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TECHNICAL ARTICLE

Reduction of Cd, Cu, Ni, and Pb Mobility by Active Si in a Laboratory Study

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Abstract Soluble forms of Si and Si-rich substances may reduce both metal mobility and toxicity. A series of column experiments were performed to investigate the influence of Si-rich materials on the mobility and leaching potential of certain metals. Column experiments were conducted using sandy soil that had been treated with various forms of a Si-rich substance, i.e. diatomaceous earth, zeolite, amorphous silicon dioxide, and concentrated monosilicic acid. The soil was also treated with soluble forms of Cd, Cu, Ni, and Pb to simulate a contaminated mine site. Application of the Si-rich materials resulted in metal immobilization and reduced leaching. It appears that monosilicic acid can cause both physical adsorption and metal precipitation within contaminated soils. Further investigations are recommended to assess the potential use of this approach for remediation of mine tailings and decontamination mine sites.

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Introduction

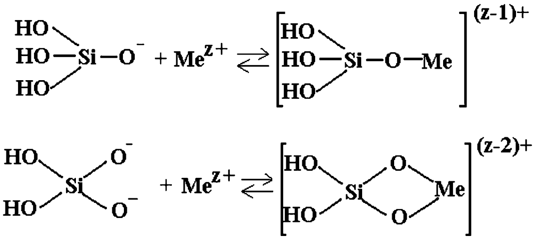
During the last century, industry and agriculture have negatively impacted the natural cycles of metals in the soil–plant system (Adriano 1986; Benavides et al. 2005). Mine operations, milling, ore concentration, and mine waste disposal can release contaminants into the soil, water, and air (Ashraf et al. 2011). As a result, areas around mine operations have been shown to have elevated concentrations of metals (Cidu et al. 2011), some of which can be toxic (Benavides et al. 2005; Vaculik et al. 2009).

Revegetation is generally implemented to protect mine sites against erosion and reduce leaching of metal contaminants into groundwater (Orlov 1992). However, because of the toxicity and low fertility levels of many mines, the revegetation of these areas is often difficult (Favas et al. 2011; Liang et al. 2012). The recovery of metal-polluted soils in mined areas is characterized by high costs and low efficiency. Methods that are currently used to regulate and manage metal mobility in the soil, such as pH adjustment or increasing adsorptive capacity by adding organic amendments, are not sufficiently effective, due to soil matrix inconsistences, which in turn is caused by the action of plants, microorganisms, and waterflow (Orlov 1992). This highlights the need for a different integrated approach to address this situation (Stupin 2009).

Silicon is one of the most abundant elements on the planet, and soil is the most silica-enriched layer of the Earth's crust; between 20 and 35 % of Si is generally found in clay soils and between 45 and 49 % is present in sandy soils (Kovda 1985). Most Si compounds in soil are crystalline forms, amorphous Si dioxide, or various forms of aluminum silicates, with quartz being the most distributed form of silica. Crystalline silica has a high resistance to weathering (Russells 1988), and together with coarse-crystalline silicates (feldspar, plagioclase, and orthoclase) and secondary or clay Si-rich minerals (kaolinite, vermiculite, and smectite), forms a soil skeleton (Orlov 1992). Fine clay minerals and amorphous silica represent the biogenic (phytoliths) and abiogenic amorphous forms or hydrated Si dioxide, which occur as a thin layer on the particle surface in the soil. Metals can react and be adsorbed by Si-rich minerals, with the absorptive capacity depending on the surface properties of the minerals (Brannvall 2006; Garcia-Sanchez et al. 1999). Natural adsorptive minerals, such as zeolites, are recommended for purification of contaminated waters (Alvarez-Ayuso et al. 2003; Babel and Kurniawan 2003; Erdem et al. 2004).

Si is known to alleviate biotic and abiotic stresses for cultivated plants (Biel et al. 2008; Ma 2003). New investigations have shown that active Si can reduce metal toxicity (Bocharnikova et al. 1999; Cunha and Nascimento 2009; Liang et al. 2005; Shi et al. 2005; Zhang et al. 2008), although the mechanism of this alleviation remains unclear. Some authors have stated that Si application to polluted soil or media can increase the metal content in the tissues of plants (Bocharnikova and Matichenkov 2007; Vaculik et al. 2009), while others have demonstrated that the metal concentration in plants is reduced by Si fertilization (Liang et al. 2005; Shi et al. 2005; Song et al. 2009).

