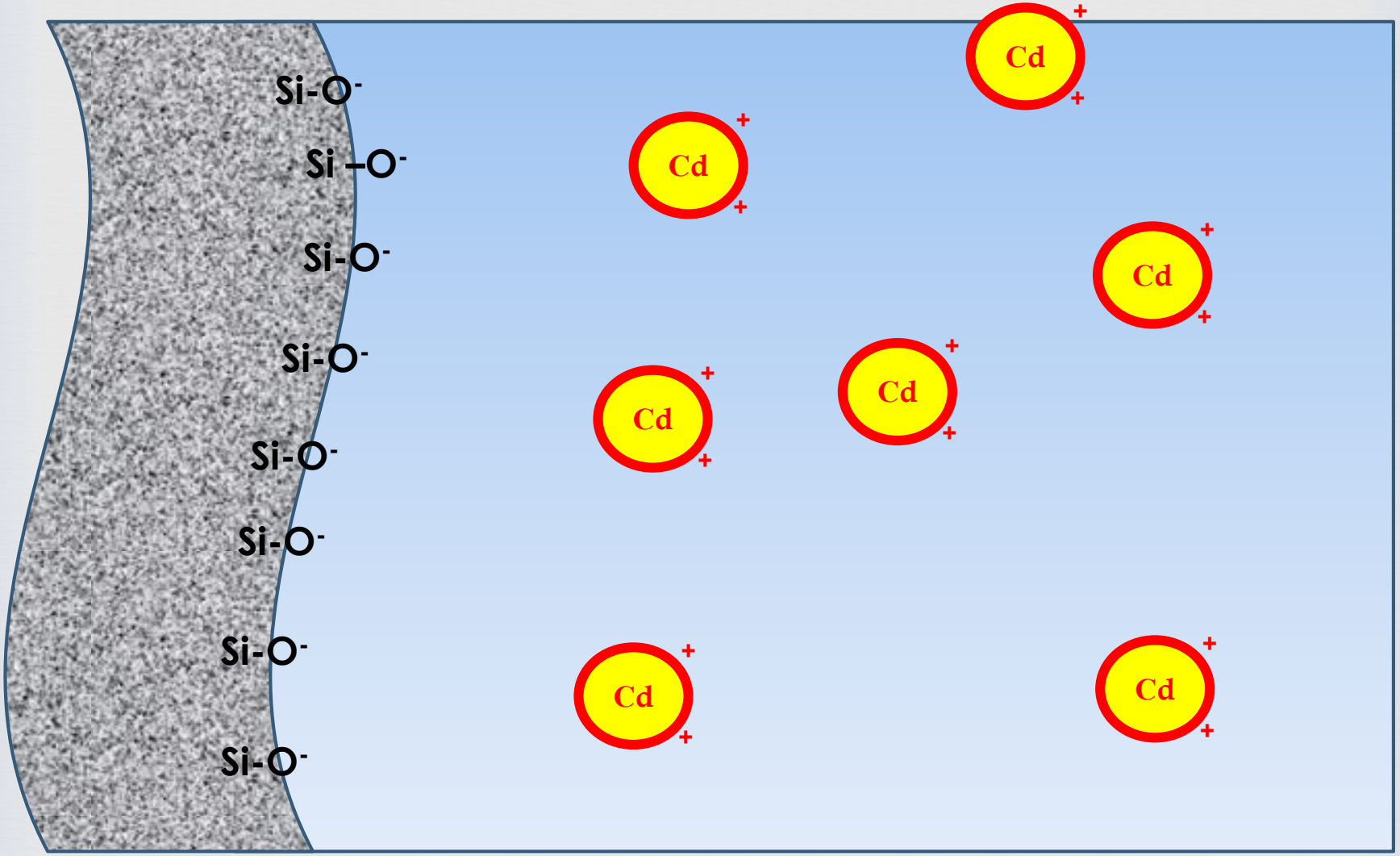
Effect of monosilicic acid concentration on Pb solubility in soil

