REMEDIATION OF CHROMIUM-CONTAMINATED SOIL USING BLAST FURNACE SLAG

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ABSTRACT
In this paper, it is attempted to study the capacity of blast furnace to stabilize Cr(VI)-contaminated soils. The slag samples are incorporated with soils in different proportions and the resulted leachate is tested using batch and column experiments to simulate static and dynamic flows. Furthermore, the mechanism by which the chromium in the soil is reduced by the iron slag is discussed. The study demonstrated that blast furnace slag can effectively stabilize Cr(VI)-contaminated soils.
Keywords: batch experiments, blast furnace slag, Cr(VI), environmental pollution, leaching testcolumn test, reduction agents, soil stabilization.

1 INTRODUCTION

Cr(VI) leaching constitutes a very challenging research area where a number of soil geochemical and mineralogical attributes play a significant role. In general, Cr(VI) is used in industrial applications such as metal plating, tannery works, anticorrosive agents, rust proofing and manufacturing of dyes and inks. The presence of chromium is wide spread in the environments like factories producing industrial inorganic chemicals and pigments, Cr plating and polishing operations, wood-preserving facilities, and petroleum refineries. It is the anthropogenic deposition of the compounds in form of chromate (CrO_4^{2-}) and dichromate ($Cr_2O_7^{2-}$) that causes environmental pollution of soil and groundwater [1].

What makes the remediation of Cr(VI)-contaminated soil complicated is the following reasons: (1) in contrast to water, the soil is complicated in its morphology, hydraulic conductivity, mineral and organic phases, and chemical and physical characteristics; (2) soil chemistry of chromium is very complex, making it difficult to predict the speciation of Cr in soil; and (3) the thermodynamic equilibrium, in general, is never reached in soils.

From the environmental point of view, the behaviour and toxic properties of chromium depend on its oxidation states. Consequently, the main criterion for the stabilization of Cr(VI)-contaminated soil by reduction is the valence state, irreversibly reducing soluble Cr(VI) to insoluble Cr(III), similar to the treatment of chromate-contaminated wastewater/groundwater. This is somehow different from the approaches used to remediate other heavy metals where the valence is not a criterion in the analysis.

Consequently, a possible strategy to remediate the Cr(VI)-contaminated soils is to reduce Cr(VI) to Cr(III). The remediation by reduction, however, is not free from disadvantages. The precipitation, sorption and redox processes are the main factors that affect the chromium species in the soil.

In order to mitigate the polluted soils with Cr(VI), remediation plans have to be both economical with low side effects. Reduction agents for Cr(VI) can be ferrous sulphate, bisulphate, and sulphides. Potential drawbacks of these agents for soil and landfill remediation include the necessity for pH adjustment prior to mixing the reducing agent such as Fe(0). This, however, depends on the chemical and physical properties of the soil and the concentrations of Cr(VI) in the soil.

The *in situ* stabilization of soil contaminated with Cr(VI) is necessary to inhibit any possible migration of chromium plume from soil to the groundwater. Additionally, from the viewpoint of construction engineering, the Cr(VI) in the contaminated soil in the ground can transport via foundation into the

building by moisture diffusion (in gas form) or by capillary transport in liquid form. This may cause health problems to the residents in the long term. For these reasons, it is necessary to remediate soil contaminated with Cr(VI) or any heavy metals, which are considered dangerous to health [2].

For the case of using iron slag in the stabilization of soils contaminated with Cr(VI), the reduction of Cr(VI) to Cr(III) and subsequent stabilization have been observed for cements containing ground granulated blast furnace slag (see e.g. [3–7]). The reason is the low redox potential of sulphur-bearing slag modified cements. In conclusion, the iron slag can be a potential reducing agent for the treatment of soils contaminated with Cr(VI) [8]. In this paper, it is attempted to study theoretically and experimentally the capacity of blast furnace to stabilize Cr(VI)-contaminated soils. The slag samples are incorporated with soils in different proportions and the resulted leachate is tested using batch and column experiments, which simulate the static and dynamic flows. Furthermore, the mechanism by which the chromium in the soil is reduced by the iron slag is discussed.

2 EXPERIMENTAL METHODS

2.1 Materials

2.1.1 Contaminated soil
For the laboratory study, soil sample was taken from a Cr(VI)-polluted site. The soil is an anthropogenic and alkaline material composed of chromate ore processing residue, mixed with lime. The source factory is a tannery whereby chromium is used in the manufacturing processes. Table 1 shows the chemical analysis of the important parameters that are related to the remediation of Cr(VI).