Previously, we suggested that the effect of soluble Si compounds on metal mobility depends on the concentration of monosilicic acid in the soil (Matichenkov 2008; Matichenkov and Bocharnikova 2001). Monosilicic acid and its anion can interact with many organic and inorganic compounds, including metals (Lindsay 1979). If the concentration of monosilicic acid is low, the resulting interaction with a metal is a soluble complex, as shown by the reaction below (Bocharnikova and Matichenkov 2007; Schindler et al. 1976):



where Me is any metal.

A high concentration of monosilicic acid can cause total precipitation of some metals by the formation of slightly soluble silicates, as shown by the following reactions (Lindsay 1979; Matichenkov 2008).

$$ZnSiO_4 + 4H^+ = Zn^{2+} + H_4SiO_4 \qquad \log Ko = 13.15$$

$$PbSiO_4 + 4H^+ = Pb^{2+} + H_4SiO_4 \qquad \log Ko = 18.45$$

The level of reduced metal mobility also depends on the adsorptive properties of the applied Si-rich minerals (Bocharnikova et al. 1999; Brannvall 2006; Matichenkov 2008). It was therefore important to investigate the interaction of different metals with various forms of Si. Considering that one of the main target for remediation of the mine tailings and waste deposits is metal detoxification and reducing the risk of secondary pollution from leaching, the main aim of our study was to determine the effect of applied liquid and solid forms of Si-rich materials on the concentration of metals, i.e. cadmium, copper, nickel, and lead.

Materials and Methods

Si-Rich Materials

The following sources of active Si were selected for the column experiments:

- amorphous silicon dioxide (ASD), a chemically pure SiO_2 (Fisher Chemicals),
- diatomaceous earth (DE), (natural silica, Synergy Fertilizers Pty Ltd, North Queensland, Australia),
- zeolite [clinoptilolite, $(Na,K,Ca)_{2-3}Al_3(Al,Si)_2Si_{13}O_{36}$-$12(H_2O)$ from the Volga region, Russia],
- monosilicic acid (ZumSil), a concentrated monosilicic acid (TerraTech Intl., Miami, FL, USA), which contains 90 % of Si as monosilicic acid and 10 % as polysilicic acid.

The selected properties of all of the tested materials are presented in Table 1.

Solid forms of Si (ASD, DE and zeolite) were analyzed using a scanning electron microscope (SEM; JEOL, Japan) together with a JFC-1600 (JEOL, Japan), which was used to apply a thin platinum layer (20 nm) onto the sample. The upper horizon of gray forest soil (45 % sand, $pH_{H_2O} = 6.8$, $C_{org} = 2.71$; CEC = 10.3 cmol +/Kg) from the southern area of the Moscow region was used in the experiment. The content of water- and acid-extractable Si in the original soil samples, as well as in soil samples after column experiment, and the original Si-rich materials were analyzed.

Water Extraction

Soluble monosilicic acid was measured in the water extracted from the fresh samples. The extraction procedure was as follows: after removing the plant roots, 6 g of soil or

Table 1 Properties of the selected Si-rich materials

Material	Modular condition	H_2O (%)	pH	Si	Fe	Ca	Mg	Na
				Total (%)				
ASD	Solid	4	7.1	44.7	nd	nd	nd	nd
DE	Solid	5	7.2	32.1	4	1.0	0.6	0.7
Zeolite	Solid	4	7.6	30.7	0.6	0.5	0.5	2.1
ZumSil	Liquid	67	14.0	20	0.01	nd	nd	10.5

Si-rich mineral was placed into 100 mL plastic vessels; 30-ml of water was added to each vessel, which was then shaken for 60 min. Then, the sample was filtered and a clean extract was analyzed for soluble monosilicic acid using the Mallen and Raily molybdate method (Iler 1979).

M HCl Procedure

Two g of an air-dried soil sample (or Si-rich mineral) was placed in a 100 mL polyethylene cup. Then, 20 mL of 0.1 M HCl was added and the mixture was agitated at 200 rpm for 30 min. After standing overnight, the mixture was shaken again for 30 min and the supernatant was centrifuged at 7000 rpm for 15 min. Si was tested in cleaned extract by the molybdate method (Iler 1979).

