

## **Soil Pollution: State-of the Art in Japan and Soil Washing Process**

*Shuzo Tokunaga*

*Department of Chemical systems*

*National Institute of Materials and Chemical Research*

*1-1 Higashi, Tsukuba, Ibaraki 305 Japan*

### **1. Introduction**

In Japan, no new agricultural soil pollution has been reported these years. However, the number of cases of soil pollution in urban area has been increasing year by year, which amounted to 232 sites in 1994(Environmental Agency, 1995). Urban soils have been polluted by various kinds of hazardous chemicals. Rainwater percolating through the soil slowly mobilizes pollutant such as chromium(VI), mercury and organochlorine compounds, which subsequently contaminates groundwater. In comparison to air and water pollution, soil pollution is difficult to detect since it takes place in invisible underground space and the effect of pollutant is persistent. Specifically in urban area, less soil pollution has been revealed due to its diversity. According to the Agricultural Soil Pollution Prevention Act and the Environmental Quality Standards for Soil Pollution, polluted soils have been remedied by the conventional methods such as soil cover, containment, stabilization, solidification, etc. Since these remedial methods are not perfect, there is always a risk of leakage of pollutant to the environment. The drastic measure to solve the soil pollution problem is to remove the pollutant from the soil. In this paper, the author describes the current state of soil pollution in Japan and soil washing process as an innovative technology for remediation of heavy-metal polluted soils.

### **2. State-of-the-Art of Soil Pollution in Japan**

#### **2.1 History of Soil Pollution and Legislation in Japan**

Table 1 shows a brief history of soil pollution and legislation in Japan. Ashio Mine Pollution is the first case of soil pollution in Japan, which took place alongside Watarase River in Tochigi Prefecture in 1880. Floods carried acid mine drainage from Ashio Mine, one of the biggest copper smelters, to the downstream, which polluted 1,460 ha of soil with copper and sulfuric acid. The polluted soil and river water seriously reduced the crop and affected the health of the inhabitants for more than 20 years. This soil pollution problem was submitted to the then National Diet. In 1902, the company agreed to pay compensation to the inhabitants and to construct drainage treatment facility. The second soil pollution came to known since 1945. Chronic cadmium poisoning called Itai-itai Disease was found among the inhabitants alongside Jinzu River, Toyama Prefecture. The peak year was 1956. This poisoning was caused by ingesting rice polluted with cadmium. The source of cadmium was mine drainage from an upstream zinc smelter. The rice produced in the polluted in the polluted paddy field contained more than 3 mg/kg of cadmium. The patient were suffered from strong pains in the joints. In 1972, after a long trial, the smelter paid compensation to the patients. Thereafter, Minamata Disease caused by

methyl mercury and PCB Poisoning occurred successively. To cope with this situation the Government has enacted the Agricultural Soil Pollution Prevention Act(Act 139, December 25, 1970), by which cadmium has been defined as a hazardous material. According to this Act, the local governments identify polluted agricultural land and take necessary countermeasure. In addition, copper and arsenic have been defined as agricultural soil pollutants in 1972 and 1975, respectively.

The number the patients amounted to 127, who were suffered from cancer and many of them got a cavity in their nose. To cope with this situation, in 1976, the Government amended the Waste Disposal and Public Cleansing Act. The guideline was set for final waste disposal facilities to control hazardous industrial wastes. However, many other cases of soil pollution in urban area were reported from various places of Japan, some of which are listed in Table 2.

Those soil pollutions were caused by improper

Table 1 History of Soil Pollution and Legislation in Japan.

1880-1902	Ashio Mine Pollution in Tochigi by acid mine drainage from a copper smelter.
1945-1972	Itai-itai Disease in Toyama by cadmium-polluted rice.
1856-1996	(Minamata Disease by methyl-mercury polluted fish).
1968-1984	(PCB Poisoning by rice oil polluted with thermal medium).
1970	Agricultural Soil Pollution Prevention Act was set for Cd.
1972	(Agricultural Soil Pollution Prevention Act was amended; Cu).
1973-1981	Chromium Slag Pollution in Tokyo by dumped Cr(VI)-containing slag; Occupational chronic Cr(VI) poisoning among the employees.
1975	(Agricultural Soil Pollution Prevention Act was amended; As).
1976	Waste Disposal and Public Cleansing Act was amended to set guideline for waste disposal facility. (Many cases of urban soil pollution were reported). (Groundwater pollution by organochlorine compounds took place).
1988	Water Pollution Control Act was amended to prohibit seepage of hazardous chemicals to groundwater.
1991	Environmental Quality Standard for Soil Pollution(10 Hazardous chemicals were defined as soil pollutants).
1994	Environmental Quality Standard for Soil Pollution was amended; additional 15 chemicals

The Chromium Slag Pollution in Tokyo is the first case of soil pollution in urban area. In 1973, a large amount of slag containing Cr(VI) was found at a subway construction site, which was dumped by a chemical industry producing chromium compounds. Dumped slag was found one after another at 172 sites and the total polluted area was 332,000 m<sup>2</sup>. At the same time, occupational health hazard by chromium was found among the employees of the same industry.

handling of hazardous materials, leakage from waste disposal site and hazardous wastes which were dumped in the past time when there were no regulations. Recent active urban development has accelerated revelation of soil pollution. Groundwater pollution subsequent to soil pollution has become a subject of public concern which was caused by organochlorine compounds. In 1988, seepage of such toxic materials to groundwater has been regulated by the amended Water

Pollution Control Act. By this Act, flow of pollutants chemicals in the list of soil pollutants. from the surface to underground is regulated and the local governments are obliged to periodically monitor the quality of groundwater.

Table 2. Cases of Urban Soil Pollution in Japan

1975 Aug.	Cr(VI) from a wood preservative factory. Stabilization by the addition of reductant and compression.
1975 Oct.	Hg-containing slag from a former sulfuric acid plant. Pavement.
1976 Oct.	Hg and Ni from the landfill site in a former chemical factory. Stabilization and concrete cut-off
1977 Sep.	Hg, Pb and Cd in a former electrochemical industry. Excavation and incineration.
1980 Jan.	Cyanogen and Cr(VI) in a former electroplating factory. Treatment by an industrial waste handling company.
1986 Mar.	Hg, As and Pb from a former national research institute. Landfilling in an industrial waste disposal area.
1986 May.	PCB in a former condenser plant. Solidification with cement.
1986 Jul.	Cyanogen in a thermal treatment plant. Containment and treatment by an industrial waste handling company.
1986 Dec.	Spill of paint containing PCB. Excavation.
1988 Aug.	Trichloroethylene from a landfill site. Excavation.
1988 Oct.	Tetrachloroethylene from a landfill site of laundry. Excavation.

