

New Use of Natural Zeolites and Clay for Environmental Protection and Remediation of Toxic Metals Contamination Sites

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Abstract

Hazardous wastes contaminated by heavy metals, arsenic, and other toxic metals were previously discharged to unlined landfills in and around industry compounds and mining facilities, or near town human lives. These wastes often provoke environmental pollution to groundwater, soils, and other local geologic units which causes serious health risk. In order to prevent the environmental pollution, natural zeolites and clay minerals with calcium compounds can be applied in two ways: One is mixing treatment of these materials to *in situ* remedy for toxic metals pollution within wastes. Ion-exchange property of zeolites and adsorption of clay minerals are effective in this treatment, which makes geochemically very stable state that reduces leaching of the toxic metals. The other is more physical way, that is a use of a mixture of clay minerals and natural zeolites for liner materials at solid waste disposal site of which impermeable property as well as adsorption successfully shields migration of toxic metals from waste sites. In this paper we report typical results of laboratory experiment and a case study of the remediation techniques by using natural zeolites and

clay minerals in solid waste disposal sites in Japan.

Keywords: Heavy metals, Contamination, Remediation, Zeolite, Clay minerals

1. Introduction

Management of hazardous waste became a major concern during last two decades. Hazardous waste is a waste material that has a potential to harm life forms and environment. If hazardous waste are introduced in any area due to a spill or other mismanagement, there may be both short- and long-term effects on human health and the ecological system. One of the major requirements in the management of hazardous waste is, therefore, selection of appropriate site based on geologic setting, proper environmental protection, and remedy of contaminated sites (Nirei,1997).

Currently available site remediation techniques can be classified on the basis of the way they treat contaminants (Soesilo and Wilson, 1997). In this classification remediation techniques may fall into three major categories, physical, chemical, and biological technologies. The physical technologies adopt various physical treatments such as heating, destruction, removal, or isolation by shielding or fixing materials. The chemical technologies normally reduce the solubility or leaching of toxic materials by using chemical treatment. This technology requires the addition of stabilizing agents that chemically stabilized given toxic material. Biological technologies generally apply activities of microorganism such as bacteria for the treatment.

However, in the case of remedial treatment for toxic metal contamination sites, these techniques previously developed have more or less weakness. For instance, one of the most popular treatment, removal of contaminated materials or physical isolation by shield involves a risk of spread of pollution. Chemical treatment is also very

popular technique but it often causes secondary pollution with artificial chemicals. Biological technologies are still immature for general uses.

We have been developing new environment-friendly remediation technique for toxic metals, Ni, Cr, Co, Cd, Cu, Pb, Zn, Hg, As, Se and so on, by using natural zeolites and clay minerals (Minato *et al.*,1996; Okano *et al.*,1996; Minato *et al.*,1997; Minato *et al.*,1998; Minato and Shibue,1999; Minato and Yoshida,1999). In this paper we describe the remediation technique by using natural zeolites and clay minerals, results of laboratory experiment and a case study in waste disposal site in Japan.

2. Role of Zeolites and Clay Minerals: Basic Principle

Heavy metal ions and other toxic cations in water can be removed by an ion-exchange process of natural zeolites (Minato,1994a,b). The chemical formula of natural zeolites is generally expressed as follows:



where the part in square brackets represents the framework atoms (aluminosilicate) and the other parts the extraframework atoms. The tetrahedrally coordinated framework cations may be substituted by Fe^{3+} to a small extent. An important chemical parameter is the ratio of $R=\text{Si}/(\text{Si}+\text{Al}+\text{Fe})$, which indicates the ion-exchangeable capacity of relevant structure (Sugiyama *et al.*,1994). Zeolites have a microporous structure, and the lattice carries a negative electric charge balanced by cations described above, which can be replaced by other cations. In particular, alkalis and alkaline earths Na, K, and Ca ions easily participate the ion-exchange process in water (Minato,1994c; Sub-committee Members from Okutama Kogyo, 1994). Thus, the ion-exchange process results in the replacement of toxic heavy metal cations with the non-toxic ions.

This process is applicable for toxic cations leached water which fills within hazardous wastes.

