

# Purification of wastewaters from mining and possibility of regulating heavy metal concentrations in environmental flows

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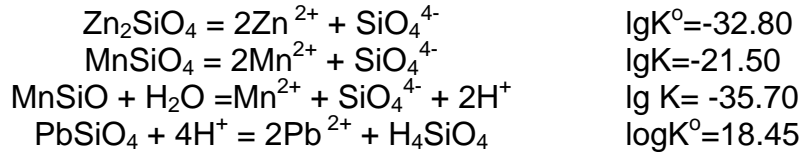
## Abstract

Human activity leads to increasing heavy metal (HM) concentrations in the natural waters as a result of applying chemicals in agriculture, industrial pollution, and bad management in storage and disposal of wastes. Mining is one of the most important businesses in Australia. Commonly wastewaters from mining operation contain significant amounts of metals, including heavy metals, so they are potential source of the emission of metals into the water system. Mine tails usually contain some amounts of HM and, what is especially important, their mobile forms. The possibility to manage HM mobility in water solutions and grounds could help to control HM input into the environmental flows and to improve aquatic ecosystem health. New innovative technologies for wastewater and mining tails treatment are required. The use of various forms of chemically active Si seems to be prospective for reducing HM amounts in the natural waters. Our preliminary study has demonstrated that active Si allows managing HM mobility. The ability of monosilicic acid as a source of active Si to impact the mobility of Cd, Cr, Ni, Cu, and Pb was studied in greenhouse experiment. Barley (*Hordeum vulgare L.*) was used as a test plant. Heavy metals were applied to soil in soluble forms before planting barley. The solution of monosilicic acid with the Si concentration of 160 ppm was applied with irrigating water at the rate of 50 mL per pot per day. Each pot had the volume of 1L. In the course of the experiment, HM concentrations were analyzed in the percolated solutions. After the experiment, biomass of barley was measured. The HM concentrations in the soil and in the plant tissue were analyzed as well. The obtained results have shown that active Si can significantly reduce HM input into aquatic ecosystems. The concentrations of all tested HM in the percolated solutions became 2- to 10-fold smaller depending on the type of HM. The HM concentrations in the plant issue were reduced 2- to 5-fold. The concentrations of mobile HM in the soil were reduced 2- to 4-fold. By this means, the application of the liquid active Si (ionized concentrated monosilicic acid) can neutralize HM in the soil or ground by transforming mobile forms into immobile ones. The demonstration test has shown that active Si substances can be successfully used for purification of wastewaters and reducing heavy metal mobility in industrial wastes. On the base of results obtained the technology for fast and effective reduction in HM input into aquatic ecosystems was elaborated. The proposed technology allows reducing HM activity in soil, water, and living organisms. This technology in the combination with bioremediation could give possibility 1) to localize polluted area; 2) to protect natural waters against HM pollution; 3) to accelerate the bioremediation processes.

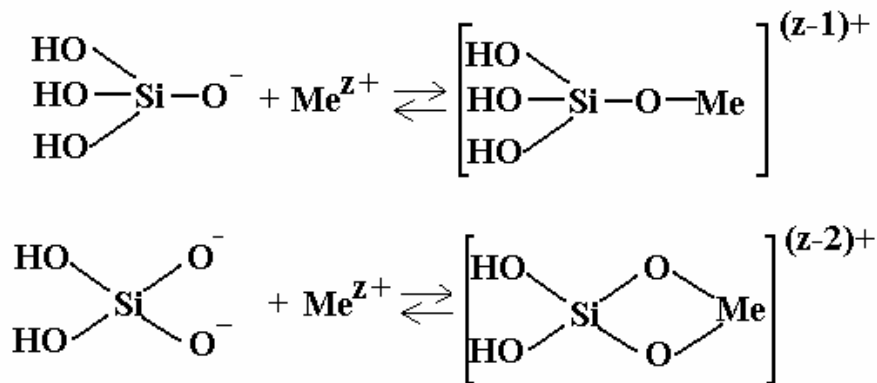
## Introduction

At presents, it has become evident that human activities have altered the natural cycles of HM. In many instances, the HM inputs from anthropogenic sources exceed the contributions from natural sources by several fold (Adriano, 1986). The ever-increasing demands for some elements, fertilizers, pesticides, land disposal techniques enhance the probability of the environmental contamination. Mining can be an important source of HM input to the environment, including natural waters. The metals are derived from exposures of minerals, mine drainage, tailings, spoil and slag deposits, and processing works (Banks, Younger et al., 1997). Significant amounts of HM to have been mined deposit in the biosphere. Pollution of river and stream waters by HM in