(Upper line: pollutant and source/Lower line: remediation method)

To take a full-scale countermeasure against complicated soil pollution problems the Environment Agency set the Environmental Quality Standard for Soil Pollution in 1991 for the 10 hazardous chemicals. According to the Standard, the local governments can inspect soil pollution and take necessary countermeasures to remedy polluted soil. In 1994, the Standard have been amended to tighten the guidelines for arsenic and lead and to include additional 15

The present guidelines are shown in Table 3. The guidelines values are defined as the concentration of each hazardous materials in the leachate obtained by contacting 10 w/v % of a soil with water(pH 5.8-6.3) for 6 h. Those standard are applied to all types of soils.

Table 3 Environmental Quality Guidelines for Solids.

Pollutant	Guideline*
Cadmium	0.01 (1 mg/kg-rice)
Total cyanogen	ND
Organophosphorus compound	ND
Lead	0.01
Chromium(VI)	0.05
Arsenic	0.01 (15 mg/kg-soil)
Total mercury	0.0005
Alkylmercuric compounds	ND
PCB	ND
Copper	(125 mg/kg-soil)
Dichloromethane	0.02
Carbon tetrachloride	0.002
1,2-Dichloroethane	0.004
1,1-Dichloroethylene	0.02
cis -1,2-Dichloroethylene	0.04
1,1,1-Trichloroethane	1
1,1,2-Trichloroethane	0.006
Trichloroethylene	0.03
Tetrachloroethylene	0.01
1,3-Dichloropropane	0.002
Thiram	0.006
Simazine	0.003
Thiobencarb	0.02
Benzene	0.01
Selenium	0.01

\* Concentration (mg/L) in leachate unless otherwise noted. Soil is treated with water, pH 5.8 -6.3 for 6 h at 10 w/v% solid concentration.

( ): for agricultural soil

ND: shall not be detected.

## 2.2 Agricultural Soil Pollution

In average, soil contain approximately 0.5, 5 and 10-20 mg/kg of Cd, As and Cu, respectively. Since use of heavy-metal-containing herbicides and insecticide (such as phenylmercuric acetate, lead arsenate and copper sulfate) has been prohibited many years ago, soil pollution by agricultural chemicals has become insignificant. Fig. 1 gives the statistics of pollutants,

polluted area and remediation of polluted agricultural soil (Kankyo Soran, 1996). Polluted agricultural land spreads widely all over Japan amounting 128 sites and 7,140 ha. Since these years no new agricultural soil pollution has been reported, these agricultural soil were polluted in the past. In many cases, these polluted sites are located in volcanic region or downstream of mining area. Volcanic activity and mining drainage supply

hazardous metals. Therefore, the major sources of agricultural soil pollution are nature-originated. Cadmium is by far the common pollutant, contaminating 6,610 ha of area. Pollution by copper and arsenic is much less.

According to the Agricultural Soil Pollution Prevention Act, the corresponding local governments have taken countermeasures to remedy the polluted sites. In the case of Cd-polluted soils, 71.1 % of the area have been already remedied. Cu- and As- polluted soils have been remedied by 86.7 % and 51.8 %, respectively. Therefore, agricultural soil pollution has been progressively improved in Japan. Such remediation measures have been implemented by low-rate loan and government subsidy.

In most cases, polluted soil have been remedied in such a way as shown in Fig. 2. Cadmium-polluted soil is treated by the soil-cover method. The polluted soil is covered with a layer of non-polluted soil of 20 -25 cm thickness so that rice grown there should not contain more than 1 mg/kg-rice of cadmium. Copper- or arsenic-polluted soil is by the dilution method. The polluted surface soil is mixed with non-polluted soil so as to reduce the copper and arsenic content to less than 125 and 15 mg/kg-soil, respectively.

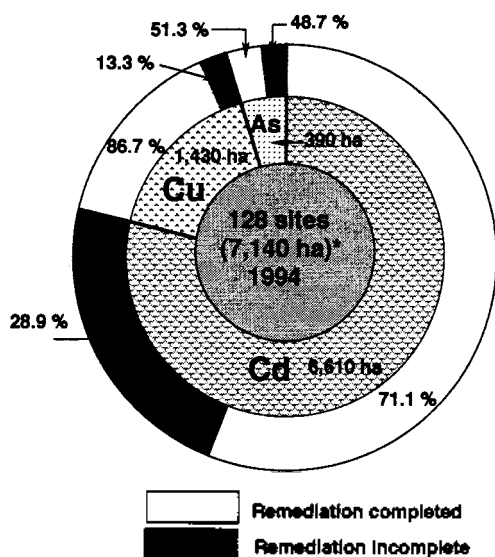


Fig. 1 Pollution of Agricultural Land and Remediation

\*Due to multiple pollution of some sites, the total area is not equal to the sum of the individual area.

(ha =  $1 \times 10^4$  m<sup>2</sup>)

### 2.3 Urban Soil Pollution

In comparison to agricultural soil pollution, urban soil pollution is complicated since (1) owner and polluter are different, in many cases, (2) pollution takes place in relatively small area, (3) pollutants are diversified, and (4) inspection by authority is limited. In 1994, soils of 232 urban area were polluted with various kinds of hazardous chemicals. Fig. 3 exhibits the classification of pollutants detected (Environmental Agency, 1995). Some sites are polluted by multiple pollutants. Pollution by inorganic materials accounts for 62.2% of the source of pollution in the order Pb>Cr(VI)>Hg>Cd>As>CN>Zn. As for organic pollutants, tetrachloroethylene, trichloroethylene and PCB account for 11.2%, 10.5% and 4.5%, respectively. Such organochlorine compounds are liable to contaminate groundwater. Industries causing urban soil pollution are in the order chemical industry > electroplating industry > electrical machinery industry > laundry.