Clay minerals, mainly montmorillonite, play an important role in this remedial treatment of hazardous waste (Table 1). The ions on the surface of clay particles may be O^{2-} or $(OH)^-$, which give the clay particle a net negative electric charge. The negative electric charge is balanced by the external adsorption of cations at the surface of particle and between the sheets. These externally absorbed cations can be replaced by other cations, which is also the ion-exchange. In the case of montmorillonite, it is well known that the crystal consists of an aluminum sheet between two silica sheets, *i.e.* a 2:1 mineral. The bond holding sheets is due to Van der Waals forces and exchangeable ions. It is very weak bond and easily broken by water or other polar or cationic organic fluids entering between the sheets. There is extensive substitution of silica and alumina, resulting in considerable charge deficiency, which results in high cation exchange capacity.

Poorly crystalline clay minerals such as allophanes also play vital role in the treatment (Table 1). They are formed from weathering process of volcanic ash under poor drainage conditions and/or humid climate. Weathering products of volcanic ash are widely distributed in Japanese island arc and one of the typical deposits is named as the "Kanto Loam". Similar products containing poorly crystalline clay minerals are expected from weathered granite, named as "Masado". In our remedial treatment, the poorly crystalline clay minerals, or even amorphous silicate, show anion exchange capacity and further crystallization which integrates existing toxic cations into the crystal structure as a trace element (Minato and Shibue, 1999).

Calcium compound such as lime (CaO) is additionally mingled with zeolites and

clay in due case. The lime normally precipitates heavy metal cations as metal hydroxide which is far less soluble and non-toxic. Its higher pH condition is preferable to further crystallization (Table 1).

3. Procedure

In general, the procedure of this treatment can be outlined by four steps (Figure 1). The first step is the characterization of contamination site. Proper site characterization is critical for appropriate site remediation planning. It is essential to describe the type of contaminants that lie in the subsurface, the characteristics of the subsurface geology and groundwater, and the movement of the contaminants in the subsurface. Its geology, mineralogy, chemical composition, groundwater, pollutants, and pollution process should be described in detail. The second step is the design of admixture for given contamination site, which is the determination of most suitable combination of natural zeolite, clay minerals, and calcium carbonate. The third step is in-door experiment for verification of the designed composition. Some adsorption tests are normally made with a standard solution of heavy metals. After the completion of these three steps, actual site remediation action, mixing of zeolites, clay minerals, and calcium carbonate with given contaminated soil, is performed (Figure 1).

Table 1: Role of natural zeolites, clayey material and calcium compound in the remedial treatment.

Material	Description	Role
Natural Zeolite	Mordenite, clinoptilolite	Ion-exchange (cations)
Natural Clayey Materials ("Kanto Loam")	Clay minerals (montmorillonite)	Ion-exchange (cations and anions)
	Poorly crystallized clay minerals	Adsorption
	Amorphous silicates	Crystallization of new mineral phase
Calcium compound	lime	pH control Precipitation of metal cations

