Applicability of Immobilizing Agents for the Remediation of Heavy Metal Polluted Soils in The Netherlands

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Accountability: This exploratory study conducted as part of The Netherlands Integrated Soil Research Programme concerns a literature review of methods for the chemical immobilization of heavy metals in polluted soils and the applicability in The Netherlands. The authors conclude that some of the methods are certainly promising for specific pollution and soil conditions in The Netherlands, but that there are no general, ready to hand receipts available for this type of problems. Each site requires its own approach, which should be tested beforehand. The authors conclude, that more research on field scale is necessary for testing selected techniques for specific situations on effectivity and durability.

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Preface

This study was conducted in the framework of The Netherlands Integrated Soil Research Programme. The objectives were to summarize the state-of-the-art and applicability of the use of adjuvants to immobilize heavy metals in the soil and to evaluate its applicability in The Netherlands. To this end an extensive literature study into the mode of action and the strengths and weaknesses of various immobilizing agents was conducted. The resulting overview was used to evaluate the applicability of the most promising immobilizing agents for the remediation of five cases of heavy metal polluted soils in The Netherlands. The study has been performed at the Research Institute for Agrobiology and Soil Fertility (AB-DLO) in Wageningen.

This report consists of two parts. The first part starts with a description of the developments in The Netherlands that have led to a new policy on issues related to soil protection and the resulting change in attitude towards novel techniques for the remediation of heavy metal contaminated soils. By means of an inventory of a series of five typical cases of heavy metal pollution in The Netherlands it will then be evaluated to what extent these examples meet the criteria to apply selected immobilizing agents as a method of soil remediation. In the second part of this study (i.e. the appendix) it is explained in more detail what is known about the various immobilization methods described in the literature.

Summary

In The Netherlands we will have to learn how to live with contaminated soils. The present government has opted for a pragmatic approach with as guiding principles *function oriented remediation* and *active soil management*. In this approach measures are to be taken with an eye on the (intended) use of the soil. To this end knowledge has to be developed (i) on the risks of soil contamination in relation to the use of that soil, and (ii) on new affordable techniques with which the risks of the presence of contaminants are reduced. A possible technique is the application of immobilizing agents. These are compounds, which, when added to the soil, make pollutants, especially heavy metals, less mobile, and hence less toxic. The effect of immobilization is that the contaminants are no longer available for plant uptake, are less toxic for the cryptobiota, and do not longer leach to the groundwater.

Remediation by means of immobilization implies that contaminants are not removed but rather are fixed in the soil in an innocuous form, or immobilized. This method does not have to be inferior to removal and replacement of the soil. An advantage is that the immobilizing agent will also catch contaminants that will be deposited later through the atmosphere. A second, additional advantage of immobilizing agents is that they often improve the soil structure, thus stimulating plant growth. Remediation by means of immobilizing agents is a relatively new, little applied technique, and there are no standard recipes available, also because of the importance of location specific factors, such as the nature of the contamination, the soil type and the soil use. Responsible application of immobilizing agents therefore requires a coupling between research and application, in which:

- soil and vegetation are analyzed for (available) heavy metals;
- to what extent and at what rate soil flora and fauna and the soil ecosystem recover;
- to what extent heavy metals still wash out;
- information is collected with which it will be possible to optimize the technique in the course of the remediation process (if necessary).

A literature search has revealed the existence of a number of promising immobilizing agents, none of which however has been tested adequately in the field. These immobilizing agents are: beringite, Al- or Al_{13}-montmorillonite, and Mn-oxide. The choice for a certain immobilizing agent depends on the location (especially the pH of the soil) and on the nature of the contaminant. Not all heavy metals show the same behaviour in the soil.

Beringite is an immobilizing agent that has been subjected to some preliminary tests in Belgium. It is a waste product of a coal mine near Beringen in Belgium. Beringite has a high affinity for Zn, Cd, Pb and Cu, and should therefore in principle be suitable for immobilization of each of these metals. However, adding beringite to the soil results in an

increase of pH, which in turn results in the solubilization of organic material in the soil solution (Dissolved Organic Carbon: DOC). Cu has a strong tendency to sorb to DOC, much stronger than the other aforementioned heavy metals. Beringite is therefore not suitable for immobilization of Cu, but it is suitable for the immobilization of Zn, Cd and Pb. The effect of beringite on Ni has not yet been described in the literature.