According to the Environmental Quality Standard for Soil Pollution, the remediation has been completed on the 149 (64.3%) sites out of the 232 sites under the guidance of the corresponding local governments. Fig. 4 shows the category of the remedial technologies applied

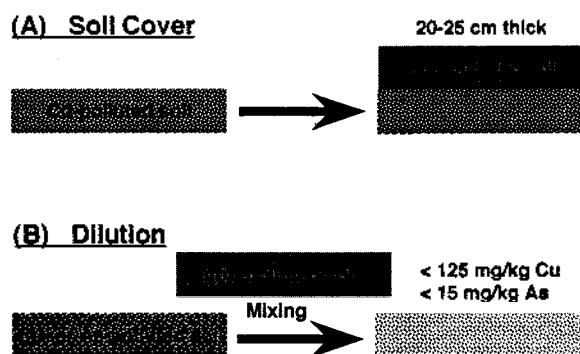


Fig. 2 Remediation of Agricultural Soils

(Environmental Agency, 1995). In some cases, two or three different technologies were applied at a site, e.g., combination of containment and stabilization or solidification. The description of some of the technologies are given below.

**Containment:** In most cases, polluted soil is excavated and transported to a containment facility where the polluted soil is confined in a large vat so that the pollutant does not spread to the environment. There are two types of containment; concrete cut-off and water-barrier. The vat of concrete cut-off is made of concrete and that of water-barrier is lined with layers of impermeability plastic sheet and clay (bentonite). Containment accounts for 30% of the remediation.

**Industrial waste handling companies:** Industrial waste handling companies treated and disposed of 25% of the polluted soils.

**Stabilization:** The mobility of pollutant is minimized by the addition of suitable chemical. For example, Cr(VI) is reduced by a reductant to Cr(III) and hydrolyzed to hydroxide, because Cr(III) is much less soluble and less toxic than Cr(VI) species. Hydrolizable heavy metals are stabilized by the addition of lime, which increases a soil pH to form less soluble hydroxide (Marschner et al., 1995). Sodium sulfide is used to stabilize soils polluted with Cd or Pd. Lead is stabilized also by the addition of phosphate (Ruby et al., 1994).

**Vacuum extraction:** Volatile and semivolatile pollutants can be extracted by driving wells in the polluted zone and sucking them with a vacuum pump. This method is effective for unsaturated zone without excavation, but not effective for saturated zone. Subsequent treatment of the gas containing pollutant is required. Vacuum extraction is suited for the removal of trichloroethylene, perchloroethylene and gasoline.

**Incineration:** The polluted soil is directly heated in a rotary kiln to decompose organic pollutants to carbon dioxide and water (Shultz et al., 1994). The incineration methods is suited for less-volatile heavy hydrocarbons.

**Thermal desorption:** The polluted soil is heated at low temperature, 150 - 700°C to vaporize pollutants (Wilson and Tamamushi, 1993; Percin, 1995). The vapor stream is usually cooled to condense liquid products. Therefore additional cleaning step is required.

**Solidification:** The polluted soil is mixed with cement to solidify so that it becomes easy to handle and the pollutant is less mobile.

### 3. Soil Washing Process

#### 3.1 Soil Pollution by Heavy Metals

Among soil pollutants, heavy metals are (1) non-volatile; vacuum extraction and thermal desorption

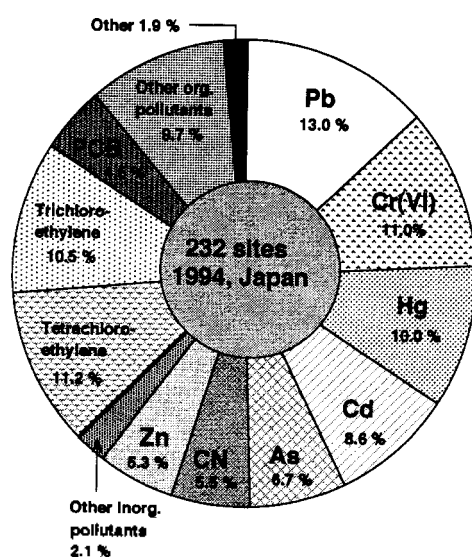
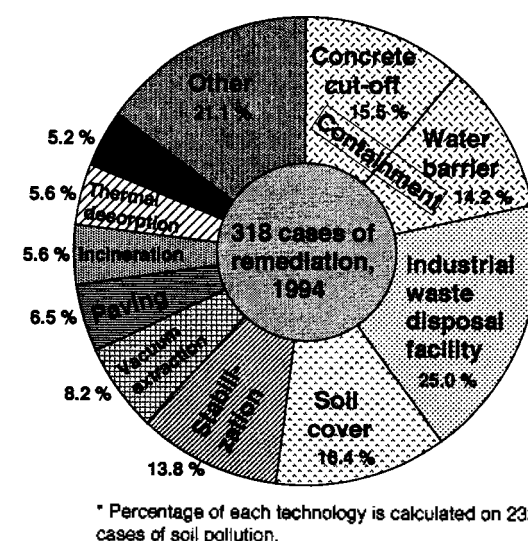


Fig. 3 Classification of Soil Pollutants in Urban Area



\* Percentage of each technology is calculated on 232 cases of soil pollution.

Fig. 4 Remediation technologies for polluted urban soils

methods are not effective remove them, but semivolatile Hg compounds can be treated by thermal desorption (Weilandt, 1994), (2) highly toxic (Niebor and Richardson, 1980); serious pollution diseases were caused by Hg, Cd and Pb in Japan, (3) non-biodegradable; soil microorganisms cannot decompose them, (4) liable to adsorption, complex formation with soil organics, precipitation as carbonate, hydroxide, sulfide, etc. (Schnitzer and Skinner, 1966; Christensen, 1984; Evans, 1989; Livens, 1991), and (5) liable to contaminate groundwater; some mobile heavy metal such as Cr(VI) and other metals solubilized such as by acid-rain leaching contaminate groundwater (Bergfeldt, 1994). Due to these properties, once soil has been polluted with heavy metal, the effects are persistent. Many cases of soil pollution by heavy metals have been reported from many places of the world (Magaritz et al., 1990; Kotuby-Amacher et al., 1992; Chung et al., 1994; Park et al., 1995). Most of the environmental methods are not clean-up technology of which effect is not permanent. There is always a risk of leakage of hazardous materials to the environment. Moreover, remediation costs have significantly increased these years. Drastics measure to solve the problems of soil pollution by heavy metal is to remove the pollutant from the soil. Soil washing process is one of the most effective and economical methods to remove heavy metal from soil. Many bench-scale studies have been reported for the removal of heavy metal. The effects of some cleaning agents are discussed below.