Column Test

Dry soil (1 kg) was treated with ASD (10 g), DE (10 g), or zeolite (10 g), and then placed into a plastic box that was 10 cm in width and length and 20 cm high. Distilled water, contaminated solution, or ZumSil (diluted with distilled water or with the contaminated solution until the monosilicic acid concentration reached 200 ppm of Si) were using for incubation. Both the treated and untreated soils were then mixed with either distilled water as a control sample or with the metal solution to 25 % moisture. Each kg of the dry contaminated soil contained 500 mg of Cd as $CdCl_2$, 400 mg Cu as $CuSO_4$, 200 mg Ni as $NiSO_4$, and 300 mg Pb as $Pb(NO_3)_2$. The soils were then incubated at a temperature of 24 °C, while soil moisture remained at 20–25 %, for 1 week.

The plastic columns used in our study had a radius of 3 cm and a height of 25 cm. The treated soil that was placed in each column had a volume of 0.5 L. A 200 mL volume of distilled water was added daily to each column using a peristaltic pump with a speed of 8.3 mL/h; the percolated solutions were collected every day for 1 week. The percolated solutions were centrifuged for 15 min at 6000 rpm to precipitate colloids and solid particles prior to analysis. After 1 week, the soil from the columns was dried at 65 °C and analyzed for Cd, Cu, Ni, and Pb in $MgCl_2$—extracts (mobile form). The standard extraction method with 0.1 N HCl was used to determine potentially mobile forms of Cd, Cu, Ni, Pb, and Si (Matichenkov 2007; McLaughlin et al. 2000; Sabienë et al. 2004). The Cd, Cu, Ni, and Pb content in the percolated solutions and in soil extracts was measured by atomic adsorption (AAS Hitachi 170-50A).

Each treatment had three replications. All data management and statistical analysis was conducted using EXCEL for Windows. $P \leq 0.05$ was considered to be substantial.

Results

The water-soluble Si content in the soil was extremely low, indicating a low concentration of active Si. All tested Si-rich materials were characterized by high concentrations of water- and acid-extractable Si (Table 2).

ASD produced the maximum monosilicic acid content (215.7 mg/kg). The lowest level of water-extractable Si was found in the zeolite (29.2 mg/kg); however, this concentration was higher than the monosilicic acid content of the untreated soil. The maximum acid-extractable Si content was found in the DE (1295.6 mg/kg) and the minimum was observed in the ASD (453.6 mg/kg).

The SEM microphotographs showed that the DE has a unique structure formed by the prehistoric skeleton of diatom algae (Supplemental Fig. 1). In contrast, the zeolites are crystals with a smooth non-porous surface (Supplemental Fig. 2). This difference causes the water- and acid-solubility of the Si in the zeolites to be less than that of the DE. The ASD are rough-surface spheres with diameters of 10–15 µm (Supplemental Fig. 3); this structure provides a high water-extraction characteristic, but low

Table 2 Water and acid-extractable Si in the tested Si-rich materials

Si-rich materials	Water-extractable Si	Acid-extractable Si
	mg/kg	
Original soil	9.5	340
ASD	215.7	453
DE	38.4	1295
Zeolite	29.2	870
LSD_{05}	1.5	16

acid-extractable Si (note: these supplemental files accompany the on-line version of this paper and can be downloaded for free).

The column test simulated the effect of Si-rich substances on the behavior of metals in polluted soils, such as might be present in mine tailings or near mine areas. The dynamics of the metal concentrations in the percolated solution are shown in Figs. 1, 2, 3 and 4. Considering that mobile forms of the metals were applied to soil and that the soil was not dried, the maximum concentration of all of the tested metals was analyzed at the start of the experiment. The concentrations of the mobile and potentially mobile forms of the metals in the soil were reduced by chemical adsorption or by leaching. The application of solid or liquid Si-rich substances dramatically reduced the leaching of Cd, Cu, and Pb; however, the dynamics and intensity of the leaching varied with the different Si forms as well as the metal. Application of DE reduced Cd leaching the most (Fig. 1); at the beginning of the experiment, the concentration of Cd in the percolated solution was 3.1 ppm, whereas in the control it was 8.7 ppm. Zeolite had a similar effect as the DE, while ZumSil and ASD were less

