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Solidification and Immobilization of Heavy metals in Soil using with nano-metallic Ca/CaO Dispersion Mixture

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Abstract. In the present work, the use of nano-metallic calcium (Ca) and calcium oxide (CaO) dispersion mixture for the immobilization of heavy metals (As, Cd, Cr and Pb) in soil was investigated. With simple grinding, 85-90% of heavy metals immobilization could be achieved, while it could be enhanced to 98-100% by grinding with the addition of nano-metallic Ca/CaO dispersion mixture. By SEM-EDS elemental maps as well as semi-quantitative analysis observed that the amount of As, Cd, Cr and Pb measurable on soil particle surface decreases after nano-metallic Ca/CaO treatment. The leachable heavy metals concentrations were reduced, to the concentration lower than the Japan soil elution standard regulatory threshold, i. e., < 0.01 mg/l for As, Cd and Pb and 0.05mg/l for Cr. Whereas, the effect of soil moisture and pH on heavy metals immobilization was not much influenced. The results suggest that nano-metallic Ca/CaO mixture is suitable to be used for the gentle immobilization of heavy metals contaminated soil at normal moisture conditions.

Key words: Solidification, immobilization, heavy metals, soil grinding, nano-metallic Ca/CaO.

Introduction

The remediation of contaminated soils follows a rapid upward trend in Japan, especially after the Soil Contamination Countermeasures Law proclamation in 2002 and enforcement in 2003 (Ministry of Environment Government of Japan, 2002). Heavy metals contaminated sites pose a serious hazard to public health and the environment. Heavy metal contaminated soils are notoriously hard to remediate. Hence, its remediation is recognized to be one of the most difficult problems to be solved by taking advantage of suitable technologies.

Typical remediation techniques for heavy metals in soil are constituted by extraction and immobilization processes. Extractive techniques may involve inorganic acids or organic acids and surfactants (Macauley and Hong, 1995). Ex-situ extractive technologies are rarely adopted because of high risks and costs related to the use of hazardous extractants, the consequent need of treating secondary wastewater and shortage of landfill sites. On the other hand, in-situ extractive technologies are constituted mainly by phytoextraction and electrokinetic extraction (Reddya et al., 2001). Phytoextraction, may require extremely long times. The efficiency of electrokinetic extraction, may be strongly affected by soil type and contaminant species to be removed. Considering the limitations of the extractive techniques described above, immobilization processes are generally preferred for treating heavy metal contaminated soils (Paff and Bosilovich, 1995). Immobilization is typically performed by mixing the contaminated soil with suitable binders, which are able to reduce heavy metals leachability through pH and alkalinity control to minimize their solubility, or by increasing adsorption, ionic exchange and precipitation of pollutants (USEPA, 1982). A variety of binders were investigated to immobilize heavy metals in soils. Mainly with hydroxyapatite, zeolites, calcium hydroxide and phosphates. On the other hand, cement based stabilization/solidification treatment process for immobilizing hazardous substances that contain heavy metals is well known (Lin et al., 1998). Unfortunately, these immobilization treatment process are wet condition, the use of cement is expensive, forming of secondary effluents and their treatment for additional cost are the main drawbacks. Therefore, the treatment under dry and water free conditions should be considered. While, our recent investigations showed that the nano-metallic Ca/CaO mixture was the most effective for hydrodechlorination about 98% of PCDDs, PCDFs and PCBs in contaminated fly ash, and also, for cesium immobilization about 96% in soil by ball milling treatment (Mitoma et al., 2011; Srinivasa Reddy et al., 2012). The high PCDDs, PCDFs and PCBs hydrodechlorination and cesium immobilization with the addition of nano-metallic Ca/CaO may be caused by the high reduction potentials and high surface area produced by ball milling. Whereas, in case of cesium immobilization, Ca/CaO and sodium phosphate (NaH_2PO_4) can also make immobile salts with moisture and CO_2 in atmosphere, including pozzolanic cement and hydraulic property, cesium would be brought into the immobile Ca/PO_4 salts (Srinivasa Reddy et al., 2012). We assumed, that the addition of the nano-metallic Ca/CaO would effectively reduce the heavy metal leaching potential from contaminated soil by its high reduction potential and high surface area with simple grinding. Therefore, in the present work, the use of nano-metallic Ca/CaO dispersion mixture for the immobilization of heavy metals (As, Cd, Cr and Pb) in contaminated soil was investigated by simple grinding process. The degree of metal immobilization was evaluated by analyzing the leachable fraction of heavy metals obtained through the application of the Japanese soil elution standards. Furthermore, the effect of soil moisture and pH on heavy metals immobilization and the mechanism was also studied.