### 3.2 Mineral Acid

In many cases, the interaction between soil and heavy metals is pH dependent. Fig. 5 shows uptake of heavy metals by four types of soil materials as a function of pH (Amfalk et al., 1996). Except Cr(VI), uptake of heavy metals increases with increasing pH. The pH value where 100% of metal is retained by the soil is in the order  $Hg > Cd > Pb > Cr(III)$ . Above these pH ranges, heavy metals form insoluble hydroxides. Although Cr(VI) does not hydrolyze, more than 60% of

Cr(VI) are removed in the pH range of 2-3, which may be retained by aluminum oxide, a major soil component (Prokish et al., 1995). Similar metal uptake sequence is reported by Lo et al. (1992), which shows that uptake of Cu and Cd is significantly affected by soil organic matter. In general, heavy metals are hardly retained by soil in low pH region, suggesting that soil-bound metals may be desorbed by decreasing pH.

For Washing polluted soil, HCl and  $HNO_3$  have been used extensively. Table 4 shows the effects of soil washing with mineral acids. A 0.1 M HCl is effective to remove Cu, Ni, Pb and Zn with 77 to 97% removal (Tuin and Tels, 1990; Reed et al., 1995). But only 32% of Pb are removed by 0.1 M HCl when it is in the form of  $PbSO_4$ (solid). In general, the concentration of HCl should be higher than 0.1M. Hydrochloric acid is not effective to remove total Cr, 7% being removed by 0.1 M HCl. Only carbonate-bound Cr(III) can be removed by acid (Wernicke et al., 1993). Even by increasing the concentration of HCl to 1 M and with prolonged treating time, the Cr removal is low. Hydrochloric acid is neither effective to remove mercury (Wasay et al., 1995).

A low concentration of nitric acid, 0.001 M, is not effective to remove Pb and Cu (Bodeker et al., 1994). By increasing the concentration of nitric acid to 0.01 M to 0.1 M, Zn, Pb, Cu and Cd can be removed with more than 70% removal.

The acid washing is advantageous in treatment of leachate containing heavy metals which can be done by a simple precipitation method. But adverse effects may occur to the soil's physical and chemical structure by using strong acid, which dissolves significant amounts of silica, aluminum and other constituents. Therefore, acid concentration should be optimized.

### 3.3 Inorganic Cleaning Agent

Table 5 shows the effects of soil washing with inorganic cleaning agents other than mineral acids. Mercuric sulfide is a common form of mercury in soils. Fig. 6 shows the results washing a soil polluted

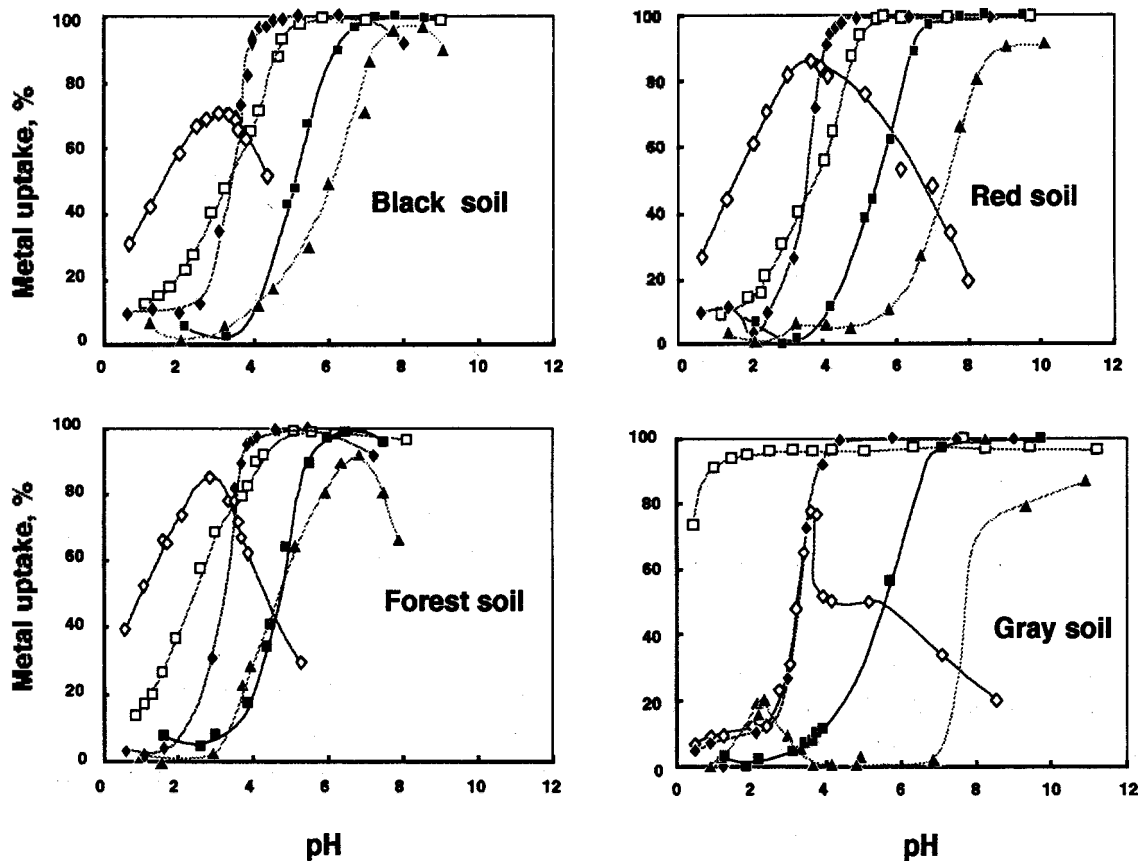


Fig. 5 Uptake of heavy metals by soils as a function of pH.