Fig. 1 Dynamics of Cd concentrations in the percolated solution

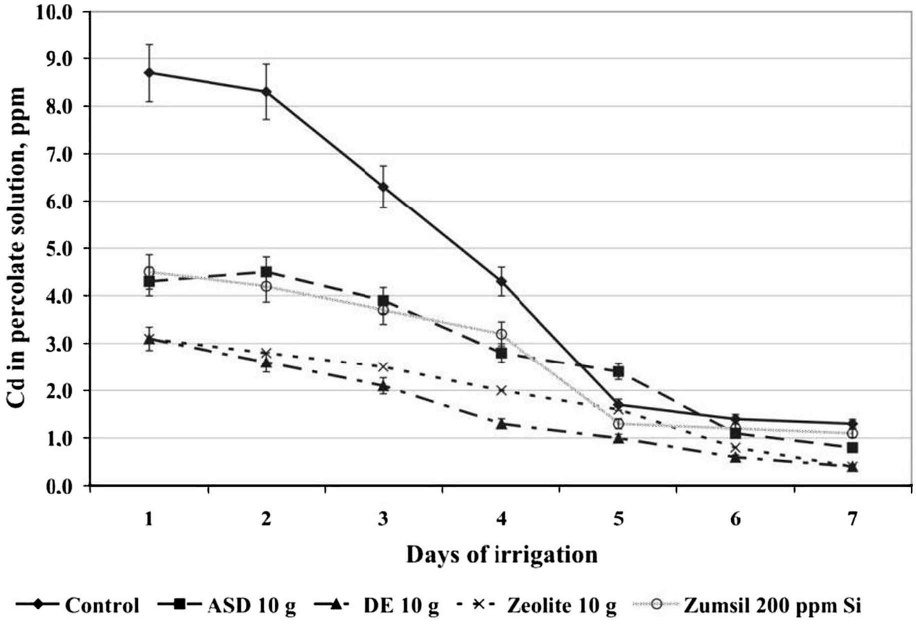
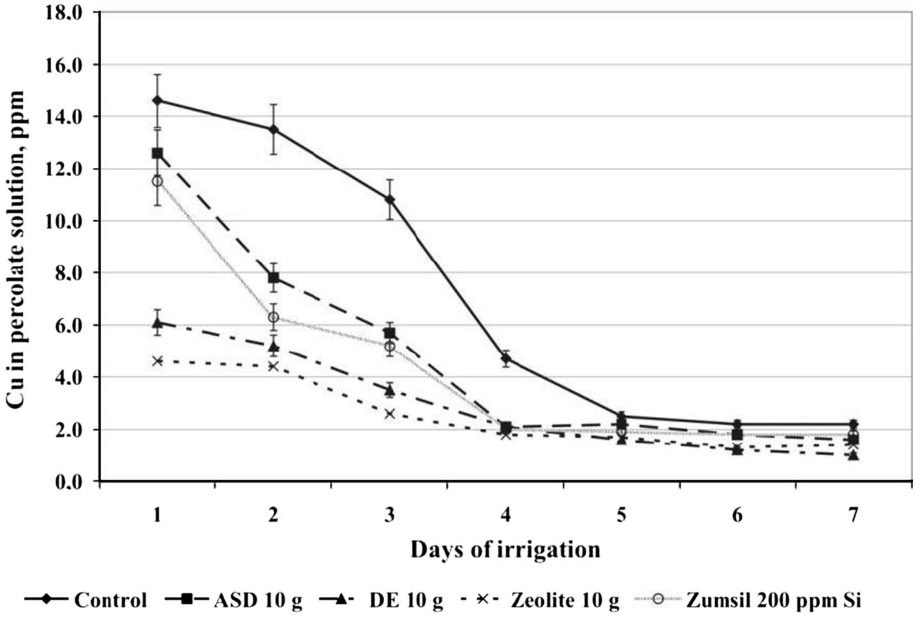