wastewater from mining operations can affect a broad area and can afflict hundreds of its inhabitants. The minimization of mining-induced contamination poses acute problem in the management of mine operation. To solve the problem, new innovative technologies are required. Using chemically active Si could be prospective in this case. Silicon is one of the most distributed elements at the Planet. Usually this element is associated with chemically inert minerals. However, all natural waters contain such chemically active form of Si as monosilicic acid. Monosilicic acid has been reported to have a double impact on the HM mobility (Bocharnikova et al., 1999; Lindsay, 1979; Schindler et. al., 1976). In water solutions, monosilicic acid at high concentrations is able to precipitate soluble HM with formation of HM-silicates:



On the other hand, a slight increase in monosilicic acid concentration in the system results in disturbing an equilibrium between mobile and immobile forms of HM and in increasing concentration of HM in the solution (Bocharnikova et. al. 1995; Schindler et. al., 1976). The mechanism of this process is related to complex formation between monosilicic acid and HM:



Where Me is any heavy metal (Bocharnikova et. al. 1995; Schindler et. al., 1976).

Nevertheless there is extremely limited data about an influence of chemically active forms of Si on HM behavior. The main aim of this study was determination of the influence of monosilicic acid on the mobility of Cd, Cr, Ni, Cu, and Pb.

### Materials and Methods

The following Si-rich materials were used in the experiment.

1. Amorphous silicon dioxide (ASD) ( $\text{SiO}_2$ , Fisher, surface area  $30 \text{ m}^2 \text{ g}^{-1}$ ) was used as a source of monosilicic acid and as a compound able to adsorb HM.
2. Zumsil (liquid Si fertilizer, Silex Inc., FL, USA) represents concentrated ionized monosilicic acid.

Selected properties of the materials investigated are presented in Table 1.

Table 1 Selected properties of Si-rich materials.

Material	pH (H <sub>2</sub> O)	Ca, %	Fe, %	Al, %	Si, %
ASD	7.0	0	0	0	46.5
Zumsil	12	0	2-3	0	16

Cultivated Spodosols (soils with organic hardpan; Ankona series) were sampled in the orange and grapefruit groves at the Indian River Research and Education Center, St. Lucie County, Florida. Soil samples were air-dried and ground to pass a 1 mm sieve. The soil had pH = 6.5 – 6.8, the content of organic matter (C) 0.7-0.8%, CEC 2.26-2.48 meq/100 g.

The experiments were conducted in plastic pots of 1L volume with barley (*Hordeum vulgare L.*) as a test plant. Twenty seeds were planted to each pot. ASD was mixed with the soil before planting at the rate equivalent to the dose of 10 t/ha. Zumsil was diluted 1:1000 and applied with irrigation water (100 ml pot<sup>-1</sup>) every day during the experiment.

During first 2 weeks all plants were growing without HM stress. Then HM were added to the pots. The design of the experiment included 3 variants: (1) without HM, (2) low level of HM (125 mg/kg of Cd as CdCl<sub>2</sub>; 150 mg/kg of Cr as CrO<sub>3</sub>; 100 mg/kg of Cu as CuSO<sub>4</sub>; 50 mg/kg of Ni as NiSO<sub>2</sub>, and 75 mg/kg of Pb as Pb(NO<sub>3</sub>)<sub>2</sub>), and (3) high level of HM (250 mg/kg of Cd as CdCl<sub>2</sub>; 300 mg/kg of Cr as CrO<sub>3</sub>; 200 mg/kg of Cu as CuSO<sub>4</sub>; 100 mg/kg of Ni as NiSO<sub>2</sub>, and 150 mg/kg of Pb as Pb(NO<sub>3</sub>)<sub>2</sub>). Three replications were conducted for each treatment. Then for next 2 weeks barley was growing under irrigation by distilled water, the percolated solutions were being collected and average samples were analyzed for monosilicic acid and HM. After 2 weeks, the shoots and roots were collected and measured separately. After finishing the experiment, the soil samples were collected and analyzed for monosilicic acid and acid-extractable Si by the methodology elaborated (Matichenkov et al., 1999). The HM compounds were sequentially extracted by MgCl<sub>2</sub> (mobile forms of heavy metals) and HCl (potentially leachable forms of heavy metals). Soil and plant samples were replicated twice from each pot. All data were subjected to a statistical analysis based on comparative methods using Duncan's multiple range tests for mean separation at the 5% level of significance (Duncan, 1955).