Materials and Methods

Heavy metals contaminated soil was synthetically prepared in laboratory having different moisture content, 1, 5 and 10%. One thousand mg/L of heavy metal (As, Cd, Cr and Pb) standard solutions was thoroughly mixed on 1 kg of sandy soil (non-polluted, commercially available mica/isinglass/fibrolite soil type, produced in Okayama prefecture, Japan). While, nano-metallic Ca/CaO (dry system) was prepared with metallic Ca and CaO through planetary ball milling process. Granular particles of metallic calcium was purchased from Kishida Chemical Co. Ltd. (99%, particle size distribution: 2.0-2.5 mm, surface area: 0.43–0.48 m^2/g). Fine grade CaO was also commercially obtained with 98% purity from Kishida Chemical Co. Ltd. Room temperature under Argon (Ar) gas atmosphere, metallic Ca and dry (825^{o}C for 2h) CaO composition (Ca/CaO = 2/5) were introduced in the planetary ball mill (Retsch PM-100; 20 pieces SUS, 32g/ball). Stirring was carried out for 1 hr at 600 rpm to a rotation-to-revolution ratio of 1 to 2. After stirring samples were collected in glass bottles, Ar gas was filled and stored to be used further treatment experiments. The maximum particle size distribution was observed at 263 nm. Heavy metal contaminated soil was grinded using a magnetic grinder (AS ONE) at 100-150 rpm in a ceramic vessel at room temperature for 6 hours under air, together with dry nano-metallic Ca/CaO dispersion mixture (1.00/0.11 (synthetically prepared heavy metal contaminated soil/nano-metallic Ca/CaO)).

After treatment without and with addition of nano-metallic Ca/CaO, the soil mixture was cooled to room temperature and performed soil elution test according with standard methods (Ministry of Environment Government of Japan, 2003). In order to determine the pH effect on immobilization efficiency, during the elution test with nano-metallic Ca/CaO treated soil sample solutions pH was also adjusted to pH 7 with concentrated HCl. Heavy metal concentrations in eluted solutions were measured using Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES; Varian, 720-ES). These experiments were repeated three times, giving similar results.

In order to elucidate immobilization mechanisms and to verify if soil alterations occurred during the treatment, the metals mapping analysis on the soil surface conducted. Scanning electron microscopy combined with electron dispersive spectroscopy (SEM-EDS; JEOL, JSM6510A equipped with a Si (Li) probe with a resolution of 138 eV) microanalysis and semi-quantitative analysis were carried out with SEM-EDS in order to analyze As, Cd, Cr and Pb distribution within the solid matrix. Generally, EDS could detect the fluorescent X-ray from the surface layer until 10 µm depth. On the other hand, X-ray diffraction (XRD) analyses were also performed in order to identify crystalline phases on the surface of solid samples, and it was carried out using a RIGAKU, RINT XRD by employing CuKα Ni-filtered radiation (λ=15.418 Å). X-ray diffraction data were collected for values of 2θ between 10° and 90°.

Results and Discussion

With nano-metallic Ca/CaO addition, after grinding, the concentration of heavy metals released in the leachate significantly decreased. While, these eluted heavy metals efficiency in the soil (1% moisture content) corresponds only to 0.02-3.8% (Fig. 1). Similar results were also observed with soil 5% and 10% moisture and at different pH conditions. Although, different soil moisture content and pH had revealed very slight, about 1%, variation on As, Cd, Cr and Pb immobilization efficiency. It was clearly observed that leachable heavy metal substantially decreases after nano-metallic Ca/CaO mixture treatment to lower than the soil leachate regulatory standard limits (< 0.01 mg/l for As, Cd and Pb and 0.05mg/l for Cr respectively) proposed by Japan soil elution standard regulatory threshold.