Phytoremediation

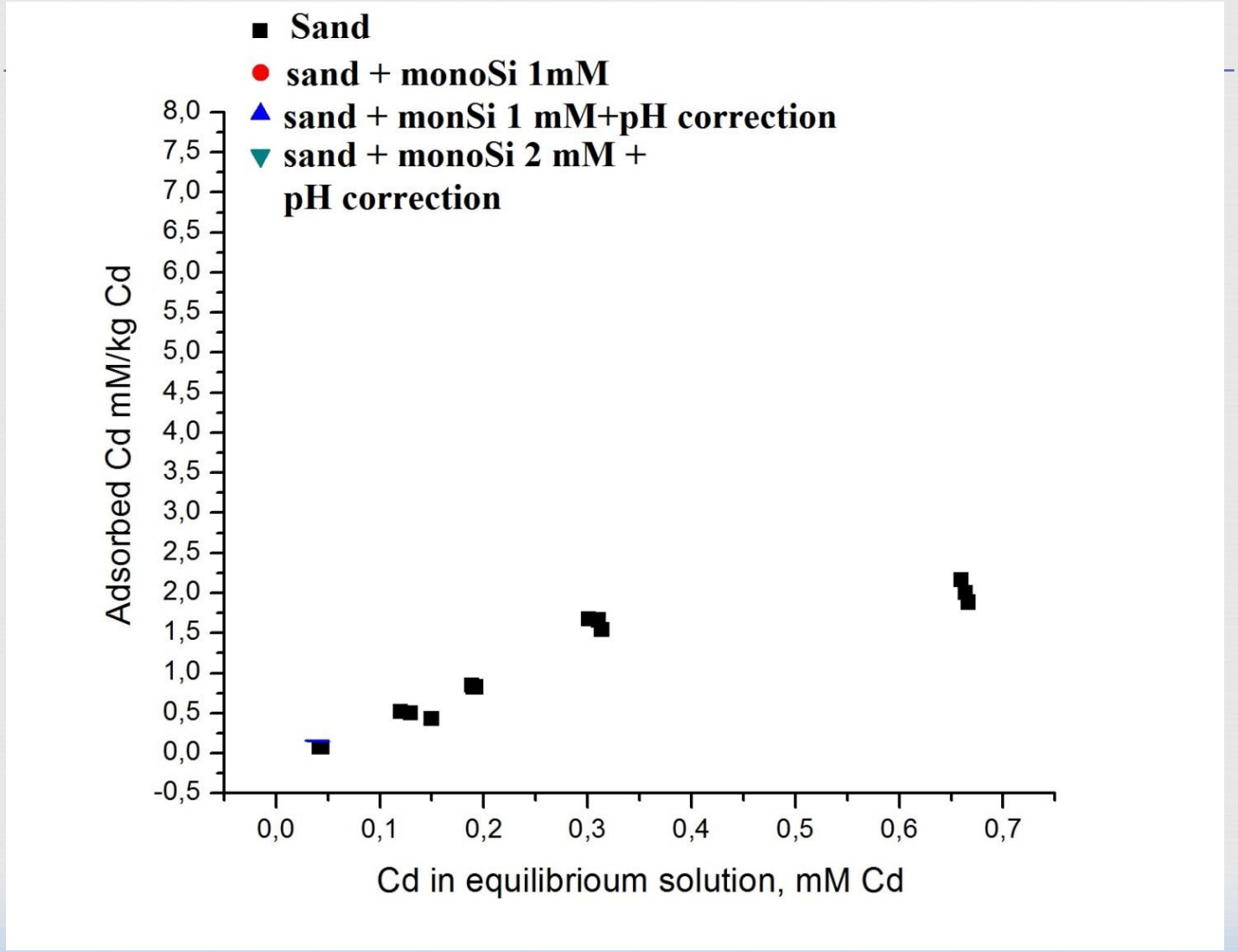
Deactivation, precipitation



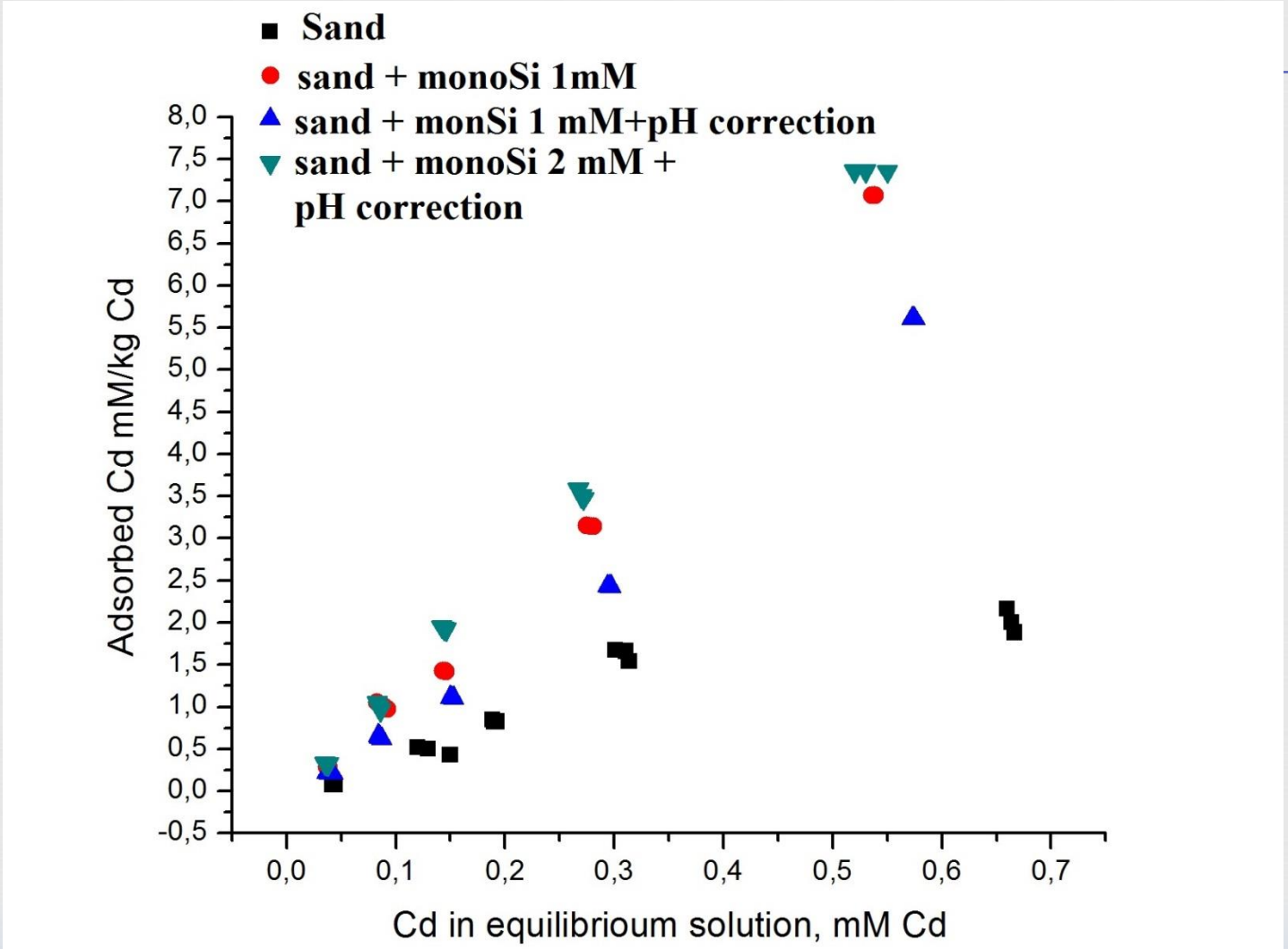
Reaction with solid Si-rich substances in soil