Fig. 2 Dynamics of Cu concentrations in the percolated solution



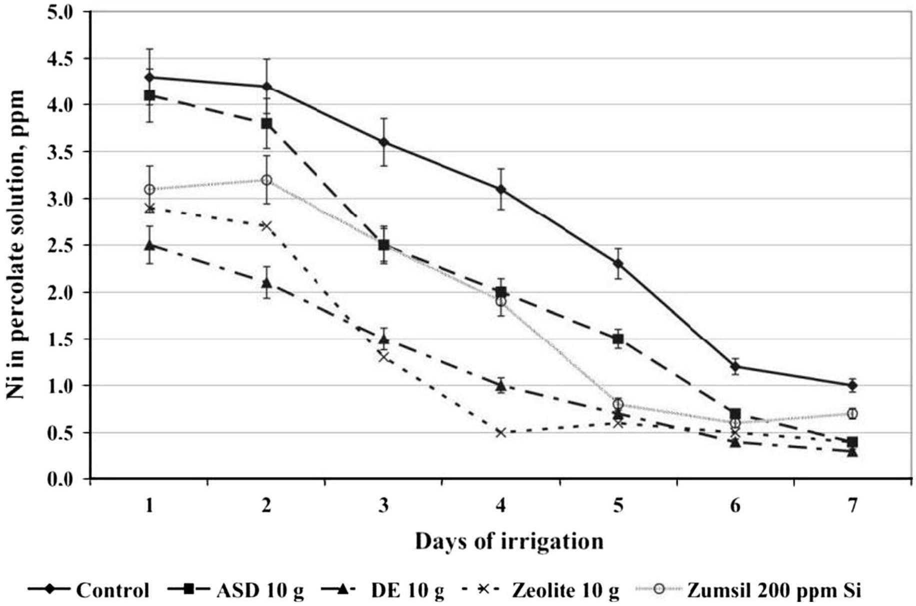


Fig. 3 Dynamics of Ni concentrations in the percolated solution

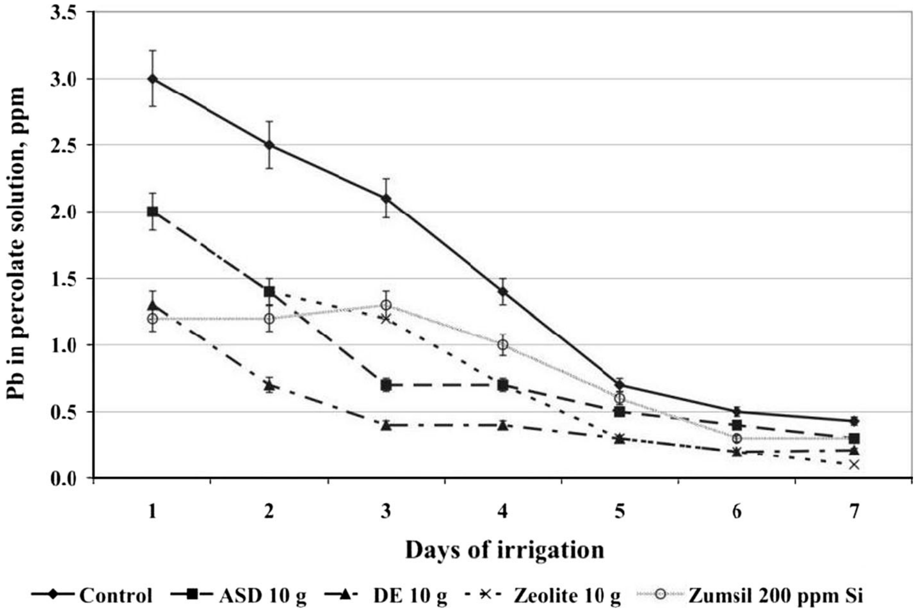


Fig. 4 Dynamics of Pb concentrations in the percolated solution

effective, producing leachate Cd concentrations of 4.5 and 4.3 ppm, respectively. This is likely because DE and zeolite affect Cd mobility by two main mechanisms: chemical adsorption of the Cd on the solid surface of the Si-rich substances and Cd precipitation by monosilicic acid within the soil solution. In contrast, ZumSil and ASD likely have only one mechanism: Cd precipitation by monosilicic acid (Bocharnikova and Matichenkov 2007).

The DE and zeolite reduced Cu leaching by more than 50 %, while ZumSil and ASD reduced Cu leaching by 15–22 % (Fig. 2). The mechanisms of the interaction between Si-rich substances and Cu are likely the same as with Cd.