## Results

The application of HM had a negative influence on the biomass of barley (Table 2). The weight of 10 shoots was reduced from 0.091 to 0.073 g or by 20%. The biomass of roots was reduced by 42.4%. As known, HM applied to soil mainly impact plant root system development (Ammosova et al., 1989). That explains more significant decrease in the biomass of roots as compared with shoots. The Si compounds applied to the pots in the absence of HM had a beneficial effect both on shoots and roots. The biomass of shoots increased by 51% and biomass of roots increased by 56% as compared with control plants. More significant plant response to the Si addition was determined for Zumsil. The optimization of Si plant nutrition alleviated HM-induced inhibition of barley growth (Table 2). For example under the treatment by Zumsil, the mass of plants exposed to HM pollution was found to be higher than that of control ones without HM pollution. The increase in the mass of barley grown under high level of HM pollution resulted from the soil treatment by Zumsil amounted to 57.5 and 124.5%, respectively for shoots and roots, in comparison with the corresponding plants in the absence of Zumsil (Table 2).

Table 2. The effect of Si-rich substances on shoot and root mass of barley under HM pollution.

	Without HM		Low level of HM		High level of HM	
	Shoots	Roots	Shoots	Roots	Shoots	Roots
	-----for 10 plants, g-----					
Control	0.091	0.163	0.083	0.121	0.073	0.094
ASD	0.133	0.231	0.122	0.229	0.107	0.171
Zumzil	0.138	0.255	0.123	0.236	0.115	0.211
LSD <sub>05</sub>	0.005	0.008	0.006	0.008	0.005	0.008

As evident from the results of total Si in the shoots and roots of barley, plant uptake and translocation of Si were influenced by both Si and HM applications (Table 3). The Si compounds increased the total Si in the shoots and roots of barley. More obvious increase was provided by Zumzil. Barley plants exposed to HM pollution in the absence of Si had slightly, not statistically significantly increased total Si in comparison with control plants. Noticeable increase in the plant total Si, especially in the root Si, as influenced by HM was observed in the pots treated with amorphous silica as compared with the corresponding variants without HM (Table 3). While in the pots treated with Zumzil, total Si in barley both in shoots and roots decreased under HM pollution.

Table 3. Total Si in barley plants as influenced by HM and/or Si applications.

	No heavy metals		Low level of heavy metals		High level of heavy metals	
	Shoots	Roots	Shoots	Roots	Shoots	Roots
	-----Si, % -----					
Control	0.58	0.88	0.62	0.95	0.62	0.91
ASD	0.73	1.39	0.76	1.64	0.94	1.81
Zumzil	0.97	1.77	0.71	1.11	0.72	1.08
LSD <sub>05</sub>	0.05	0.07	0.05	0.07	0.05	0.07

The Spodosol investigated was very low in monosilicic acid and acid-extractable Si (Matichenkov et al., 2002) (Table 4). The application of the HM to control pots had no significant effect on the contents of water- and acid-extractable Si compounds in the soil. The soil treatment with Si-rich materials increased the content of both forms of active Si (Table 4). The combined soil treatment by Si-rich substances and HM resulted in slight increase in monosilicic acid and acid-extractable Si forms in the soil.

Figures 1 and 2 show the HM concentrations in percolated solutions.

Table 4. Monosilicic acid, acid-extractable Si, and pH in Spodosol as influenced by HM and Si applications.

	No heavy metals			Low level of heavy metals			High level of heavy metals		
	Monosilicic acid	Acid-extractable Si	pH	Monosilicic acid	Acid-extractable Si	pH	Monosilicic acid	Acid-extractable Si	pH
	-----Si mg/kg -----			-----Si mg/kg -----			-----Si mg/kg -----		
Control	7.9	139.4	6.2	8.1	138.6	6.2	8.2	136.5	6.3
ASD	16.2	185.6	6.3	16.8	158.7	6.2	16.2	185.2	6.2
Zumsil	12.5	178.4	6.8	15.2	179.3	6.7	13.5	175.6	6.7
LSD <sub>05</sub>	0.5	4.0	0.2	0.5	4.0	0.2	0.5	4.0	0.2

Figure 1. HM in percolated solutions under low level of pollution.