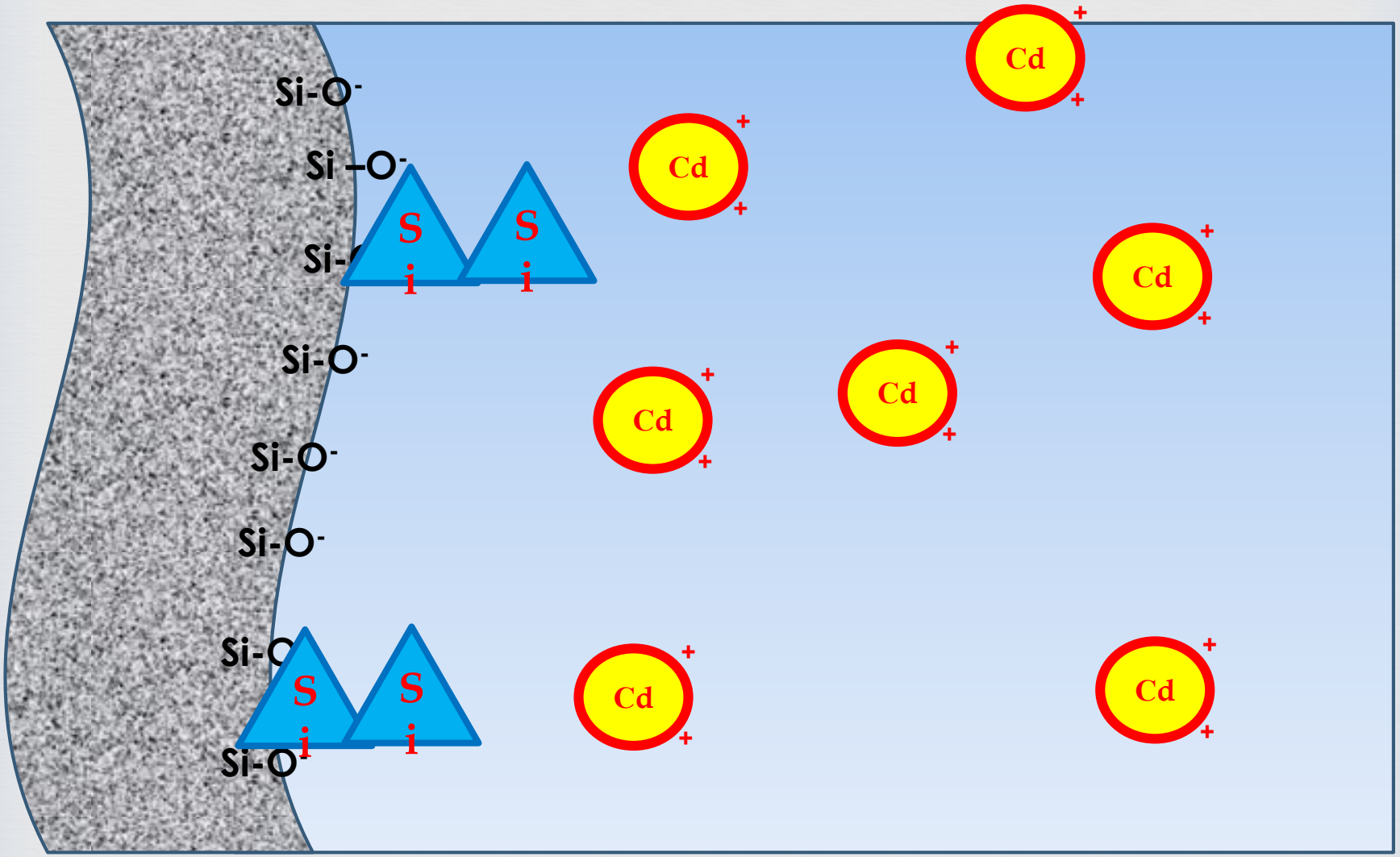
Adsorption test



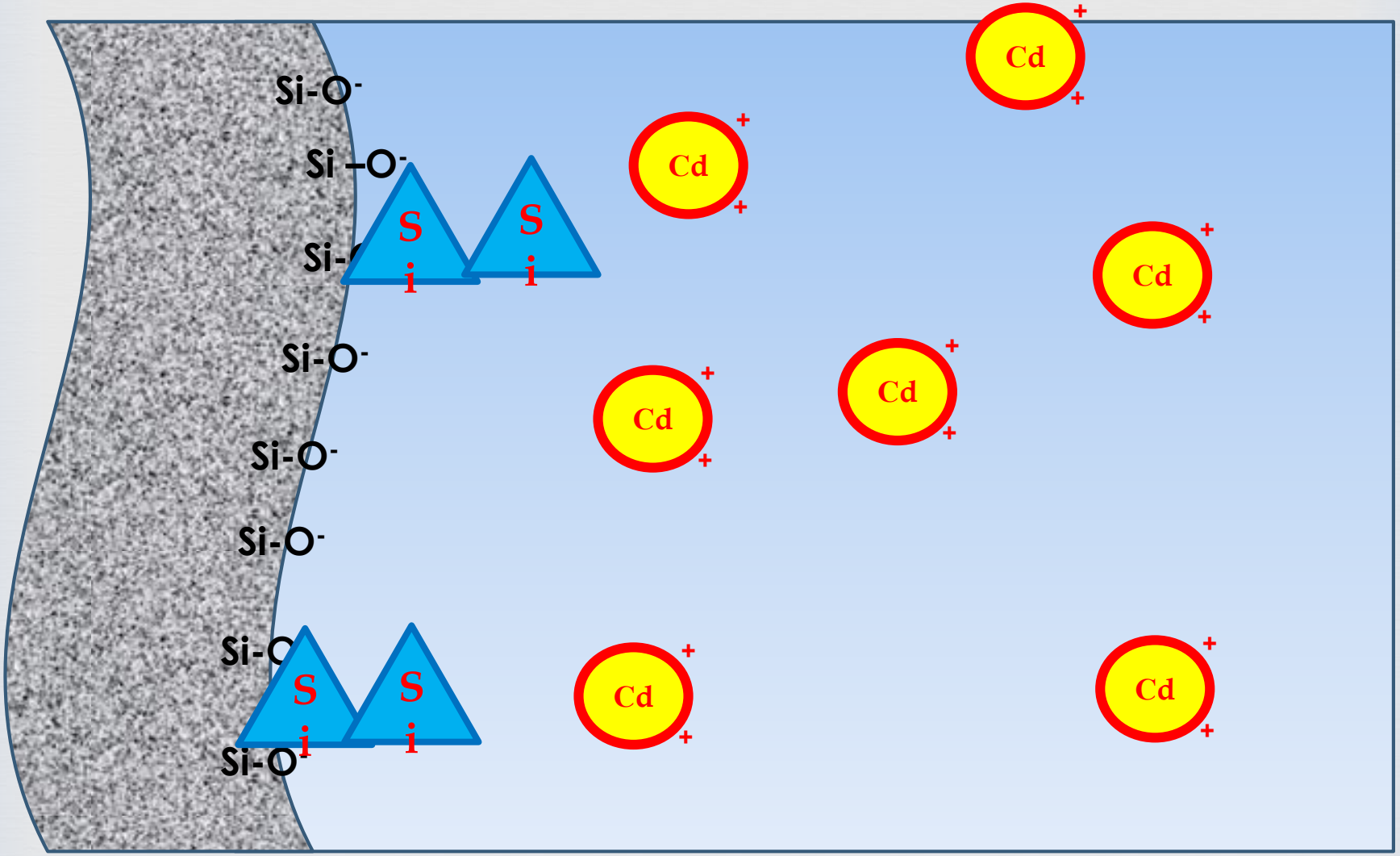
Adsorption test



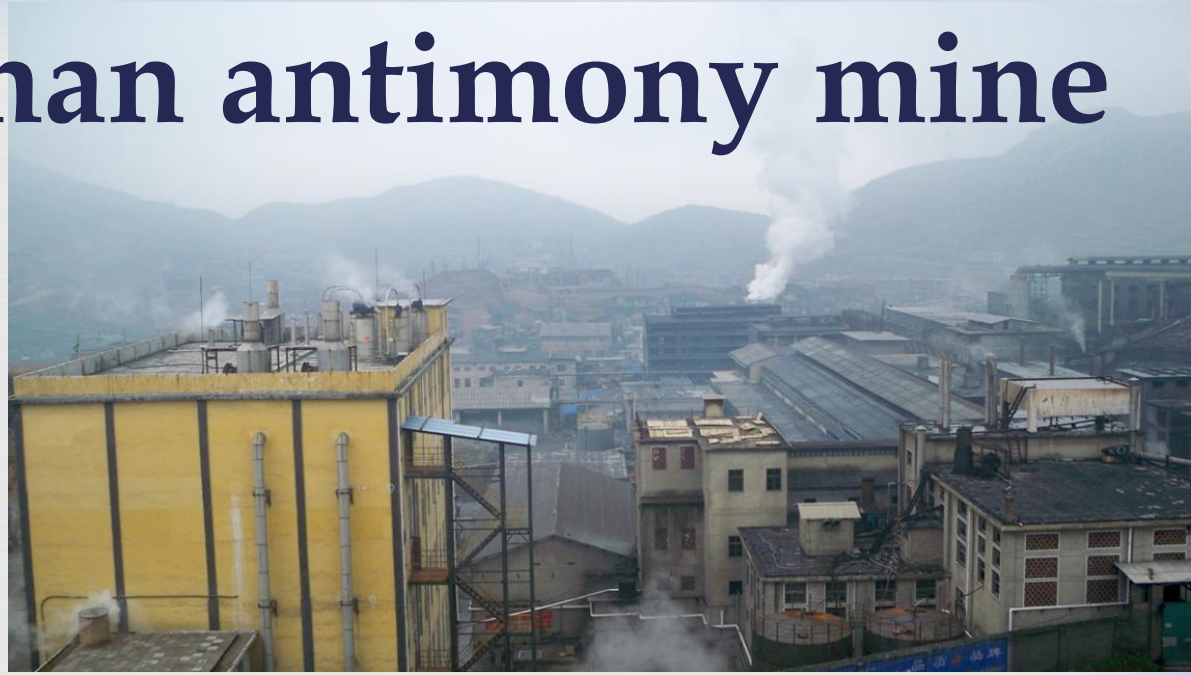
Reaction with solid Si-rich substances in soil