Maximum reduction of Ni leaching occurred in the soil treated by the DE and zeolite. The effect of ASD was initially minimal compared to the control sample, though reduced Ni leaching occurred in the middle of the test (Fig. 3). As for Pb, the maximum reduction of metal leaching was associated with DE (Fig. 4).

The monosilicic acid content in the original soil was very low, according to the soil classification of plant-available Si (Matichenkov 2007), and the acid-extractable Si content was deficient (Table 3). Application of Si-rich materials increased the content of both tested forms of Si. The largest increase of monosilicic acid was noted in the soil treated with ZumSil; the monosilicic acid increased the

Table 3 Water and acid-extractable Si in the soil after the column test

Soil treatment	Water-extractable Si Si (mg/kg)	Acid-extractable Si
Control	9.8	332
ASD	35.8	465
DE	26.3	697
Zeolite	16.1	576
ZumSil	38.7	408
LSD_{05}	1.5	15

Table 4 Metal concentration in the soil after the column test

Treatment	Mobile metals ($MgCl_2$ extraction)		Potentially mobile metals (0.1 n HCl extraction)	
	mg/kg	Reduction (%)	mg/kg	Reduction (%)
Cadmium (Cd)				
Control	28.5		58.6	
ASD	9.9	65.3	36.9	37.0
DE	2.6	90.8	1.9	96.7
Zeolite	3.6	87.1	26.3	55.1
ZumSil	7.2	74.7	12.9	77.9
Cupper (Cu)				
Control	24.2		163.4	
ASD	19.8	18.2	103.4	36.7
DE	11.2	53.7	114.2	30.1
Zeolite	20.4	15.7	143.4	12.2
ZumSil	13.3	45.0	93.4	42.8
Nickel (Ni)				
Control	13.4		21.9	
ASD	7.4	44.8	5.6	74.4
DE	2.8	79.1	1.3	94.0
Zeolite	6.6	50.7	0.9	95.9
ZumSil	2.5	81.3	4.3	80.4
Lead (Pb)				
Control	3.2		24.4	
ASD	1.1	65.6	8.3	65.9
DE	1.8	43.8	11.2	54.1
Zeolite	1.9	40.6	12.4	49.2
ZumSil	0.8	75.0	8.5	65.2
LSD_{05}	0.2		0.4	

Si content from 9.8 ppm in the control to 38.7 ppm. The greatest acid-extractable Si content was in the DE-treated soil, at 697.5 ppm Si.

The amount of mobile and potentially mobile metals present in the soil after the experiments was changed by the Si treatment (Table 4). The concentration of Cd in the soil was reduced by 65–90 % for mobile and by 37–96 % for potentially mobile forms, with the best results obtained with the DE, while ASD treatment was least effective. The content of mobile Cu in the soil was reduced by 15–53 %, with zeolite being the least effective. For potentially mobile Cu, DE was the most effective, while zeolite was again the least effective.

The concentration of the tested forms of Ni in the soil after the experiment was reduced by 44–81 % for mobile and by 74–95 % for potentially mobile forms. ZumSil was the most effective, while ASD was the least effective. The mobile Pb content in the soil was reduced by 40–75 %, while potentially mobile Pb was reduced by 9–65 %, with ZumSil showing the best results.

Discussion

In the study, the application of solid or liquid forms of active Si significantly reduced the leaching of Cd, Cu, Ni, and Pb from contaminated soil and decreased the concentrations of mobile and potentially mobile metals. The data obtained is in accordance with other investigations (Cunha and Nascimento 2009; Liang et al. 2005; Shi et al. 2005; Zhang et al. 2008). It is important to note that all of the applied forms of Si increased the content of water-extractable Si and acid-extractable Si in the soil. The reduction of mobile and potentially mobile metal concentrations were more intensive for Cd and Ni than for Cu and Pb.