As can be seen, the soil is highly polluted with Cr due to its proximity to the pollution point source. The chemical analysis of the soil is carried out according to references [9–12].

2.1.2 Blast furnace slag
In the first stage of moulding steel, impurities in the form of iron byproducts (e.g. furnace slag) will be removed. The second stage of steel manufacturing is to clean up the steel and free it once again from the iron impurities. The byproducts in the second stage are denoted blast-furnace slag (BFS); particle size is 1–3 mm. The main usage of this slag is to use it as a membrane for different applications such as for dams, etc.; BFS can also be used in the manufacturing of some construction materials. Other applications are the production of mineral wool or using it as cement substitutes in masonry mortars. Disposal of this slag bears economical costs in addition to the responsibility of ensuring disposal in landfill sites in accordance with environmental regulations. From a chemical

Table 1: Chemical analysis of the soil.

Parameter	Concentration mg/kg
Cr	7,308.41
Mn	276.77
Sulphide	1.25
Organic matter	217.15
pH of the soil	
pH	10.3

point of view, the slag is a complex combination of chemicals, metal oxides such as sulphur, calcium and iron. For the study, BFS is used (black-coloured and has high bulk density (about 2,000 kg/m^3), particle size: 1–3 mm). Table 2 shows solid matter analysis of the BFS. The results suggest that iron slag is a high alkaline material.

2.2 Extraction method and batch experiments

The amount of Cr in the soil is determined by using acid extraction method. Soil samples of 1 gm are digested by 20 ml half-concentrated (7 N HNO$_3$) and put in oven at 125 °C for 30 min [9, 12]. After cooling off and decanting, the extract is made up to 100 ml. The batch experiments are conducted by adding an amount of slag corresponding to a specific percentage of total solids together with soil. Then, the total solids are mixed with deionized ID water corresponding to the liquid/solid (L/S) ratio. The samples are weighted and mixed homogeneously in a 50-ml beaker with deionized ID water according to L/S ratio. Two replicates for each L/S- and mix ratios are used. The samples are then measured for pH at time = 0 and put in a shaker at 190 puk/min, which is little above middle velocity for an efficient rate of mixing. At different times, the leachate from the batches for Cr analysis is taken and centrifuged for around 12 min to isolate the precipitants (usually Cr(III)) from the liquid phase (usually Cr(VI)). The supernatant is then transferred immediately to glass samples and acidified to pH < 1 and refrigerated for later analysis of total dissolved chromium. The concentration of total Cr is determined by flame-emission atomic absorption spectroscopy. The solution's pH in the batch experiments is measured using pH colour strips readable to 0.3 pH unit precision. The pH is determined using a combination of pH electrode, calibrated using pH 4, pH 7 and pH 9 standard buffers.

2.3 Mix proportions of soil samples with slag and water

For batch experiments, different mixtures between BFS and soil mixtures are made. The mix proportions of batches used for analysis are shown in Table 3.

2.4 Column experiments

To assess the effectiveness of blast furnace slag to reduce Cr(VI) to Cr(III) under dynamic flow conditions, column experiments are conducted. For the column experiment, two acrylic columns each with a diameter of 5.35 cm are used (Fig. 1). The internal length of each column is 25.2 cm and the total volume amounts to 566.5 cm^3. At the lower end of the columns, a layer of quartz sand and a filter paper (0.45–1.0 μm) is laid to secure horizontal spreading of the added water and to hinder the mixture from infiltrating into the percolate. The columns are closed in both ends with a cover of acryplast. The first column is packed with layers of reactive mixtures of soil and slag 80% BFS:20% soil; soil

Table 2: Solid matter analysis.

Parameter	Value
Alkalinity	15.5 eq./kg TS
pH	11.5
TS g/kg	870 g/kg

Table 3: Mix proportions of soil samples with BFS.