Reaction with solid Si-rich substances in soil

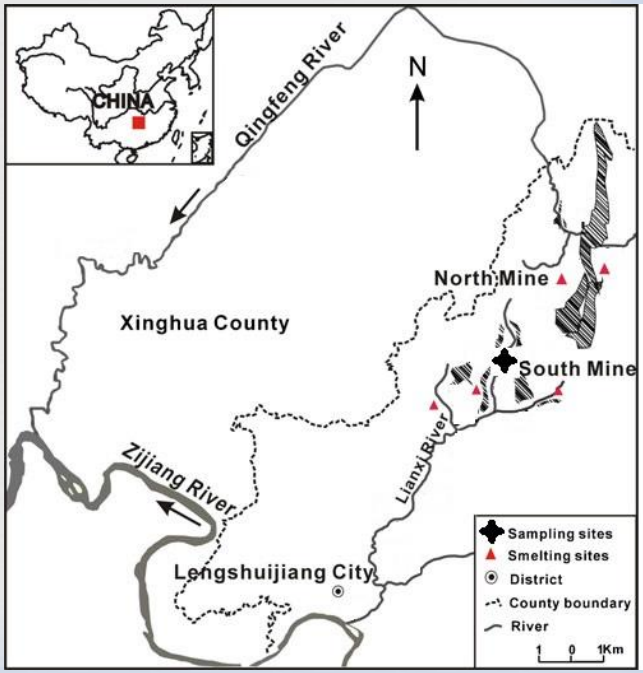


Xikuangshan antimony mine



The largest antimony deposit in the world.