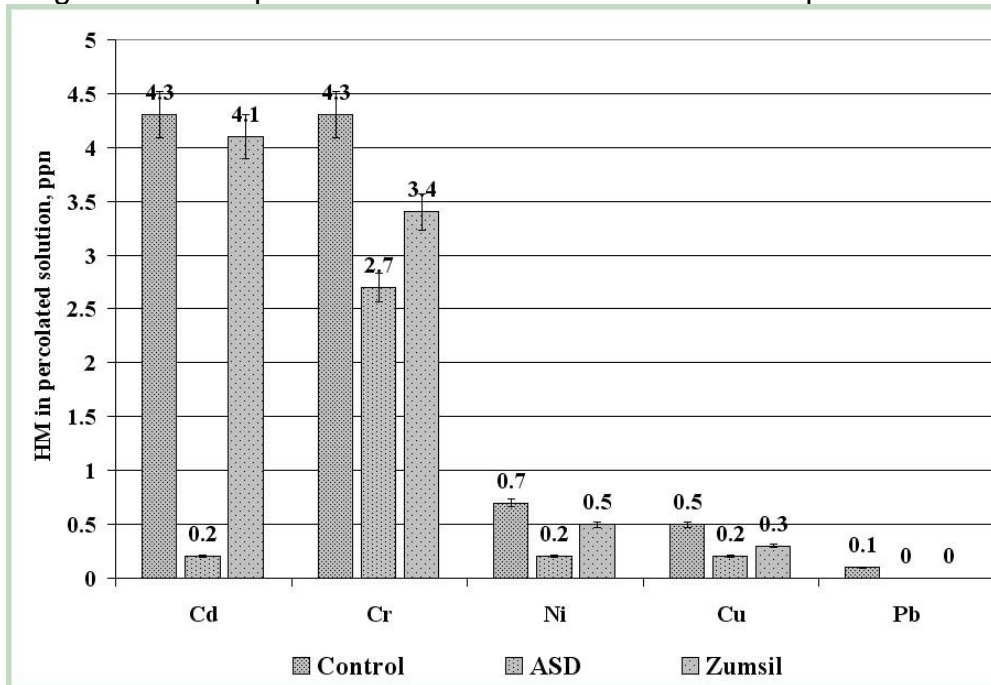
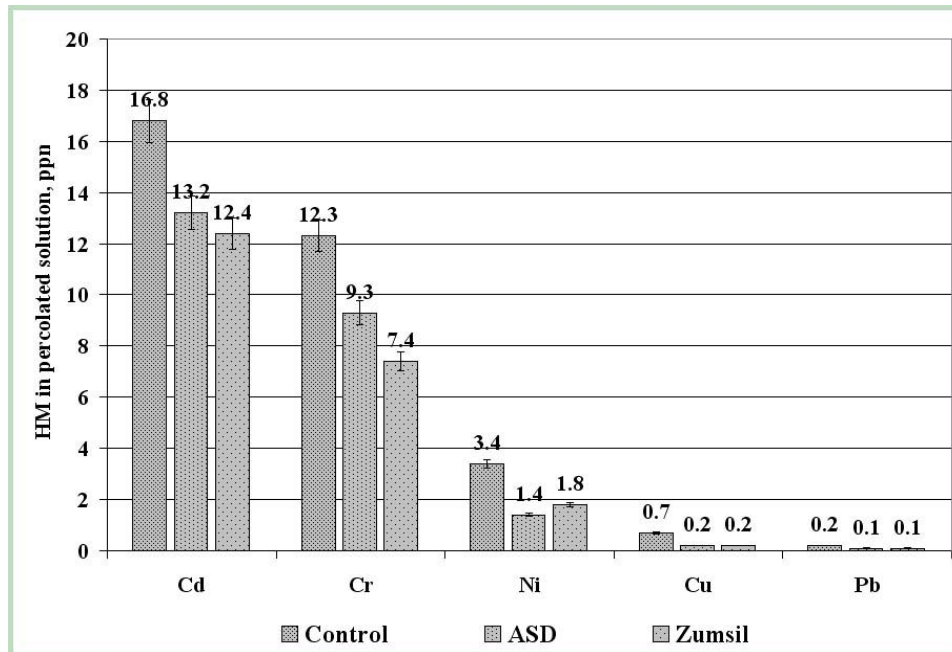


Figure 2. HM in percolated solutions under high level of pollution.