Batch	Soil, g	BFS /FS, g	ID. water, ml	L/S ratio	Soil:BFS ratio
A	5	5	20	2:1	1:1
B	2	8	20	2:1	1:4
C	2.5	2.5	25	5:1	1:1
D	1	4	25	5:1	1:4
E	2.5	2.5	40	8:1	1:1
F	1	4	40	8:1	1:4
G	2.5	2.5	50	10:1	1:1
H	1	4	50	10:1	1:4
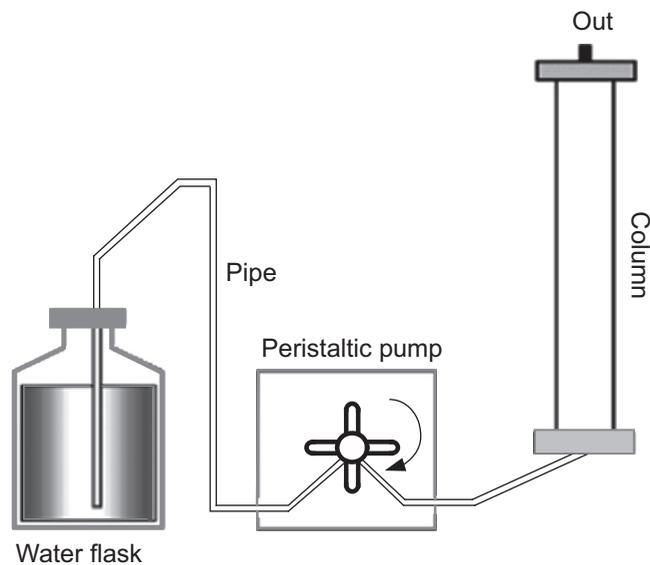
Figure 1: Set-up of the column experiment. A peristaltic pump is a type of positive displacement pump used for pumping the water through the column.

Table 4: Parameters for the column experiments.

Column	Wt of empty column, g	Total dry wt, g	Total wt saturated, g	Net wt soil dry, g	Net wt. saturated soil, g	Wt. water, g	Porosity %	Density, g/cm^3	Mix ratio soil: BFS
Control	323	680.4	1067.5	357.4	744.5	387.1	68%	0.631	100% soil
BFS	300.3	882.6	1140.9	582.3	840.6	258.3	45%	1.028	1:4

particle size is <1 mm. The second column is packed with soil only, without any reactive reductant to control the results. The tap water is used to simulate groundwater and rain water. It is attempted to make the flow rate through the columns constant in the interval of 80–90 ml/h to simulate the groundwater velocity. After reaching the saturation state, the columns are weighted to calculate the volume of water in the pores. Table 4 shows the parameters for the column experiments.

3 RESULTS AND DISCUSSION

3.1 Batch experiments

3.1.1 Effects of L/S ratio and time
Figures 2 and 3 show the mix- and L/S-ratio effect on the removal of chromium from the leachate after mixing BFS with soil; the results concern the case in which soil:BFS ratios are 1:4 (batch
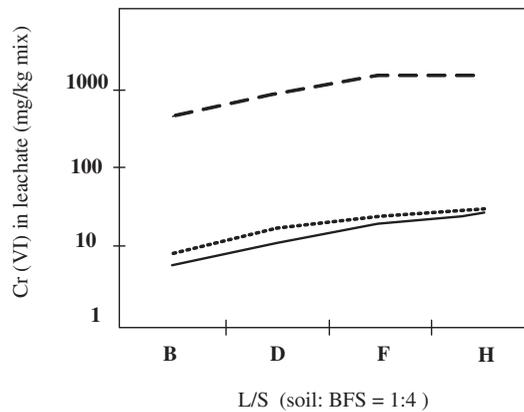
Figure 2: L/S, mix ratio of batches with BFS (soil:BFS = 1:4) versus Cr(VI) concentrations in leachate. (- - -) control samples; (…) after 4 days; (—) after 7 days.
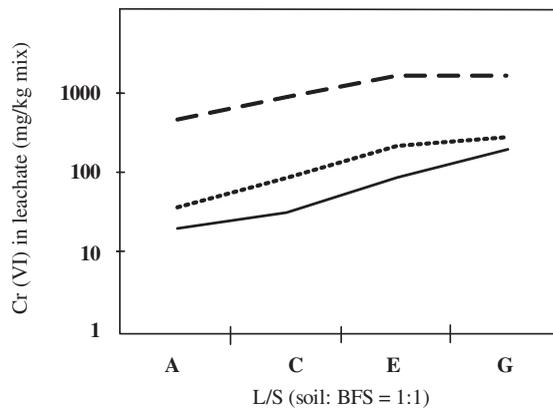
Figure 3: L/S, mix ratio of batches with BFS (soil:BFS = 1:1) versus Cr(VI) concentrations in leachate. (- - -) control samples; (…) after 4 days; (—) after 7 days.