The annual production capacity of the Xikuangshan Sb mine is 40,000 metric tons of Sb products and 40,000 metric tons of zinc ingots.



Concentration of selected pollutants in waste-water from Xikuangshan mine area.

Element	As	Cd	Cu	Hg	Ni	Pb	Se	Sb
	----------ppm----------							
MPC*	0,05	0,005	0,001	0,005	0,01	0,006	0,01	0,05
Waste-water	7,9	0,25	0,54	0,14	0,020	1,42	13,3	14,5

*MPC- maximum permissible concentration for water (Russian Federation)

Content of mobile and potentially mobile pollutants

	As	Cd	Cr	Hg	Ni	Pb	Se	Sb
	----------mg kg-1----------							
Mobile forms (0,1 n HCl)								
Contaminated site	30, 4	5,2	2,7	0,83	1,64	15,6	17,43	45,2
Potentially mobile forms (2 n HNO_3)								
Contaminated site	140,2	5,11	3,82	n/d	4,97	83,6	n/d	176,4

Complex solution of the problem

Xikuangshan mine

Sb, Se, As problems

Metallurgical enterprise

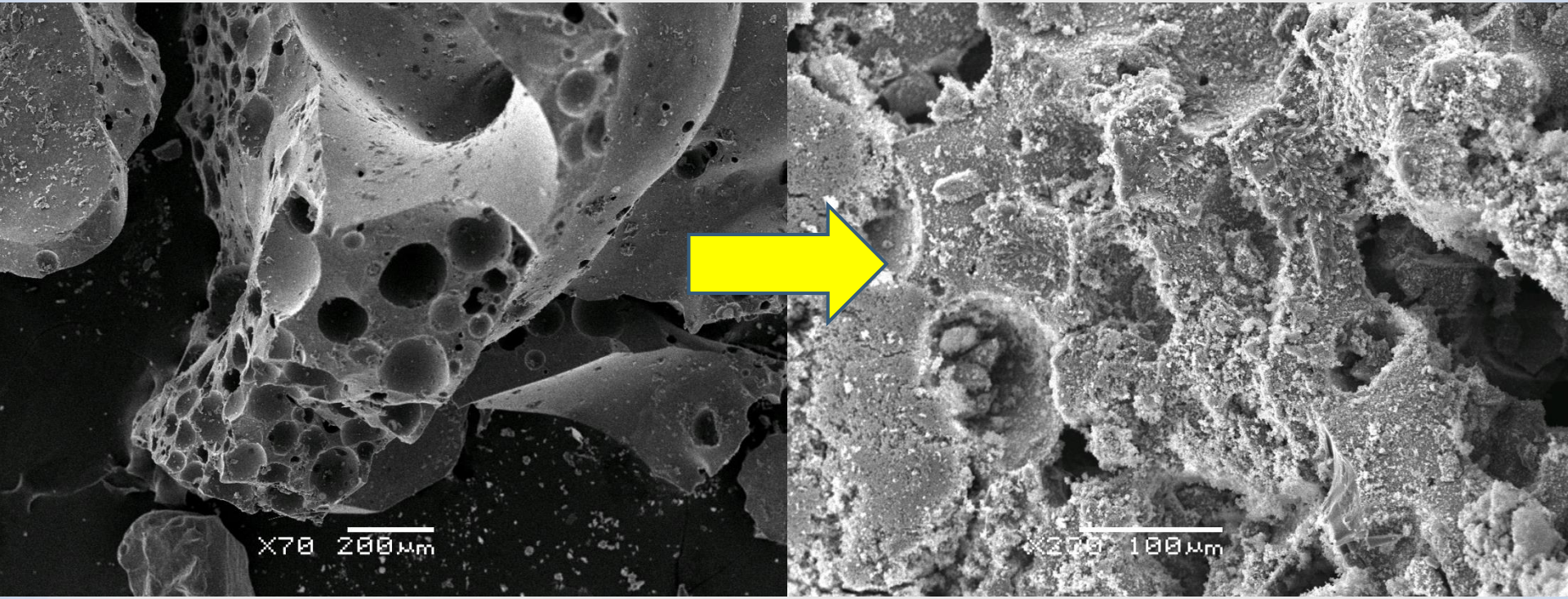
Slag utilization problem

Lengshuijiang Iron & Steel Co. Ltd.

The company mainly produces, processes and markets screw steel, steel wire, hot-rolled steel plate and fasteners with using iron ore from Australia. Founded in 1958, after 50 years the production scale of enterprises has reached 3 million tons of steel production, steel production 3.2 million tons. Total assets 4,000,000,000 yuan now, annual sales income of over 10 billion yuan. Enterprise ranked top 500 Chinese enterprises, China's top 500 manufacturing, iron and steel enterprises in the world 200 strong, reinforced concrete rolled ribbed steel in 2007 was "Hunan Provincial Famous Brand" title.