As evident from the results, ASD was very effective in reduction of HM leaching under low level of pollution (Figure 1). For example, the leaching of Cd decreased from 4.3 to 0.2 ppm. Zumsil provided less significant decrease in the HM concentrations in percolated solutions especially for Cd. While under high level of pollution, the decreasing effect of Zumsil on the mobility of HM, except Ni, was more considerable than that of ASD (Figure 2).

The concentrations of Cd, Cr, Cu, Ni, and Pb in the  $MgCl_2$ - and HCl-extracts from the Spodosol are shown in Table 5. The concentrations of mobile and potentially mobile forms of HM were found to be increased by the HM application. The soil treatment with the silicon compounds provided remarkable reduction in the content of the both forms of HM. Under low level of HM pollution, the decreasing effect of amorphous Si on mobile and potentially mobile forms of all HM tested was more obvious as compared with Zumsil (Table 5). On average, the application of Si-rich materials reduced the concentration of mobile forms of HM ( $MgCl_2$ -extractable) by 20 to 60% and potentially mobile forms (HCl-extractable) by 10 to 50% (Table 6).

Table 6. Heavy metals in MgCl<sub>2</sub>- and HCl-extracts from Spodosol.

	No heavy metals		Low level of heavy metals		High level of heavy metals	
	Mg Cl <sub>2</sub> extraction	0.1 n HCl extraction	Mg Cl <sub>2</sub> extraction	0.1 n HCl extraction	Mg Cl <sub>2</sub> extraction	0.1 n HCl extraction
	-----Cd, mg/kg -----					
Control	0.18	1.40	5.32	13.44	17.7	29.80
ASD	0.08	0.80	0.90	4.16	14.66	24.12
Zumsil	0.18	1.12	4.50	9.96	16.7	27.24
	-----Cr, mg/kg -----					
Control	0.06	0.52	4.88	9.24	12.68	13.96
ASD	0.02	0.52	3.08	3.28	10.58	6.44
Zumsil	0.09	0.64	4.06	14.56	8.06	7.48
	-----Cu, mg/kg -----					
Control	0.30	2.92	0.69	16.8	0.72	40.52
ASD	0.11	2.08	0.24	5.04	0.26	34.60
Zumsil	0.16	2.56	0.42	12.16	0.28	40.60
	-----Ni, mg/kg -----					
Control	0.06	0.6	0.72	5.68	3.72	15.96
ASD	0.02	0.28	0.26	1.88	2.42	12.24
Zumsil	0.02	0.32	0.58	2.08	2.96	10.12
	-----Pb, mg/kg -----					
Control	0.01	0.04	0.08	0.18	0.22	0.56
ASD	0.01	0.01	0.08	0.04	0.12	0.44
Zumsil	0	0.04	0.14	0.08	0.19	0.04
LSD <sub>05</sub>	0.01	0.01	0.03	0.40	0.50	0.50

## Discussion

The active Si compounds applied to the Spodosol were responsible for reduced concentrations of mobile forms of HM in the polluted soil and in the percolated solutions. It is known that increased pH can lead to reduction in the mobility of HM in the soil (Adriano, 1986). The application of Zumsil resulted in slight increase in the soil pH level, while amorphous silica had no effect on the pH of the soil. The reducing effect of amorphous silica on HM mobility was more apparent than that of Zumsil, but it can not be related to a change in the soil pH. These results suggest that interaction between Si and HM occurs in the soil, in the case of ASD, probably by the formation of HM silicates or by the HM adsorption on silica surface. In the case of Zumsil, two different mechanisms providing reduction in HM mobility seem to be involved: increasing soil pH level and precipitation of HM by monosilicic acid.

The demonstration test has shown that active Si substances can be successfully used for purification of wastewaters and reducing heavy metal mobility in industrial wastes. On the base of results obtained, the technology for fast and effective reduction in HM input into aquatic ecosystems was elaborated. The proposed technology allows reducing HM activity in soil, water, and living organisms. This technology in the combination with bioremediation could give possibility 1) to localize polluted area; 2) to protect natural waters against HM pollution; 3) to accelerate the bioremediation processes.

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