codes: B, D, F, H) and 1:1 (batch codes: A, C, E, G), respectively. For the soil mix ratio 1:4, the optimum L/S ratio is 2:1; after 7 days from mixing, 98.7% Cr(VI) was reduced by BFS. For the soil mix ratio 1:1, the removal of chromium is 70% less than for the mix ratio 1:4 for L/S = 2:1. Once again, the optimum L/S = 2:1. Consequently, the BFS has a good capacity for the removal of Cr(VI) from the leachate as compared with the control soil samples, which contains only chromium (without a reductant). The results indicate that as the percentage of the slag incorporated increase, the removal of Cr(VI) also increases. However, higher L/S values are not favoured for the stabilization process. Additionally, the time of reaction has an influence and that after a definite time most of the Cr(VI) is reduced. A timeframe in which reaction stabilizes and most of Cr(VI) is reduced can be set to 7 days.

3.1.2 Reaction effect on pH

The reaction effect is shown in Fig. 4. As can be seen, the reaction between the slag and Cr(VI) in soil particles increases the hydrogen ion concentrations. In this manner, the reaction is alkalinity generating and acidity consuming. Within time, pH increases. Obviously, the BFS adds hydroxides to the leachate through the hydration of metal oxides contained in the slag.

3.1.3 The effect of pH modification

The effect of pH modification on the reduction process is carried out by adjusting the pH to 5 for 24 h by using pH static. The results demonstrated that the acidification reduces the efficiency of BFS as a reductant. It is thought that the process of continuous addition of acid will desorb the Cr(VI) particles and lead to migration of Cr(VI) thereby increasing its concentrations in the leachate.

3.1.4 Effect of particle size

The results are shown in Figs 5 and 6. As expected, the mix proportion soil:BFS = 1:4 (batch B) is more effective than the mix ratio 1:1 (batch A). The results suggest that smaller particle sizes are favoured by the reduction and the efficiency of stabilization increases as particle sizes decreases. It is noteworthy to indicate here that smaller particle size in general is the significant contributor to the obtained results.
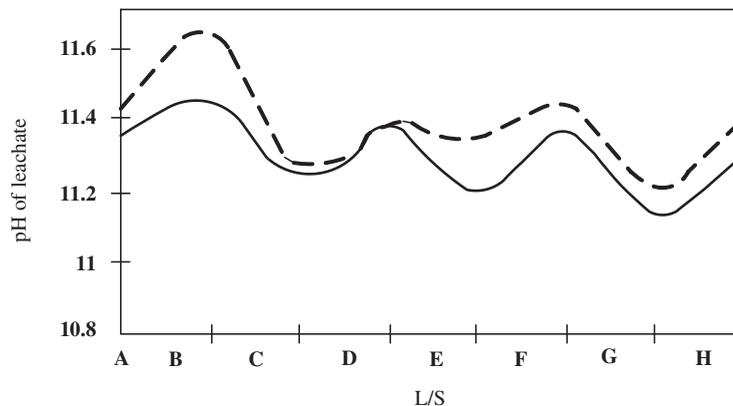