By SEM microstructure analysis, blending the heavy metals contaminated soil with nano-metallic Ca/CaO decreased the production and development of the core particles and would be caused the hydration products to coat the aggregates extremely. This fact probably indicates that a certain amount of heavy metals was entrapped inside new aggregates produced during the nano-metallic Ca/CaO treatment. Furthermore, from SEM-EDS 3D elements maps, it is also possible to observe that, the amount of Cd, Cr and Pb detectable on the soil particle surface decreases after nano-metallic Ca/CaO treatment (Fig. 2). On the other hand, Ca mass percent increased. The reduction of As, Cd, Cr and Pb amount on soil particle surface is a possible explanation for increase of immobilization efficiency with nano-metallic Ca/CaO treatment, by enclosed/bided soil surface with Ca associated compounds. Furthermore, XRD analysis the major phases identified in soil before treatment was quartz and clay minerals kaolinite and bentonite. When the same soil was subjected to grinded with nano-metallic Ca/CaO peaks related to Ca crystalline phases ($CaCO_3/Ca(OH)_2$) appeared in addition to quartz, kaolinite and bentonite. This probably indicates that main amount of enclosed/bided materials was Ca associated complexes.

The most probable mechanism for the enhanced heavy metals immobilization capacity with nano-metallic Ca/CaO treatment may be probably ascribed to phenomena such as adsorption and entrapment of heavy metals into new formed aggregates due to prompting aggregation of soil particles and enclosed/bided with Ca associated immobile salts as schematically shown in Fig. 3. It is possible to assume that when soil is contaminated, heavy metals is adsorbed onto soil particles (Fig. 3a) through a surface coordination process. During grinding in the presence of nano-metallic Ca/CaO, soil particles are subjected to collisions that may promote aggregation and breakage phenomena as well as accumulation of crystalline defects and vacancies amorphization (Montinaro et al., 2007). When aggregation occurs in the presence of nano-metallic Ca/CaO, the amount of heavy metal adsorbed on the surface of two overlapping particles may be entrapped within the new formed aggregates (Fig. 3b). Moreover, it is also possible to assume that heavy metal complexes may diffuse within the crystalline reticulum of soil particles thus leading to a very efficient chemical entrapment of heavy metal within the soil in presence of nano-metallic Ca/CaO. On the other hand, nano-metallic Ca/CaO could make immobile salts with moisture and CO_2 in atmosphere, including pozzolanic cement and hydraulic property, hence heavy metals (As, Cd, Cr and Pb) would be brought into the immobile Ca salts, therefore, the surfaces of soil might enclosed/bided with Ca associated ($CaCO3/Ca(OH)_{2)}$ salts (Fig. 3b). In this way, the amount of heavy metals exposed to the leaching accomplishment is reduced thus determining a enhanced immobilization capacity with nano-metallic Ca/CaO treatment. These results appear to be promising and the simple grind with nanometallic Ca/CaO addictive may be considered potentially applicable for the remediation of heavy metals contaminated soil.

Conclusions

With simple grinding, 85-90% heavy (As, Cd, Cr and Pb) metals immobilization could be achieved in soil, and enhanced about 98-100% of heavy metals immobilization with nano-metallic Ca/CaO dispersion mixture by grinding. The leachable heavy metals concentrations were reduced, after nano-metallic Ca/CaO treatment to a concentration lower than the Japan soil elution standard regulatory threshold. SEM-EDS elements map as well as semi- quantitative analysis, observed that the amount of As, Cd, Cr and Pb detectable on soil particle surface decreases after nano-metallic Ca/CaO treatment. The results suggest that nano metallic Ca/CaO mixture is a suitable treatment for the gentle immobilization of heavy metals in polluted soil. The addition of nano-metallic Ca/CaO that enhanced heavy metals immobilization in soil at normal moisture conditions is an innovative approach for the remediation of soils polluted with heavy metals.