In general, the best results regarding metal mobility were obtained with DE. We suggest that this is due to the very fine surface structure of DE, which can clearly be observed with the SEM. The application of a liquid form of Si was also noted to significantly influence metal mobility. This suggests a dual mechanism reaction, with the first reaction directly between the monosilicic acid and the metal, while the second is chemical or physical adsorption by Si-rich surfaces. In order to understand which mechanism takes priority, coefficients were calculated to show the correlations between various soil parameters such as metal mobility, potential metal mobility, and the concentrations of monosilicic acid and acid-extractable Si. Based on the available literature, the acid-extractable Si is related to the Si-rich surface of the soil minerals (Barsykova and Rochev 1979; Matichenkov 2008; Matichenkov and Bocharnikova 2001). Higher correlation coefficients are associated with primary processes that occur in the soil matrix. The results of these calculations are presented in Table 5.

According to these calculations, mobile Cd concentrations are more related to adsorption than to the reaction between monosilicic acid and Cd in the soil. For Cu, Ni, and Pb, the influence of monosilicic acid is more important than the adsorptive capacity of the Si-rich minerals. This

Table 5 Post-experimental correlation between mobile and potentially mobile metals to the concentrations of monosilicic acid and acid-extractable Si

Metal	Mobile metals		Potentially mobile metals	
	Water-extractable Si	Acid-extractable Si	Water-extractable Si	Acid-extractable Si
Cd	−0.52	−0.79	−0.54	−0.74
Cu	−0.63	−0.59	−0.98	−0.21
Ni	−0.71	−0.61	−0.53	−0.76
Pb	−0.94	−0.21	−0.86	−0.46

was also demonstrated by the reduced content of these elements in the soil after the experiment.

Conclusions

Summarizing the results of the experiment on metal immobilization in soil by Si-rich materials, DE and ZumSil reduce metal mobility better than the zeolite we tested and the ASD. This was due the reaction between monosilicic acid and the metals as well as surface adsorption. Also, the rate of metal movement through the soil varies with the metal present. The maximum reductions of metal mobility were obtained for Cd and Ni, while Cu and Pb were less affected.

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References

Adriano DC (1986) Trace elements in the terrestrial environment. Springer, New York City

Alvarez-Ayuso E, Garcia-Sanchez A, Querol X (2003) Purification of metal electroplating waste waters using zeolites. Water Res 37:4855–4862

Ashraf MA, Maah MJ, Yusoff I (2011) Heavy metals accumulation in plants growing in ex tin mining catchment. Int J Environ Sci Technol 8(2):401–416. doi:10.1007/BF03326227

Babel S, Kurniawan TA (2003) Low-cost adsorbents for heavy metals uptake from contaminated water: a review. J Hazard Mater B97:219–243. doi:10.1016/S0304-3894(02)00263-7

Barsykova AG, Rochev VA (1979) The influence of silica-gel-rich fertilizers on mobile silicic acid in soil and on available it for plants. In: Shvejkina RV (ed), The control and management of the macro- and micro-element content on media ural region, proceedings, vol 54. Sverdlovsky ACI, pp 84–88

Benavides MP, Gallego SM, Tomaro ML (2005) Cadmium toxicity in plants. Braz J Plant Physiol 17:21–34. doi:10.1590/S1677-04202005000100003

Biel KY, Matichenkov VV, Fomina IR (2008) Protective role of silicon in living systems. In: Martirosyan DM (ed) Functional foods for chronic diseases. Advances in the development of functional foods, vol 3. D&A Inc, Richardson, pp 208–231

Bocharnikova EA, Matichenkov VV, Snyder GH (1999) The management of heavy metal behavior and mobility in the soil–plant system. In: Proceedings, 31st mid-atlantic industrial and hazardous waste conference, pp 614–622

Bochrnikova EA, Matichenkov VV (2007) Effect of active silicon on mobility of cadmium in the soil–plant system. In: Proceedings of international scientific conference on modern problems in soil contamination, Moscow State University, pp 62–65

Brannvall E (2006) An experimental study on the use of natural zeolite for Cu, Pb and Zn immobilization in soil. Mineralogy 56:1–4

Cidu R, Frau F, Da Pelo S (2011) Drainage at abandoned mining sites: natural attenuation of contaminants under different seasons. Mine Water Environ 30:113–126

Cunha KPV, Nascimento CW (2009) Silicon effects on metal tolerance and structural changes in maize (*Zea mays*, L.) grown on cadmium and zinc enriched soil. Water Air Soil Pollut 197:323–330. doi:10.1007/s11270-008-9814-9