Figure 4: L/S for different mix ratios of batches with BFS versus pH of the leachate. (---) after 7 days; (—) after 4 days.
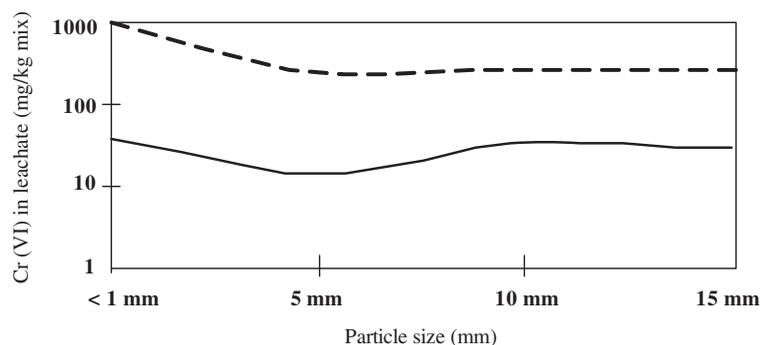
Figure 5: Effect of soil particle size on the reduction of Cr(VI) by BFS for batch A (soil:BFS mix proportionality is 1:1). Time of measurement is after 3 days and L/S = 2:1. (---) control (100% soil); (—) batch A.
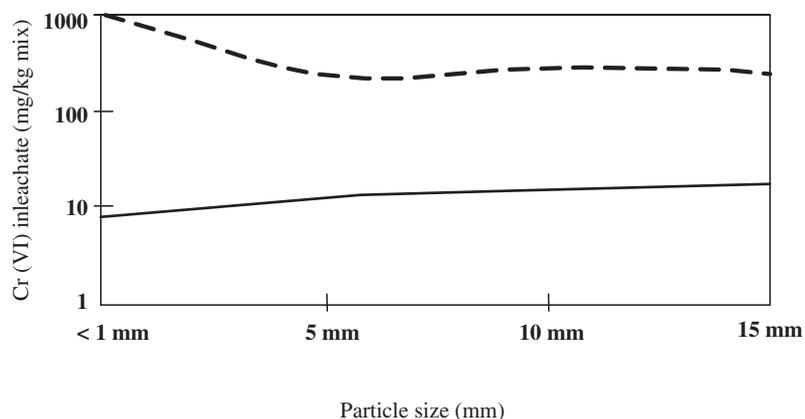

Figure 6: Effect of soil particle size on the reduction of Cr(VI) by BFS for batch B (soil:BFS mix proportionality is 1:4). Time of measurement is after 3 days and L/S = 2:1. (---) control (100% soil); (—) batch B.

3.2 Column experiment

3.2.1 Control column
The effect of total volume of the pores in the porous packing (expressed as specific pore volume) on the leachate parameters, Cr(VI) concentrations and pH, is shown in Figs 7 and 8. For the control column (Fig. 7), the chromium measured in the effluent due to dynamic flow shows a decreasing trend with increasing pore volume and time. The water flow through column and the gradual release of Cr from soil matrix to the water would have direct impact on pH of the leachate at the outlet (Fig. 8). On the other hand, pH of the leachate is highly alkaline. With decreasing Cr release from soil particles due to washing of the column with water flow, both the pH and the hydrogen ion concentrations decrease slowly. The trend in pH fluctuation with fluctuations in Cr concentration in the leachate is similar to the batch experiments discussed previously. For the mixture column, it is shown in Fig. 7 that most of Cr reduction occurs after a specific time from running the water flow through the column, approximately after 15 h from running the experiment.
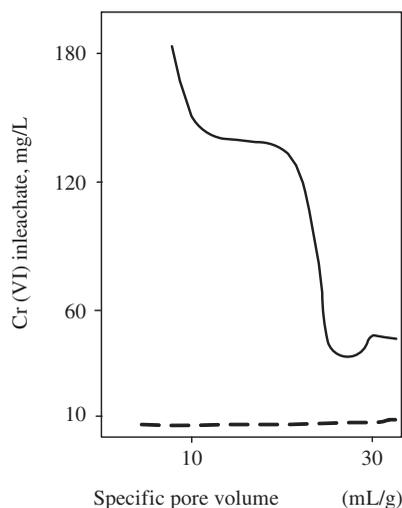
Figure 7: % Pore volume versus Cr(VI) in the leachate for different columns. (---) soil mixture with BFS; (—) control (100% soil). The soil and BFS are mixed in their dry solid state, and soil particle size is <1 mm.
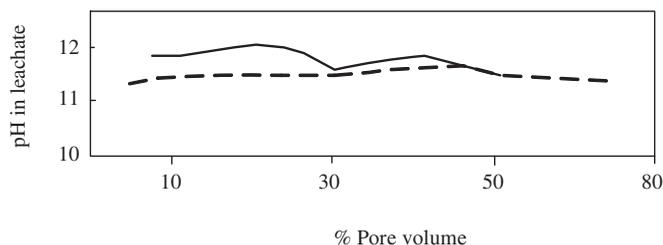

Figure 8: % Pore volume versus pH of the leachate. (---) soil mixture with BFS; (—) control (100% soil). BFS and soil are mixed in their dry solid state, and soil particle size is <1 mm.