Contrary to Cu, Ni, Zn, Cd and Pb are not only poorly soluble at high pH, but they also do not sorb significantly to DOC in the soil solution. Al- or Al_{13}-montmorillonite and Mn-oxide are in principle suitable immobilizing agents for each of these heavy metals. Their effect can be enhanced by using them in combination with lime to increase the pH of the soil. The best way to immobilize Cu is by adding Al- or Al_{13}-montmorillonite, or Mn-oxide to the soil without additional measures to increase the pH of the soil. Under reducing conditions Mn-oxide will dissolve, and hence heavy metals sorbed to Mn-oxide will be remobilized. This characteristic makes Mn-oxide less suitable for use in wet areas.

The final choice between the techniques mentioned above will have to be based on the effectiveness of the immobilizing agents and the stability of the effects under field conditions. There is an urgent need for additional research into the effectiveness and stability of immobilizing agents in the field.

Samenvatting

Op 16 juni 1997 heeft het kabinet besloten het beleid aangaande de bodem-verontreinigingsproblematiek te herzien. De nieuwe aanpak steunt op twee principes: *functiegericht saneren* en *actief bodembeheer*. Bij deze aanpak worden de te implementeren maatregelen afgestemd op het (beoogde) gebruik van de bodem. Hiertoe moet kennis worden ontwikkeld over risico's van bodemverontreiniging in relatie tot bodemgebruik en over nieuwe technieken waarmee de risico's van de verontreiniging worden gereduceerd, technieken die uiteraard betaalbaar en technisch uitvoerbaar moeten zijn. Een veelbelovende techniek is de toepassing van immobilisatoren. Immobilisatoren zijn stoffen die aan de bodem worden toegevoegd om met name anorganische verontreinigingen zoals zware metalen (Cu, Zn, Cd e.d.) te binden c.q. te immobiliseren. Het effect van immobilisatie is dat de verontreinigende stoffen niet meer beschikbaar zijn voor plant- en gewasopname, niet meer toxisch zijn voor het bodemleven, en niet meer uitspoelen naar het grondwater.

Sanering door middel van immobilisatoren betekent dat de verontreinigende stoffen niet worden verwijderd, maar in onschadelijke vorm in de bodem worden vastgelegd of geïmmobiliseerd. Deze methode hoeft echter niet inferieur te zijn ten opzichte van verwijderen en vervangen van de grond. Een voordeel is namelijk dat de aanwezige immobilisator nieuwe (door atmosferische depositie aangevoerde) verontreinigende stoffen wegvangt. Een tweede, bijkomend voordeel van immobilisatoren is dat vaak de bodemstructuur verbeterd wordt, zodat er een betere planten- en gewasgroei mogelijk is. Sanering door middel van immobilisatoren is een relatief nieuwe, nog weinig toegepaste techniek en er zijn geen standaard-recepten, mede vanwege locatiespecifieke factoren, zoals de aard van de verontreiniging, het bodemtype en het bodemgebruik. Voor een verantwoorde toepassing van immobilisatoren dient daarom de uitvoering te worden gekoppeld aan onderzoek, waarin:

- grond en vegetatie worden onderzocht op gehaltes aan beschikbare zware metalen;
- wordt nagegaan in hoeverre en met welke snelheid het bodemleven en het bodem-ecosysteem zich herstellen;
- in hoeverre zware metalen nog uitlogen;
- kennis wordt verzameld waarmee het mogelijk wordt om de techniek gedurende het saneringsproces (eventueel) te wijzigen en te perfectioneren.

Uit literatuuronderzoek komt naar voren dat er momenteel een aantal veelbelovende immobilisatoren beschikbaar is, die echter nog geen van alle voldoende getest zijn op veldschaal. Deze immobilisatoren zijn: beringiet, Al- of Al_{13}-montmorilloniet en Mn-oxide. De keuze voor een immobilisator hangt af van de locatie (met name de zuurgraad van de grond) en de aard van de verontreiniging. Niet alle zware metalen gedragen zich hetzelfde in de bodem.

Beringiet is een immobilisator die al op beperkte schaal uitgetest is in de Belgische Kempen. Het is een restproduct van een kolenmijn bij Beringen (België). Beringiet heeft een hoge affiniteit voor Zn, Cd, Pb en Cu, en zou dus in principe geschikt zijn voor immobilisatie van elk van deze metalen, ware het niet dat toevoegen van beringiet aan de grond ook leidt tot een stijging van de pH van de bodem. Een dergelijke stijging van de pH leidt tot het in oplossing gaan van organisch koolstof (DOC). Cu heeft een sterke neiging om te sorberen aan DOC, veel sterker dan voornoemde andere metalen. Beringiet is dus niet geschikt voor immobilisatie van Cu, maar wel voor immobilisatie van Zn, Cd en Pb. Het effect van beringiet op Ni is niet beschreven in de literatuur.