■ Cd ◆ Cr(III) ◇ Cr(VI) ▲ Hg □ Pb (Arnfolk *et al.*, 1996)

mainly by mercuric sulfide with various cleaning agents (Wasay *et al.*, 1995). Hydrochloric acid nor 0.05 M EDTA is not effective to remove mercury. An acidic 0.1 M KI solution shows very high percentage removal of mercury. The mechanism of the removal is formation of soluble mercuric iodide complex,  $\text{HgI}_4^{2-}$ . The leachate containing  $\text{HgI}_4^{2-}$  can be successfully treated with activated carbon in the neutral pH range.

Usually it is difficult to remove Cr by acid washing. But, 70 - 85% of Cr in soil can be extracted with a hot 0.46 M sodium hypochlorite solution at pH 8.5 (Tuin and Tels, 1990). Sodium hypochlorite is also effective to remove Zn.

Calcium chloride works to remove Zn, Pb and  $\text{PbSO}_4$  (Bodeker *et al.*, 1994; Reed *et al.*, 1995). The mechanism of the desorption is thought to be cation exchange reaction. Cation exchange reaction is one of

the major mechanisms of retention of heavy metals by soils. Such heavy metals can be desorbed by the addition of a secondary exchange cation of higher affinity to the soil. For this purpose  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  ions are used. Originally, both Ca and Mg are abundant in soils and harmless.

### 3.4 Chelating Agent

Some chelating agents form soluble metal complexes and hence are utilized to extract soil-bound metals. Ethylenediaminetetraacetic acid (EDTA), nitrilotriacetic acid (NTA) and diethylenetriamine pentaacetic acid (DTPA) have been studied extensively. Table 6 shows the effects of soil washing with these chelating agents. A 0.01 M EDTA solution is effective to extract Pb in the form of  $\text{Pb(II)}$ ,  $\text{PbSO}_4(\text{s})$  and  $\text{PbCO}_3(\text{s})$  with 100% removal from soils (Reed *et al.*,



1995). The Pb removal from soils containing 10,000 mg/kg are 64.2 and 19.1 % for EDTA and NTA, respectively (Peter and Shem, 1992). Extraction with EDTA is rapid and pH-insensitive whereas that with NTA is slow and pH-dependent. A  $3 \times 10^{-3}$  M EDTA and DTPA (pH 6) are effective to completely remove Zn from soil containing 4,450 mg/kg of Zn (Davis and Singh, 1995). By increasing NTA concentration from  $10^{-5}$  M to  $10^{-3}$  M (pH 6), the Cu removal increases from 16% to 59%; similarly the Zn removal increase from 13% to 44% (Linn and Elliott, 1988).

By using chelating agents heavy metals can be removed with high percentage removal, but the problems are (1) cost of chelating agents, (2) difficulty of leachate treatment because some chelate complexes are highly stable, and (3) environmental safety (Sorvari and Sillanpaa, 1996); NTA is biodegraded without producing metabolite, therefore, has been utilized as detergent. DTPA is degradable with producing several

metabolites. EDTA is non-degradable (Stumpf et al., 1996).

### 3.5 Naturally Occurring Organic Acid

Some naturally occurring organic acids are used for soil washing, because of their effects to lower pH value and to form soluble metal complexes. The advantages of such organic acids are (1) low cost, (2) biodegradable, therefore friendly to the environmental, and (3) less destructive to soil structure than mineral acids. Table 7 shows the effects of soil washing with naturally occurring organic acids.

A 0.1 M acetic acid is effective to remove Pb, Cu, Cd and Zn with more than 50% removal (Reed et al., 1995; Farrah and Pickering, 1978). Whereas 1.67 M acetic acid gives lower removal for Pd and Cu, since the metal constants are low (Bodeker et al., 1994). In general, it is more difficult to remove less amount of heavy metals since they are more strongly bound to the

Table 4 Effect of soil washing with mineral acids.

Cleaning agent	Metal	Content mg/kg-soil	Removal %	First Author year
0.1 M HCl	Cu	2,158	92	Tuin, 1990
0.1 M HCl	Ni	2,100	77	Tuin, 1990
0.1 M HCl	Pb	428	79	Tuin, 1990
0.1 M HCl	Zn	1,185	75	Tuin, 1990
0.1 M HCl	Pb	500	85	Reed, 1995
0.1 M HCl	PbCO <sub>3</sub> (s)	10,000	97	Reed, 1995
0.1 M HCl	PbSO <sub>4</sub> (s)	10,000	32	Reed, 1995
0.1 M HCl	total Cr	588	7	Tuin, 1990
1 M HCl	Cr(III)	1,500	low	Wernicke, 1993
0.01 M HCl	Hg	47,100	10	Wasay, 1995
0.001 M HNO <sub>3</sub> (pH 3.0)	Pb	192	6	Boedeker, 1994
0.001 M HNO <sub>3</sub> (pH 3.0)	Cu	109	9	Boedeker, 1994
0.001 M HNO <sub>3</sub> (pH 3.0)	Zn	805	64	Boedeker, 1994
0.01 M HNO <sub>3</sub> (pH 2.0)	Zn	4,450	81	Davis, 1995
0.1 M HNO <sub>3</sub> (pH 1.4)	Pb	2,211	90-95	Farrah, 1978
0.1 M HNO <sub>3</sub> (pH 1.4)	Cu	678	70-85	Farrah, 1978
0.1 M HNO <sub>3</sub> (pH 1.4)	Cd	1,199	70-85	Farrah, 1978
0.1 M HNO <sub>3</sub> (pH 1.4)	Zn	698	70-85	Farrah, 1978

Table 5 Effect of soil washing with inorganic cleaning agents

Cleaning agent	Metal	Content mg/kg-soil	Removal %	First author year
0.1 M KI(pH 1.5)	Hg	47,100	100	Wassy, 1995
0.46 M NaOCl(pH 8.5)	total Cr	588	70-85	Tuin, 1990
0.2 M NaOCl	Zn	4,450	64	Davis, 1995
0.01 M CaCl <sub>2</sub>	Cu	98	5	Linn, 1988
0.01 M CaCl <sub>2</sub>	Zn	225	27	Linn, 1988
0.023 M CaCl <sub>2</sub>	Pb	192	27	Boedeker, 1994
0.023 M CaCl <sub>2</sub>	Cu	109	9	Boedeker, 1994
0.023 M CaCl <sub>2</sub>	Zn	805	89	Boedeker, 1994
1.0 M CaCl <sub>2</sub>	Pb	500	78	Reed, 1995
1.0 M CaCl <sub>2</sub>	PbSO <sub>4</sub> (s)	10,000	96	Reed, 1995
1.0 M CaCl <sub>2</sub>	PbCO <sub>3</sub> (s)	10,000	14	Reed, 1995

Table 6 Effect of soil washing with chelating agents.