Slag

Slag activation



1 kg of Slag + 20 mL 20% (Si) of monosilicic acid, drying at +65°C

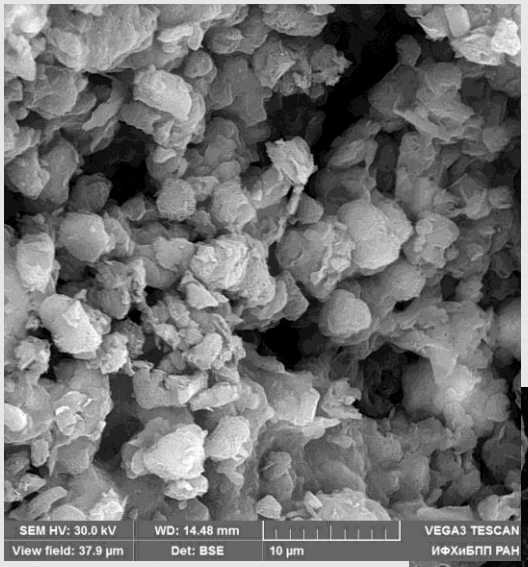
To determine the possibility to resolve the problem using local sources:

a) column test with Si-based substances;

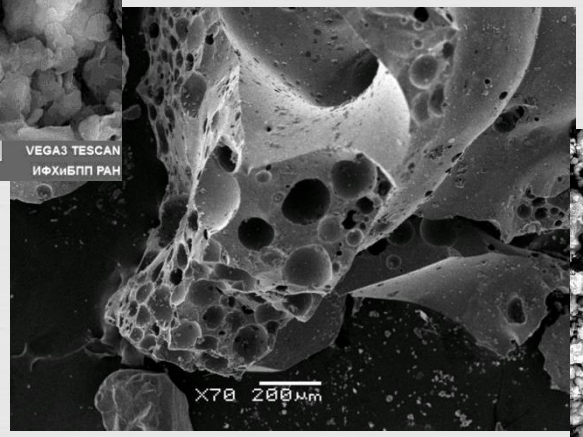
b) greenhouse (incubation) test with Si-based substances.

Materials:

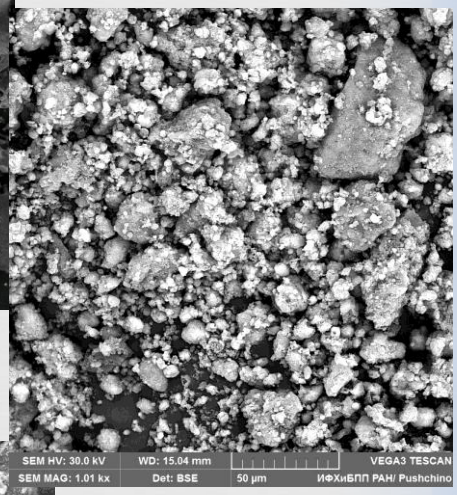
Zeolite



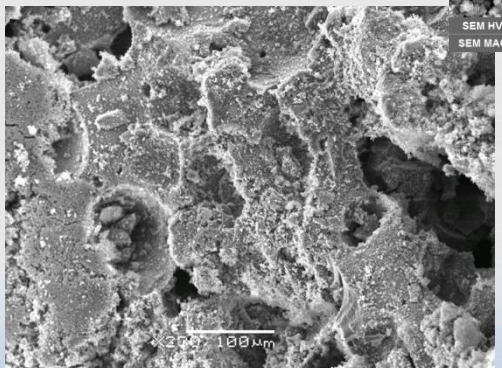
Slag



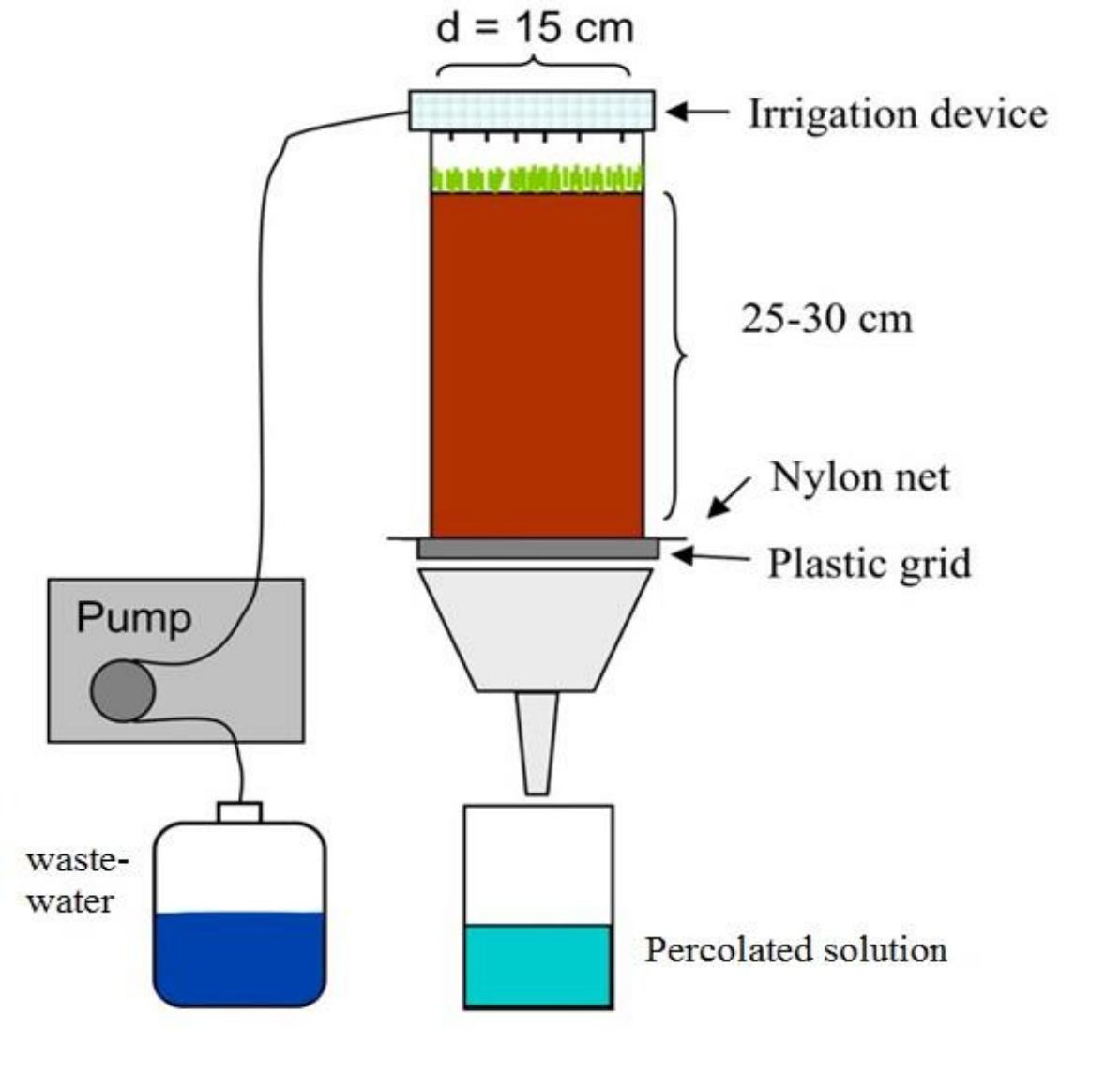
Activated zeolite (A-Zeolite)