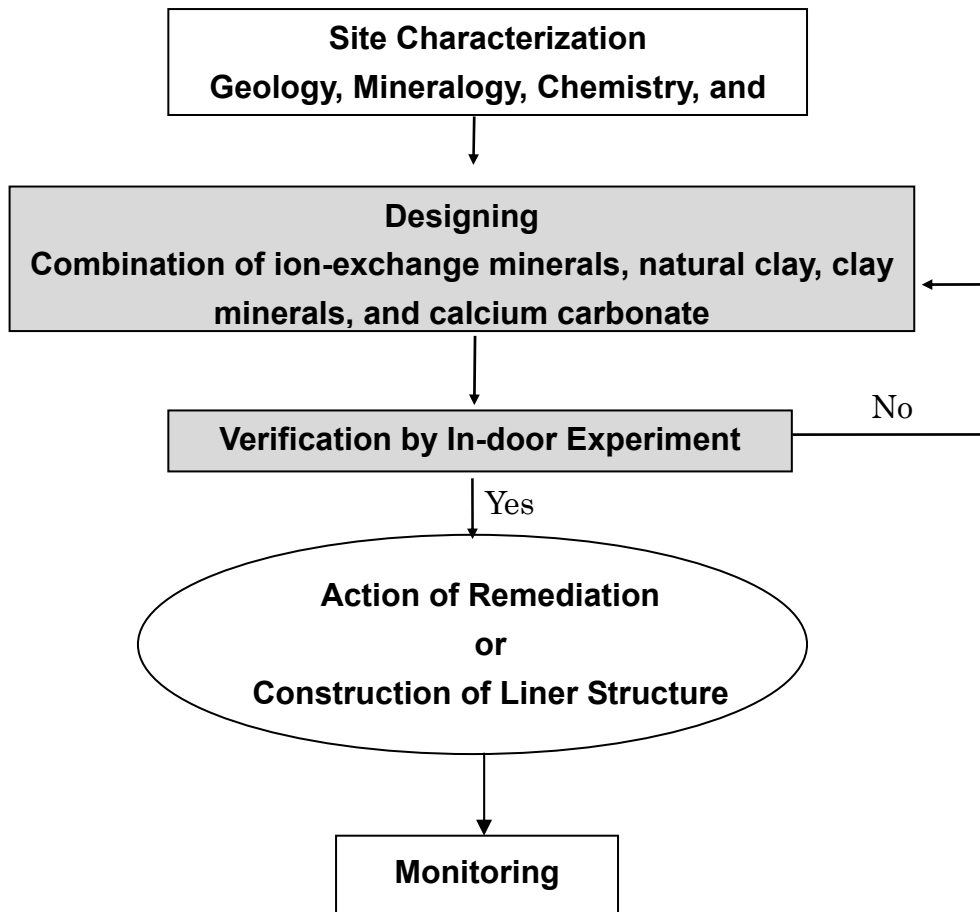


Figure 1: Flowchart of site remediation or environmental protection program by using natural zeolites and clay.

4. Experiment

An in-door adsorption and ion-exchange experiment was made for 2.0ppm standard solutions of toxic metals (Zn, Cd, Cu, Cr, Pb, Ni, As). The results verified that ion-exchange process rapidly exceeds when zeolites, mordenite and clinoptilolite, were added into the solutions (Figure 2). The results also showed that ion-exchange and/or adsorption process were more effective when calcium compound (lime) and “Kanto Loam” were mingled with the zeolites. It is probably caused by rapid precipitation of heavy metal by lime and adsorption by clay minerals.

Table 2 and Figure 3 show another experimental result of adsorption, ion-exchange, and precipitation by using zeolites (mordenite and clinoptilolite) and lime (CaO). It is clear that copper(low concentration), lead, zinc, mercury, and arsenic became insoluble by using the admixture of zeolites (more than 5wt%) and lime (5wt%). High concentration of copper (1030.2mg/l), chromium, and cadmium were drastically decrease the solubility while still some portions were soluble. In this experiment we compared specimen with and without oil (machine oil) contamination which is common in solid waste disposal site in industry compounds. The results show that the presence of oil gives little influence to the capacity of ion-exchange, adsorption and precipitation of metal.