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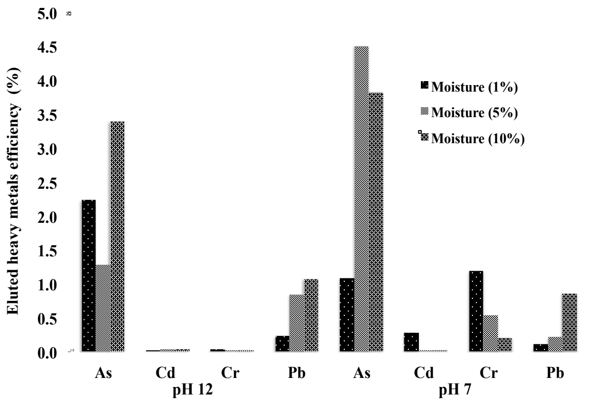


Fig. 1. Eluted heavy metals efficiency in soil with various moisture and at pH conditions after nano-Ca/CaO treatment.

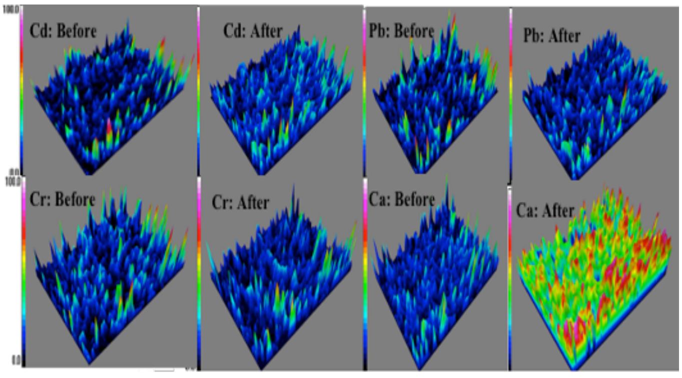
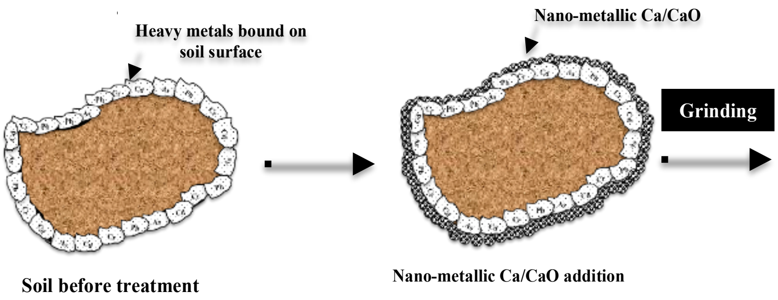
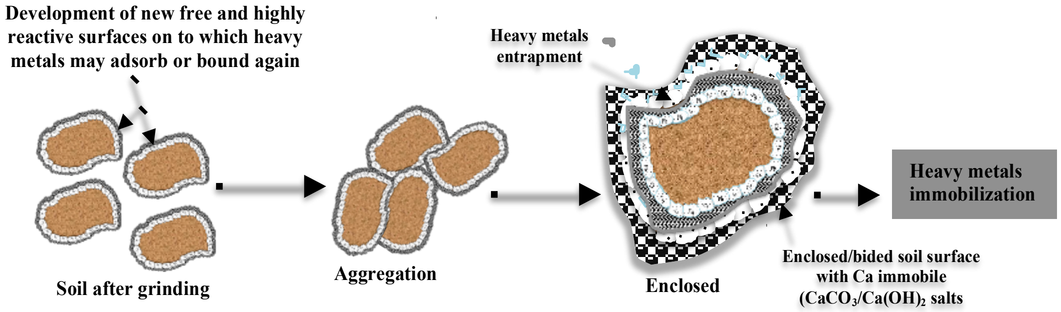


Fig. 2. SEM-EDS 3D elements map of heavy metals contaminated soils before and after nano-metallic Ca/CaO treatment.



a: Heavy metals adsorption and nano-metallic Ca/CaO addition on soil



b: Aggregation/soil surface bided/heavy metals immobilization

Fig. 3. Schematic representation of possible mechanisms which may determine the enhanced heavy metals immobilization efficiency in soil after grinding with nano-metallic Ca/CaO: (a) heavy metals adsorption and nano-metallic Ca/CaO addition; (b) aggregation and surface bided.

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