Cleaning agent	Metal	Content mg/kg-soil	Removal %	First author year
0.001 M EDTA(pH 7.2)	Pb	2,211	90-95	Farrah, 1978
0.001 M EDTA(pH 7.2)	Cu	678	90-95	Farrah, 1978
0.001 M EDTA(pH 7.2)	Cd	1,199	90-95	Farrah, 1978
0.001 M EDTA(pH 7.2)	Zn	698	90-95	Farrah, 1978
0.01 M EDTA	Pb	500	100	Reed, 1995
0.01 M EDTA	PbSO <sub>4</sub> (s)	10,000	100	Reed, 1995
0.01 M EDTA	PbCO <sub>3</sub> (s)	10,000	100	Reed, 1995
0.03 M EDTA(pH 6)	Zn	4,450	100	Davis, 1995
0.05 M EDTA	Hg	47,100	17	Wasay, 1995
0.1 M EDTA	Pb	10,000	64.2	Peters, 1992
0.00001 M NTA(pH 6)	Cu	98	16	Linn, 1988
0.0001 M NTA(pH 6)	Cu	98	39	Linn, 1988
0.001 M NTA(pH 6)	Cu	98	59	Linn, 1988
0.00001 M NTA(pH 6)	Zn	225	13	Linn, 1988
0.0001 M NTA(pH 6)	Zn	225	31	Linn, 1988
0.001 M NTA(pH 6)	Zn	225	44	Linn, 1988
0.1 M NTA	Pb	10,000	19.1	Peters, 1992
0.03 M DTPA(pH 6)	Zn	4,450		Davis, 1995

EDTA: ethylenediaminetetraacetic acid

NTA: nitrilotriacetic acid

DTPA: diethylenetriaminepentaacetic acid

Table 7 Effect of soil washing with naturally occurring organic acids

Cleaning agent	Metal	Content mg/kg-soil	Removal %	Fisrt Author year
0.1 M Acetic acid	PbSO <sub>4</sub> (s)	10,000	89	Reed, 1995
0.1 M Acetic acid	PbCO <sub>3</sub> (s)	10,000	71	Reed, 1995
0.1 M Acetic acid(pH 2.9)	Pb	2,211	50-65	Farrah, 1978
0.1 M Acetic acid(pH 2.9)	Cu	678	50-65	Farrah, 1978
0.1 M Acetic acid(pH 2.9)	Cd	1,199	50-65	Farrah, 1978
0.1 M Acetic acid(pH 2.9)	Zn	698	50-65	Farrah, 1978
1.67 M Acetic acid(pH 3.6)	Pb	192	11	Boedeker, 1994
1.67 M Acetic acid(pH 3.6)	Cu	109	12	Boedeker, 1994
1.67 M Acetic acid(pH 3.6)	Zn	805	85	Boedeker, 1994
0.1 M Oxalic acid(pH 3.3)	Pb	2,211	90-95	Farrah, 1978
0.1 M Oxalic acid(pH 3.3)	Cu	678	70-85	Farrah, 1978
0.1 M Oxalic acid(pH 3.3)	Cd	1,199	90-95	Farrah, 1978
0.1 M Oxalic acid(pH 3.3)	Zn	698	90-95	Farrah, 1978
0.26 M Citric acid(pH 7)	Cu	327	47	Leidmann, 1944
0.26 M Citric acid(pH 7)	Ni	85	42	Leidmann, 1944
0.26 M Citric acid(pH 7)	Cd	46	75	Leidmann, 1944
0.26 M Citric acid(pH 7)	Zn	1,646	56	Leidmann, 1944
0.26 M Citric acid(pH 7)	Cr	246	28	Leidmann, 1944
0.26 M Citric acid(pH 7)	Pb	1,328	23	Leidmann, 1944
0.52 M Citric acid(pH 5)	Pb	192	46	Boedeker, 1994
0.52 M Citric acid(pH 5)	Cu	109	22	Boedeker, 1994
0.52 M Citric acid(pH 5)	Zn	805	77	Boedeker, 1994
0.01 M Sodium citrate(pH 7.8)	Pb	2,211	50-65	Farrah, 1978
0.01 M Sodium citrate(pH 7.8)	Cu	678	50-65	Farrah, 1978
0.01 M Sodium citrate(pH 7.8)	Cd	1,199	90-95	Farrah, 1978
0.01 M Sodium citrate(pH 7.8)	Zn	698	90-95	Farrah, 1978
5 % Glycine(pH 7.0)	Cu	2,403	94.7	Fischer, 1993
5 % Glycine(pH 7.0)	Ni	1,074	84.9	Fischer, 1993
5 % Glycine(pH 7.0)	Zn	6,240	69.9	Fischer, 1993
5 % Glycine(pH 7.0)	Cd	51	61.3	Fischer, 1993
5 % Glycine(pH 7.0)	Pb	3,100	9.4	Fischer, 1993
Grass silage juice(pH 7.0)	Cu	327	75	Leidmann, 1944
Grass silage juice(pH 7.0)	Ni	85	35	Leidmann, 1944
Grass silage juice(pH 7.0)	Cd	46	31	Leidmann, 1944
Grass silage juice(pH 7.0)	Zn	1,646	23	Leidmann, 1944
Grass silage juice(pH 7.0)	Cr	246	5	Leidmann, 1944
Grass silage juice(pH 7.0)	Pb	1,328	2	Leidmann, 1944

soil. Oxalic acid is effective to remove Pb, Cu, Cd and Zn with high removals (Farrah and Pickering, 1978). The removals of Pb, Cu and Zn by citric acid are lower than those of oxalic acid (Leidmann et al., 1994; Bodeker et al., 1994). Citric acid has a significant effect on the interaction of Hg with kaolinite (Singh et al., 1996). A 0.01 M sodium citrate (pH 7.8) is also effective to remove Pb, Cu, Cd and Zn (Farrah and Pickering, 1978).