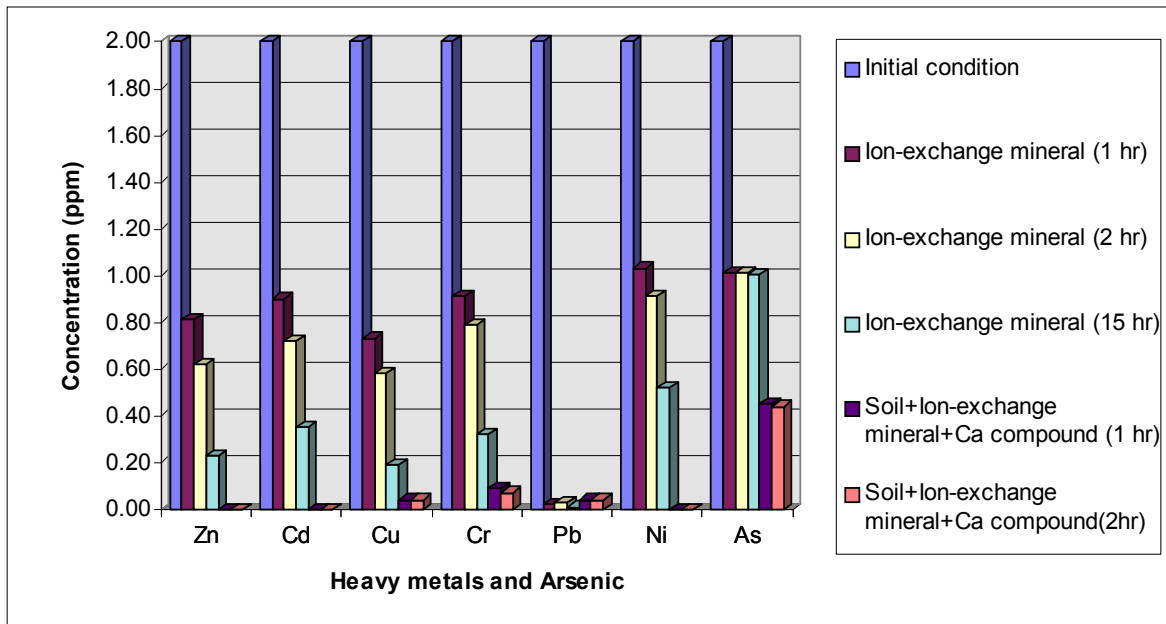


Figure 2: Adsorption test by zeolites (mordenite+clinoptilolite) and “Kanto Loam” among different 2.0ppm solutions of toxic metal cations. The ‘Ca compound’ means lime (CaO). The number of hour (hr) indicates the duration of adsorption treatment, and each bar indicates the concentration of given element after the adsorption (Minato and Shibue, 1999).

Table:2 Results of adsorption/precipitation test by zeolites (mordenite+clinoptilolite) and lime (CaO). Lower table shows the results by the specimens with oil contamination, while upper one shows without oil contamination. Oil contamination has no remarkable influence to ion-exchange and adsorption. Copper(1) indicate low concentration specimen, while copper(2) high concentration one.

(unit: mg/l)

Without oil	Copper(1)	Copper(2)	Lead	Chromium	Cadmium	Zinc	Mercury	Arsenic
	Cu ²⁺	Cu ²⁺	Pb ⁴⁺ ,Pb ²⁺	Cr ³⁺	Cd ²⁺	Zn ²⁺	Hg ₂ ²⁺ ,Hg ²⁺	As ³⁺ ,As ⁵⁺
Initial condition	0.936	1030.2	2.960	1.762	0.945	1.378	1	0.41
Zeolite5%+Lime5%	<0.001	315.5	0.003	0.309	0.009	<0.001	<0.0005	<0.005
Zeolite10%+Lime5%	<0.001	246.0	<0.001	0.247	0.010	<0.001	<0.0005	<0.005
Oil contamination	Copper(1)	Copper(2)	Lead	Chromium	Cadmium	Zinc	Mercury	Arsenic
	Cu ²⁺	Cu ²⁺	Pb ⁴⁺ ,Pb ²⁺	Cr ³⁺	Cd ²⁺	Zn ²⁺	Hg ₂ ²⁺ ,Hg ²⁺	As ³⁺ ,As ⁵⁺
Initial condition	0.936	1030.2	2.960	1.762	0.945	1.378	1	0.41
Zeolite5%+Lime5%	<0.001	273.5	<0.001	0.343	0.010	<0.001	<0.0005	<0.005
Zeolite10%+Lime5%	<0.001	297.6	0.005	0.257	0.011	<0.001	0.0005	<0.005

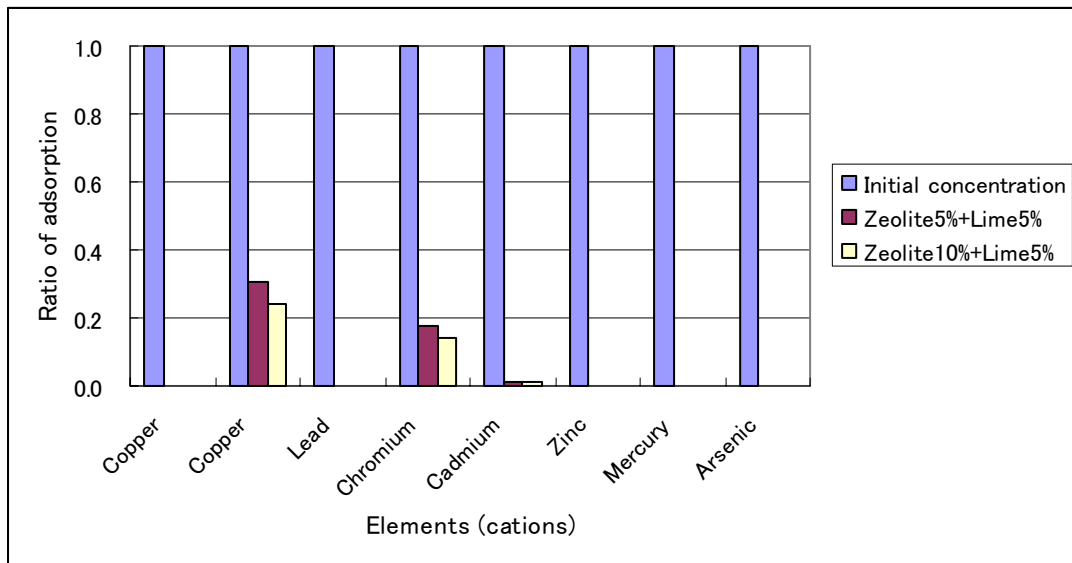


Figure 3: Adsorption rate for each element with different admixture.