Activated slag (A-Slag)



Column test


d = 15 cm
Irrigation device
25-30 cm
Nylon net
Plastic grid
Pump
waste-
water
Percolated solution

Column test

Element	As	Cd	Cu	Hg	Ni	Pb	Se	Sb
	----------ppm----------							
MPC*	0,05	0,005	0,001	0,005	0,01	0,006	0,01	0,05
Waste-water	7,9	0,25	0,54	0,14	0,02	1,42	13,30	14,51
Zeolite	5,4	0,12	0,33	0,09	0,01	0,93	10,32	5.6
Slag	7,5	0,20	0,50	0,10	0,01	1,21	11,46	10,2
A-Zeolite	1,2	0.03	0,12	0.03	n/d	0,34	4,52	2,5
A-Slag	0,4	0.04	0,08	0.03	n/d	0,32	2,45	2,1
LSD_{05}	0,1	0.01	0,02	0.01	0,01	0,03	0,10	0,3

*MPC- maximum permissible concentration for water (Russian Federation)
n/d – not detectable level

Greenhouse test

Materials (quartz sand:tailings – 1:1);

Application rate: 10 t ha^{-1};

Zeolite, Slag, Activated zeolite, Activated Slag;

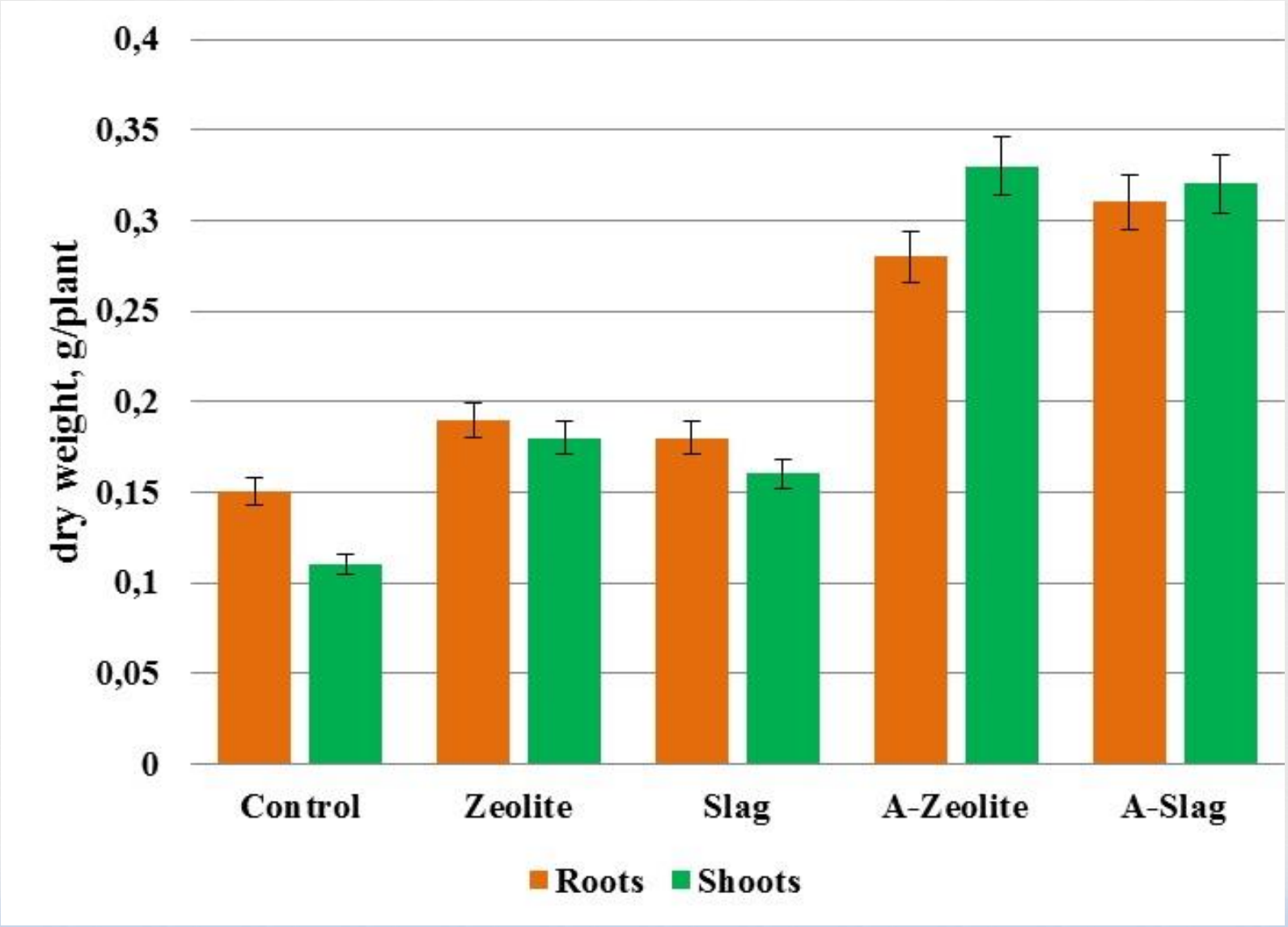
Plant: rice (*Oryza sativa* L.);