A 5% glycine, an amino acid, can remove 94.7% of Cu, 84.9% of Ni, 69.9% of Zn, 61.3% of Cd and 9.4% of Pb after 8 d from highly polluted bentonite (Fischer et al., 1993). The metal removal reduces when it is applied to polluted peat.

Grass silage juice contains aliphatic acids (e.g. acetic acid, lactic acid) and amino acids (e.g. alanine, leucine, valine) and is effective to remove Cd and Zn from a sandy silty loam polluted by sewage sludge (Leidmann et al., 1994).

### 3.6 Biosurfactant

Some biosurfactant produced by organisms from stable complexes with heavy metals and hence can be used to remove heavy metals from soils (Miller, 1995). In general biosurfactants are colloidal of which molecular weight is less than 1500. As shown in Table 8, a rhamnolipid biosurfactant (monovalent anion) produced by *Pseudomonas aeruginosa* is effective to remove Pb, Cd and Zn from soil (Herman et al., 1995). According to the stability constant, the rhamnolipid has a heavy-metal selectivity in the order  $Pb \approx Cd > Zn$ . Similarly to chelating agents, biosurfactants are expensive, but their advantages are (1) environmental

safety (biodegradable), (2) selectivity of heavy metals due to their different chemical structures, and (3) possibility of reuse/regeneration by acid treatment.

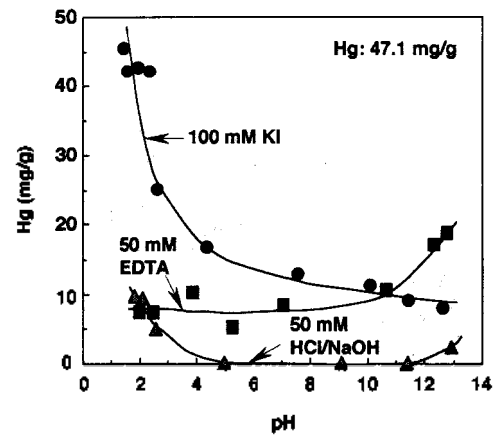


Fig. 6 Extraction of mercury from soil with different cleaning agents as a function of pH. (Wasay et al., 1995)

### 4. Soil Flushing Process

By using an effective cleaning agent, an in-situ soil flushing process can be schemed as shown in Fig. 7. The polluted soil is confined within the original place by water-tight sheet piles which reach the impermeability layer. Cleaning solution is sprayed over the soil and heavy metals are solubilized. The leachate is sucked by a pump to the surface through the well. The leachate containing heavy metal is treated by a conventional method and may be regenerated to recycle. This procedure is continued until the soil meets the standard. The in-situ method is more advantages

Table 8 effect of soil washing with biosurfactant

Cleaning agent	Metal	Content mg/kg-soil	Removal %	First Author year
0.0125 M Rhamnolipid	Cd	164	2.2	Herman, 1995
0.08 M Rhamnolipid	Cd	164	55.9	Herman, 1995
0.05 M Rhamnolipid	Pb	406	27.5	Herman, 1995
0.08 M Rhamnolipid	Pb	406	41.6	Herman, 1995
0.08 M Rhamnolipid	Zn	41.8	41	Herman, 1995

than ex-situ method because there is no excavation and transportation of soils. Selection of cleaning agent is more important and the criteria are effectiveness, cost, environmental safety and selectivity for heavy metal.

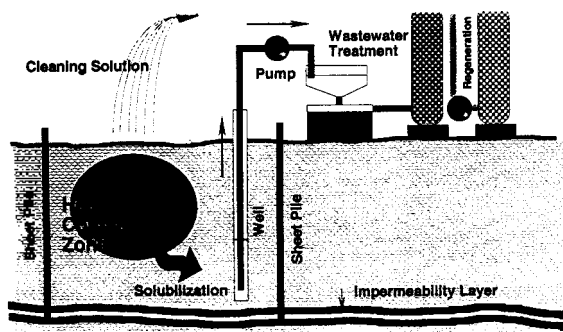


Fig. 7 Scheme of in-situ soil flushing method

## References

- 1) Arnfalk, P., Wasay, S.A., and Tokunaga, S. (1996) A comparative study of Cd, Cr(III), Cr(VI), Hg and Pb uptake by minerals and soil materials. *Water, Air & Soil Pollut.* 87, 131-148.
- 2) Berfeldt, B. (1994) Solution and exchange processes in the unsaturated soil water zone and effects on the groundwater *Karlsruher Geochem. Hefte* 4, 266 pp.
- 3) Bodeker, H., Schlaak, M., Siefert, E., and De Vries, J. (1994) Elution von Schwermetallen aus Biomüll und Kompost durch schwache organische Säuren. *Müll und abfall* 26(12), 816-827(in German)
- 4) Christensen, T.H.(1984) Cadmium soil sorption at low concentrations: 1. Effect of time, cadmium load, pH and calcium. *Water, Air, and Soil Pollut.* 21, 105-114.
- 5) Chung, I.K., Hong, S.S., and Yun, I. (1994) A survey of soil pollution in Pusan City Area, *Yakhak hoeji* 38(6), 725-732(in Korean)
- 6) Davis, A., and Singh, I., (1995) Washing of zinc(II) from polluted soil column. *J. Environ. Eng. (N.Y.)* 121(2), 174-185.
- 7) Environment Agency, Japan (1991) Environmental Quality Standards for Soil Pollution. Notification No. 46 of the Environment Agency, August 23, 1991(in Japanese)
- 8) Environment Agency, Japan (1994) Environmental Quality Standards for Soil Pollution. Notification No. 25 of the Environment Agency, February 21, 1994(in Japanese)
- 9) Environment Agency, Japan (1995) '94 Survey report on soil pollution and countermeasure June 27, 1995(in Japanese)
- 10) Evans, L.J. (1989) Chemistry of metal retention by soil, *Environ. Sci. Technol.* 23(9), 1046-1056
- 11) Farrah, H., and Pickering, W.F. (1978) Extraction of heavy metal ions sorbed on clays. *Water, Air, and Soil Pollut.* 9, 491-498.
- 12) Fischer, K., Rainer, C., Bieniek, D., and Kettrup, A. (1993) Extraction of heavy metals from polluted materials by amino acids. *Polluted Soil '93*, 1157-1158.
- 13) Herman, D.C., Ariola, J.F., and Miller, R.M. (1995) Removal of cadmium, lead, and zinc from soil by a rhamnolipid biosurfactant. *Environ. Sci. Technol.* 29, 2280-2285.
- 14) Kankyo Soran (1996) *Tsusan Shiryō Chosa Kai*, pp. 456(in Japanese).
- 15) Keller, L., Copper, D., and Volchek, K. (1993) The removal of heavy metals from soil washing rinsewaters and fines. *Procs. 10th Tech. Seminar on Chemical Spills*, sept. 7-8, 1993, New Brunswick, Canada.
- 16) Kotuby-Amacher, J., Gambrell, R.P., and Amacher, M.C. (1992) The distribution and environmental chemistry of lead in soil at an abandoned battery reclamation site. in *Engineering Aspects of Metal-Waste Management*. ed. Iskandar I.K., and Selim, H.M., Lewis Publishers, pp. 1-24.
- 17) Leidmann, P., Fischer, K., Bieniek, D., Nuflein, F., and Kettrup, A. (1994) Removal of heavy metals from polluted soil with grass silage juice. *Chemosphere* 28(2), 383-390.
- 18) Linn, J.H., and Elliott, H.A. (1988) Mobilization of Cu and Zn in contaminated soil by nitrilotriacetic acid.