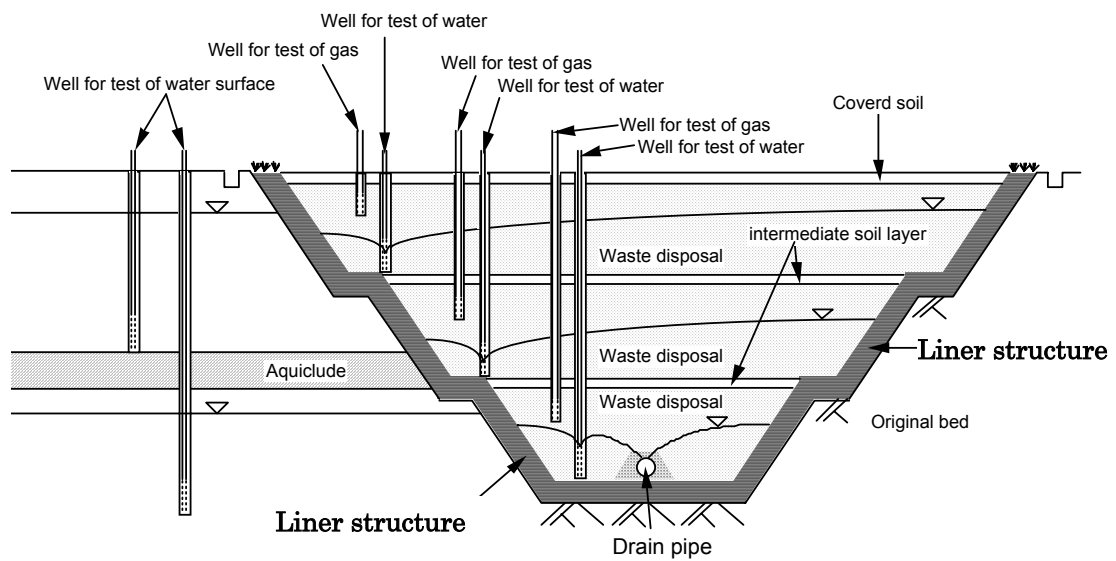


Figure 4: Schematic cross section of waste disposal site with liner structure by natural clayey material mixed by zeolites ('water shielding material'; Minato and Shibue, 1999).

5. Liner Technology

In waste disposal site, waste materials from towns, raw waste and burned ash, are

accumulated in natural area isolated by artificial liners of rubber, plastics, or cement. Harmful water contaminated by toxic metal ions migrates into local groundwater, when the liner structure is damaged owing to aging of liner materials and so on. The damage of liner structure brings out environmental problems in surrounding area of the waste disposal site (Nirei,1997; Suzuki,1997). To avoid the risk of damage of liner, an admixture of natural clay with zeolites can be used for liner materials(Minato *et al.*, 1996; Minato and Shibue, 1999; PAT.Japan H8-197376 "Sealingsoil™"). It is an application of remedial treatment based on ion-exchange, adsorption, and mineralization process by natural materials, which was mentioned in previous chapter (see chapters 2 and 3).

Natural clayey materials containing clay minerals, poorly crystallized clay minerals, and hydrous amorphous silicates should be used for the liner materials (Minato *et al.*,1996; Okano *et al.*,1996; Minato *et al.*,1998; Figure 4). The clayey materials successfully seal off the harmful water formed in the waste disposal site, and they are much more stable against physical disturbances. No damage of liner due to aging can be presumed but become more stable by further crystallization. This technique for liner material in waste disposal site was named as 'Sealingsoil™' in commercial name.

6. Concluding Remarks

The characteristics of the environmental protection and site remediation technique we proposed are as follows: (1) perfectly on-site remediation technique and possible to re-use the remediated soils, (2) only natural mineral materials are employed in the treatment, (3) based on adsorption, ion-exchange, and crystallization of new phase, (4) generally applicable for toxic metal cations.

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