3 weeks;

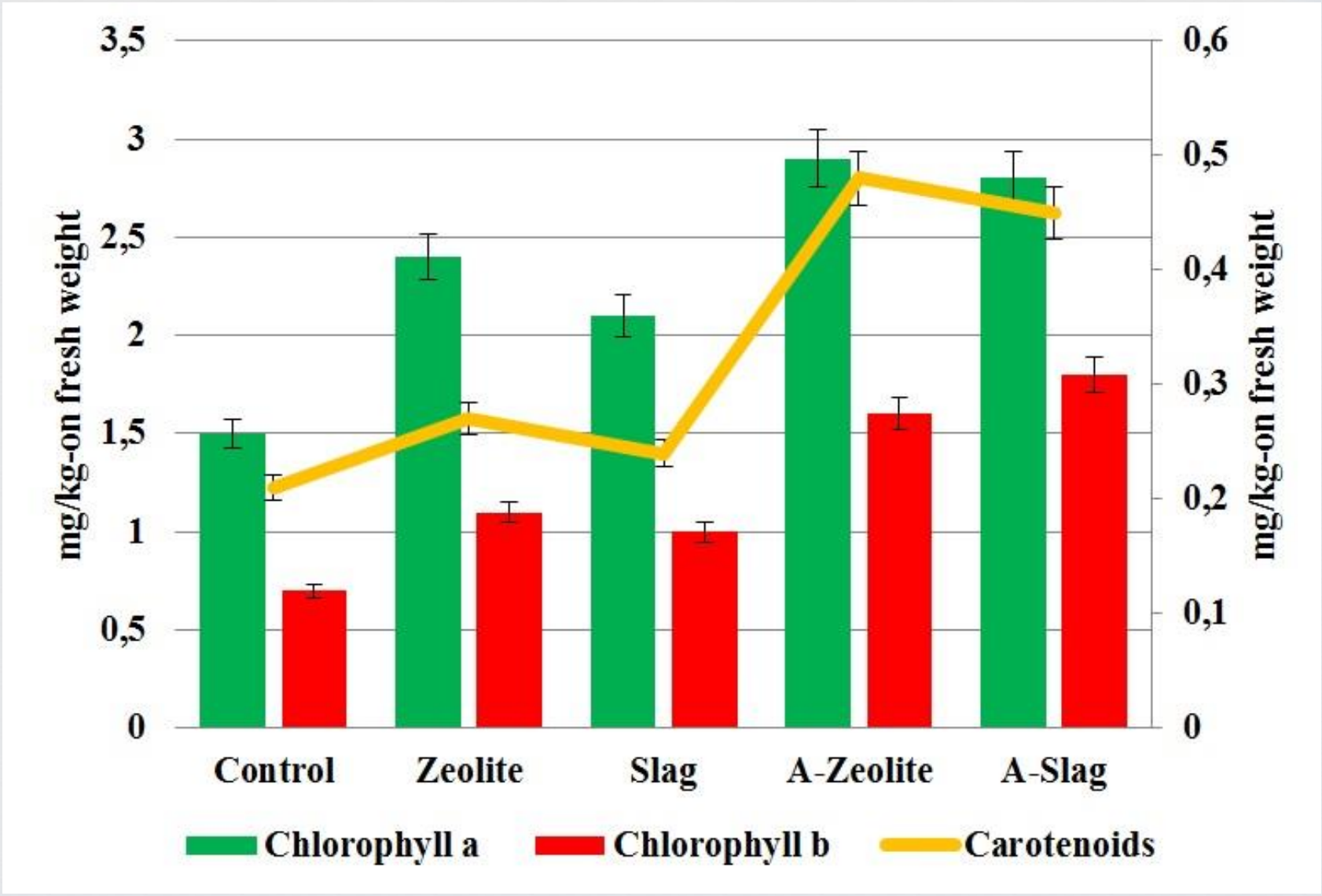
Biomass;

Chlorophyll content.

Effect of Si-rich materials on rice biomass



Effect of Si-rich materials on chlorophyll content in rice leaves



Mobile forms (0.1 n HCl-extractable) of pollutants in greenhouse test, mg kg^{-1}

	As	Cd	Cu	Hg	Sb	Pb
Control	30.5	5.4	25.3	0.82	6.6	12.3
Zeolite	3.4	2.1	10.4	0.34	3.5	4.5
Slag	15.6	3.2	18.9	0.57	4.4	7.6
A-Zeolite	2.1	0.6	4.5	0.05	0.4	0.4
A-Slag	2.0	0.6	5.0	0.04	0.6	0.5
LSD_{05}	0.2	0.1	0.2	0.01	0.1	0.1

Potentially mobile forms (2 n HNO_3-extractable) of pollutants in greenhouse test, mg kg^{-1}

	As	Cd	Cu	Hg	Sb	Pb
Control	128	6.7	78	n/d	10.3	80
Zeolite	35	4.3	43	n/d	4.5	45
Slag	89	5.5	66	n/d	7.6	76
A-Zeolite	12	1.2	12	n/d	1.2	21
A-Slag	25	1.3	14	n/d	1.1	18
LSD_{05}	5	0.2	4	-	0.2	3

Mechanisms

Chemical interaction between monosilicic acid and heavy metal with the formation of slightly soluble or insoluble silicates.

Inorganic pollutants are chemically adsorbed on the surface of Si-rich materials.

Both metal and non-metal pollutants are physically adsorbed by Si-rich substances.

Improved plant Si nutrition provides enhancement of plant defense system against pollutant-induced toxicity.

Conclusions

The data obtained has demonstrated high potential of Si-rich substances to reduce the toxicity and mobility of pollutants at a contaminated site.

Silicon-rich substances (local industrial by-products) can be used as filters for reducing the concentrations of metal and non-metal pollutants in mine or industrial waste-waters.

Thank you for attention!