Erdem E, Karapinar N, Donat R (2004) The removal of heavy metal cations by natural zeolites. J Colloid Int Sci 280:309–314. doi:10.1016/j.jcis.2004.08.028

Favas PJ, Pratas J, Gomes MEP, Cala V (2011) Selective chemical extractions of heavy metals in tailing and soils contaminated by mining activity: environmental implications. J Geochem Explor 111(3):160–171. doi:10.1016/j.gexplo.2011.04.009

Garcia-Sanchez A, Alastuey A, Querol X (1999) Heavy metal adsorption by different minerals: application to the remediation of polluted soils. Sci Total Environ 242(1):179–188. doi:10.1016/S0048-9697(99)00383-6

Iler RK (1979) The chemistry of silica. Wiley, New York

Kovda VA (1985) Soil biogeochemistry. Nauka Press, Moscow

Liang Y, Wong JWC, Wie L (2005) Silicon-mediated enhancement of cadmium tolerance in maize (*Zea mays* L.) grown in cadmium contaminated soil. Chemosphere 58:475–483. doi:10.1016/j.chemosphere.2004.09.034

Liang X, Chen Y, Wu X, Zhang F (2012) Progress on phytoremediation of manganese mine wasteland. J Cent South Univ For Technol 12:34–39

Lindsay WL (1979) Chemical equilibria in soil. Wiley, New York City

Ma JF (2003) Function of silicon in higher plants. Prog Mol Subcell Biol 33:127–147

Matichenkov VV (2007) Soil gradation on deficiency of plant available silicon. Agrochemistry 7:22–31

Matichenkov VV (2008) Role of mobile compounds of silicon in plants and soil–plants system. Doctoral Dissertation. Institute Basic Biological Problems RAS, Pushchino, Russia (in Russian)

Matichenkov V, Bocharnikova E (2001) The relationship between Si and soil physical and chemical properties. In: Datnoff L, Snyder G, Korndorfer G (eds) Silicon in agriculture, studies in plant science. Elsevier, Amsterdam, pp 209–219. doi:10.1016/S0928-3420(01)80017-3

McLaughlin MJ, Zarcinas BA, Stevens DP, Cook N (2000) Soil testing for heavy metals. Commun Soil Sci Plant Anal 31(11–14):1661–1700. doi:10.1080/00103620009370531

Orlov DS (1992) Soil chemistry. Moscow State University Press, Moscow

Russell EW (1988) Soil conditions and plant growth. In: Russell EW, Wild A (eds) Russell's soil conditions and plant growth. Longman Scientific, London, pp 775–779

Sabienë N, Brazauskienë DM, Rimmer D (2004) Determination of heavy metal mobile forms by different extraction methods. Ekologija 1:36–41

Schindler PW, Furst B, Dick R, Wolf PO (1976) Ligand properties of surface silanol groups. I. Surface complex formation with Fe^{3+}, Cu^{2+}, Cd^{3+}, and Pb^{2+}. J Colloid Int Sci 55(2):469–475

Shi XH, Zhang CC, Wang H, Zhang FS (2005) Effect of Si on the distribution of Cd in rice seedlings. Plant Soil 272:53–60. doi:10.1007/s11104-004-3920-2

Song A, Li Z, Zhang J, Xue G, Fan F, Liang Y (2009) Silicon-enhanced resistance to cadmium toxicity in *Brassica chinesis* L. is attributed to Si-suppressed cadmium uptake and transport and Si-enhanced antioxidant defense capacity. J Hazard Mater 172:74–83. doi:10.1016/j.jhazmat.2009.06.143

Stupin DY (2009) Soil pollution and new technologies for their restoration. Lan Press, St. Petersburg

Vaculik M, Lux A, Luxiva M, Tanimoto E, Lichtscheidl I (2009) Silicon mitigates cadmium inhibitory effects in young maize plants. Environ Exp Bot 67:52–58. doi:10.1016/j.envexpbot.2009.06.012

Zhang Ch, Wang L, Nie Q, Zhang W, Zhang F (2008) Long-term effects of exogenous silicon on cadmium translocation and toxicity in rice (*Oryza sativa* L.). Environ Exp Bot 62:300–307. doi:10.1016/j.envexpbot.2007.10.024