- Water, Air, Soil Pollut. 37, 449-458.
- 19) Livens, F.R. (1991) Chemical reactions of metals with humic material. *Environ. Pollut.* 70(3), 183-208.
  - 20) Lo, K.S.L., Yang, W.F., and Lin, Y.C. (1992) Effects of organic matter on the specific adsorption of heavy metals by soil. *Toxicol. Environ. Chem.* 34, 139-153.
  - 21) Mgaritz, M., Amiel, A.J., Ronen, D., and Wells, M.C. (1990) Distribution of metals in a polluted aquifer: a comparison of aquifer suspended materials to fine sediments of the adjacent environment. *J. Contam. Hydrol.* 5, 333-347.
  - 22) Marschner, B., Henke, U., and Wessolek, G. (1995) Effects of melioative additives on the adsorption and binding forms of heavy metals in a contaminated topsoil from a former sewage farm. *Z. Pflanzenernahr. Bodenk.* 158, 9-14.
  - 23) Miller, R.M. (1995) Biosurfactant-facilitated remediation of metal-contaminated soils. *Environ. Health Perspect. Suppl.* 103 (Suppl. 1), 59-62.
  - 24) Niebor, E. and Richardson, D.H.S. (1980) The replcement of the nondescript term 'heavy metals' by a biologically and chemically significant classification of metal ions. *Environ. Poll. Ser. B* 1, 3-26.
  - 25) Park, C.Y., Park, Y.S., and Jeong, Y.J. (1995) Contamination of heavy metals in soil in the Kwangyang mine area, Han'guk Chawon Konghak Hoechi 32(2), 163-174(in Korean)
  - 26) ercin, P.R. (1995) Application of thermal desorption technologies to hazardous waste sites. *J. Hazard. Materials* 40, 203-209.
  - 27) Peters, R.W., and Shem, L. (1992) Use of chelating agents for remediation of heavy metal polluted soil. in *Environmental Remediation*, American Chemical Society, pp. 70-84.
  - 28) Reed, B.E., Moore, R.E., and Cline, S.R. (1995) Soil flushing of a sandy loam polluted with Pb(II), PbSO<sub>4</sub>(s), PbCO<sub>3</sub>(s) or Pb-naphthalene: Column results *J. Soil Contam.* 4(3), 243-267.
  - 29) Ruby, M.V., Davis, A., and Nicholson, A. (1994) In situ formation of lead phosphate in soils as a method to immobilize lead. *Environ. Sci. Technol.* 28, 646-654.
  - 30) Schnitzer, M., and Skinner, S.I.M. (1966) Organometallic interactions in soils. V. Stability constants of Cu<sup>++</sup>, Fe<sup>++</sup>, and Zn<sup>++</sup>-fulvic acid complexes. *Soil Sci.* 102(6), 361-365.
  - 31) Shultz, D.W.R., Shultz, S.R., Pinion, J.G., and Pennell, C. (1994) Incineration treatability results for contaminated soil and drummed wastes from a Superfund site. *Procs. 48th Ind. Waste Conf.* 1993, 355-365.
  - 32) Singh, J., Huang, P.M., Hammer, U.T., and Liaw, W.K. (1996) Influence of citric acid and glycine on the adsorption of mercury(II) by kaolinite under various pH conditions. *Clays clay Miner.* 44(1), 41-48.
  - 33) Sorvari, J., and Sillanpaa, M. (1996) Influence of metal complex formation on heavy metal and free EDTA and DTPA acute toxicity determined by *Daphnia magna*. *Chemosphere* 33(6), 1119-1127.
  - 34) Stumpf, M., Ternes, T.A., Schuppert, B., Haberer, K., Hoffmann, P., and Ormer, H.M. (1996) Sorption and degradation of NTA, EDTA, and DTPA during underground passage. *Vom wasser* 86, 157-171(in German).
  - 35) Tuin, B.J.W., and Tels, M. (1990) Removing heavy metals from polluted clay soils by extraction with hydrochloric acid, EDTA or hypochlorite solutions. *Environ. Technol.* 11, 1039 -1052
  - 36) Wassy, S.A., Amfalk, P., Tokunaga, S. (1995) Remediation of a soil polluted by mercury with acidic potassium iodide. *J. Hazard. Materials* 44(1), 93-102.
  - 37) Weilandt, E. (1994) Treatment of mercury-contaminated soils. *Umwelt* 24(10), 502-504(in German).
  - 38) Wernicke, G., Wienberg, R., Gerth, J., Wilichowski, M., Forstner, U., and Werther, J. (1993) Methods of treating soil polluted with chromium. *Altastensanierung* 93, 4th Int. KfK/TNO Kongr. 2, 1497-1498(in German).
  - 39) Wilson, D.J., and Tamamushi, K. (1993) Low-temperature thermal treatment of contaminated solis: Simple mathematical models. *Sep. Sci. Technol.* 28(15&16), 2351-2375.