4 DISCUSSION

The slag is a complex material composed mainly of SiO_2, Al_2O_3, CaO, P_2O_5, TiO_2, MgO, FeO, MnO and sulphur compounds. The Fe(II) in the form of FeO and the sulphur compounds in addition to the lower redox potential in the slag act as reduction agents. The other important chemical in the slag is Mn(II) in the form of MnO due to its ability to be oxidised to Mn(VI/III) an then re-oxidize Cr(III) to Cr(VI). MnO can be oxidized by oxygen to MnOOH, which is capable to re-oxidize Cr(III) to Cr(VI). Consequently, considering that the reducing agents must irreversibly reduce Cr(VI) to Cr(III), the effectiveness of iron slag to stabilize Cr(VI)-contaminated soils depends on the high contents of sulphur and Fe(II) compounds as well as its low content of MnO.

The other mechanism by which Cr(VI) is removed from the leachate is the adsorption capacity; the compounds $SiO/Al_2O_3/MgO/CaO/MnO$ in the slag can undergo hydration and adsorb Cr(VI) and the main mechanism will not be mere reduction but an adsorption process. The adsorption capacity of the slag can be attributed to its content of these metal oxides since these oxides have the

ability to adsorb Cr(VI) after its release from soil matrix in addition to its high alkalinity which supports the adsorption. The process of continuous addition of acid can desorb Cr(VI) and lead to migration of Cr(VI), thereby increasing its concentrations in the leachate. This is the reason why such high concentrations of Cr(VI) was found in the leachate of 80% BFS:20% soil (Fig. 4). Consequently, the results suggest that Cr(VI) leaching is not only a function of reduction of Cr(VI). More specifically, a significant portion of the immobilized Cr(VI) at a high pH is bound to calcium aluminium chromate hydrate crystalline compounds. The presence of sulphate (usually present in iron slag) has also been shown to play a very important role in Cr(VI) immobilization by the formation of calcium aluminium sulphate chromate insoluble crystalline compounds.

The following *in situ* remediation plan to stabilize Cr(VI)-contaminated soil is suggested:

1. In case of *in situ* treatment, iron slag should be incorporated into the typically subsurface soil materials.
2. The soil pH should be investigated and monitored. This is important to control the effectiveness of using BFS as a reducing agent. The chemical reactions governing reduction of Cr(VI) decrease pH. The adsorption process of Cr(VI) is important specially in planning stabilization method. Cr(VI) can adsorb to the soil particles and it can depend on: pH, soil minerals, and the concentrations of competing ions.
3. In case of chromate-contaminated sites that are underlain by layers rich of organic matter, these layers must not be changed physically or chemically. The reason is that the organic matter can reduce the soluble Cr(VI) leaching downward from these soils.

5 CONCLUDING REMARKS

Alkaline soils contaminated with hexavalent chromium Cr(VI) can effectively be stabilized with BFS. The reduction capacity of the slag is attributed to its content of FeO, FeS, and SO_2 contained in the slag in addition to its lower redox potential Eh and adsorption capacity. It has been amply demonstrated that Cr(VI) leaching is not only a function of reduction of Cr(VI). More specifically, a significant portion of the immobilized Cr(VI) at a high pH is bound to calcium aluminium chromate hydrate crystalline compounds. The presence of sulphate (usually present in iron slag) has also been shown to play a very important role in Cr(VI) immobilization by the formation of calcium aluminium sulphate chromate insoluble crystalline compounds.

The effect of particles size, L/S ratio, time and pH was studied on the reduction of Cr(VI) in the soils and found that in most cases L/S = 2:1 and particles size of soil <1 mm resulted in lowest Cr(VI) concentration, after reduction occurrence among the samples studied.

The feasibility of using iron is demonstrated as concentrations up to 1,000 mg Cr(VI)/kg in the leachate of an alkaline soil is reduced to 0.7 mg Cr(VI)/kg mix after 12 days, but to less than 5 mg Cr(VI)/kg mix after 7 days. Small particle size and L/S ratio are, in most cases, favoured by the reducing agents to stabilize the contaminated soil.

From the economical point of view, the iron slag is very cheap material as compared with other reduction agents of chromium-contaminated soils (e.g. zero-valent iron). Consequently, the treatment of soils contaminated with chromium by iron slag is both cost-effective and practical.

As a last observation, from the environmental point of view, the stabilization of Cr(VI)-contaminated soils by blast furnace slag must not lead to creating extraneous pollutant by-products. Therefore, a comprehensive study on this matter is needed in order to justify the use of the method.

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