In tegenstelling tot Cu zijn Ni, Zn, Cd en Pb niet alleen slecht oplosbaar bij hogere pH, maar sorberen zij ook niet of nauwelijks aan DOC in het bodemvocht. Al- of Al_{13}-montmorilloniet en Mn-oxide zijn in principe geschikte immobilisatoren voor elk van deze zware metalen. Hun effect kan nog versterkt worden door ze te gebruiken in combinatie met kalk om zo de pH van de grond omhoog te brengen. De beste wijze om Cu te immobiliseren is door toevoegen van Al- of Al_{13}-montmorilloniet, of Mn-oxide zonder additionele pH verhogende maatregelen. Onder reducerende omstandigheden kan Mn-oxide oplossen, zodat geïmmobiliseerde zware metalen geremobiliseeerd worden. Deze eigenschap maakt Mn-oxide minder geschikt voor gebruik in natte gebieden.

De uiteindelijke keuze tussen bovenbeschreven technieken zal gemaakt moeten worden op basis van de effectiviteit van de immobilisatoren en de duurzaamheid van de effecten onder veldomstandigheden. Er is behoefte aan aanvullend onderzoek om de effectiviteit en duurzaamheid van immobilisatoren op veldschaal te testen.

1. Introduction

In The Netherlands we will have to learn how to live with contaminated soils. The present government has opted for a pragmatic approach with as guiding principles *function oriented remediation* and *active soil management*. In this approach measures are to be taken with an eye on the (intended) use of the soil. To this end knowledge has to be developed (i) on the risks of soil contamination in relation to the use of that soil, and (ii) on new affordable techniques with which the risks of the presence of contaminants are reduced. A possible technique is the application of immobilizing agents. These are compounds, which, when added to the soil, make pollutants, especially heavy metals, less mobile, and hence less toxic.

Much general information is available on the mode of action of the various immobilizing agents. For the interested reader this information has been summarized and discussed in the second part of this brochure (i.e. the appendix). In the first part the available knowledge will be focused on the Dutch situation. To this end five cases of heavy metal polluted soils in The Netherlands have been selected. After a short general introduction these specific cases will be described to outline how immobilizing agents could be used to remediate these sites. Thus the emphasis is on the criteria that decide which method is best.

This study focuses on heavy metals. Organic contaminants fall outside the scope of the present study. The applicability of immobilization methods to remediate the large areas of phosphate enriched soils in The Netherlands has been discussed recently (Chardon *et al.* 1996). Ironically, one of the methods proposed in the literature to remediate Pb contaminated soils is by adding phosphate in order to precipitate Pb in the form of Pb phosphate minerals. In our perception this is like "driving out the devil with Beelzebub".

1.1 Policy developments

In the last decade the hope that within the foreseeable future spatial planning in The Netherlands can take place without having to pay attention to soil pollution has evaporated. Shortly after the scare of the first case of serious soil pollution (Lekkerkerk, 1980) this was still quite different. An evaluation of the total problem at that time suggested a clean-up operation of about 1 billion guilders. Based on this figure the consensus was to get it over with as soon as possible and clean-up the polluted sites rapidly. Gradually this attitude turned out to be too optimistic. Ten years later it was clear that The Netherlands had no less than 100,000 seriously polluted sites, and that cleaning up all these cases would require an enormous effort with a price tag of more than 100 billion guilders. With this amount of money involved complete clean-up of all the polluted soil in The Netherlands becomes unrealistic. This awareness has resulted in stagnation of

the remediation efforts and has hampered the connected spatial and economic processes in the areas involved.

Against this background a number of initiatives were taken in the 1990s to come to a new soil protection policy, which included an evaluation of the Soil Protection Act, and an interdepartmental policy analysis with regard to soil remediation which has culminated in a process of policy renewal with regard to soil remediation (BEVER). The government has recently come to the conclusion that: *Soil remediation is too expensive and the output of the soil clean-up operation is too low, because per unit of time too little cases are treated. Furthermore the size of the soil pollution problem relative to the available means results in stagnation of spatial and economic processes. The result is social damage, little support for soil remediation, a low level of investments, and a negative effect on the quality of the environment.* The government therefore stands for a new approach with as guiding principles function oriented remediation and active soil management.

1.2   Function oriented soil remediation and active soil management

Function oriented soil remediation means that the measures that are to be taken are tailored towards the desired soil usage. This implies that the regulatory process is no longer based on "multifunctionality, unless", but on an evaluation of the remediation result that has to be achieved; a process where controlling the exposure and dispersal risks comes first, but where special attention is paid to the function and usage of the soil. By that, function oriented remediation differs from the present policy on soil pollution which is based on a choice between either complete removal of the pollution, or isolation, containment and control. Consequently under the new policy there will be more cases in which pollution will remain in the soil than there would have been under the old rules and regulations. That is why function oriented soil remediation has to be embedded in active soil management. Active soil management encompasses the chain prevention-management-remediation-maintenance with the objective to achieve sustainable soil usage. From a perspective of soil remediation active soil management aims at creating boundary conditions for dealing with soil pollution. Important elements in soil management are:

• protection of clean soils;
• optimal use of polluted soils;
• improving the quality of polluted soils where necessary and possible;
• managing and controlling the quality of and activities in and on the soil.

1.2.1 Mobility of contaminants as a starting point for measures and research

A policy based on a function oriented approach towards polluted soils requires that a distinction is made between mobile and immobile contaminants. Mobile contaminants (compounds that are not bound to the soil, thus moving with the water in the soil, volatile compounds) would have to be removed from the soil as far as this is economically feasible, and if this is not so they have to be controlled. With regard to immobile contaminants (compounds that are bound to the soil and do not move) at least unacceptable exposure of humans and ecosystems is precluded under the present or intended use of the location. Actual implementation of this policy requires thorough knowledge of the mobility of the contaminant in real situations of soil pollution. Presently much knowledge is available on the soil parameters that affect mobility, but this knowledge is mainly based on experiments in the laboratory and on theoretical models. Much less is known about the mobility of contaminants in field situations, so this aspect requires further research. In this context it is important to be aware that the mobility of compounds can be influenced. This offers opportunities for strategies aiming at a reduction of risks for humans and the environment. Because mobility strongly depends on soil factors like pH, organic matter and clay content manipulation of these parameters can lower the mobility of contaminants in the soil.

Some of these measures will have only a limited duration of effectiveness. Liming of soils, with the objective to keep the pH high will for example have to be repeated frequently. But some measures are expected to be long lasting. When for example the clay content of the soil is raised it is to be expected that the immobilizing effect of the added clay particles will have a lasting effect on the mobility of contaminants. That is why recently much attention has been paid to the possibility to apply immobilizing agents with a long lasting effect.

1.3   Immobilizing agents

Immobilizing agents are compounds that are added to the soil with the objective to specifically bind or immobilize inorganic compounds such as heavy metals (Cu, Zn, Cd, etc.). The effect is that metals are no longer available for plant uptake, are no longer toxic for organisms living in and on the soil, and are no longer a source for dispersion via wash out. Examples of immobilizing agents are beringite (research of the University of Limburg, Diepenbeek, Belgium), montmorillonites (Institute of Terrestrial Ecology, ETH-Zürich, Switzerland), and manganese oxides (Wageningen Agricultural University, The Netherlands). Remediation by means of immobilizing agents therefore implies that the contaminants are not removed, but are rendered harmless by immobilization in the soil matrix. Now that remediation less often has to imply that all contaminants are physically removed immobilization becomes an attractive alternative. Figure 1 shows

schematically the effects of the *in situ* addition of immobilizing agents on the size of the mobile and immobile fractions of heavy metals in the soil.
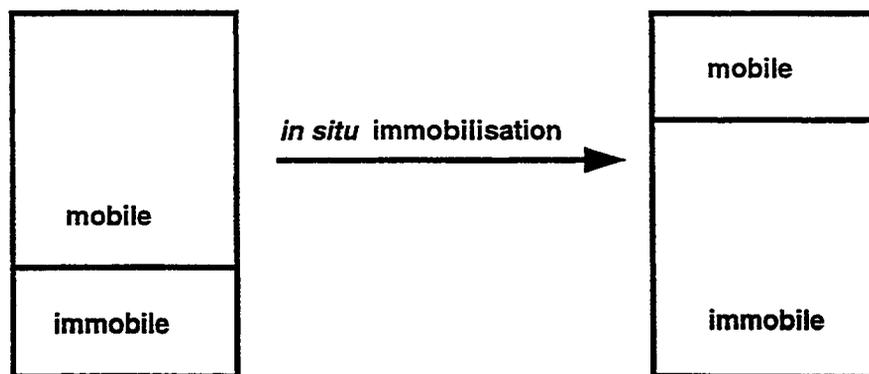

Figure 1.   Effects of the *in-situ* addition of immobilizing agents on the mobile and immobile fractions of metals in the soil (after Krebs, 1996).

1.3.1 Principles

The principle of the application of heavy metal immobilizing agents is based on the awareness that the effects of heavy metals on plants and other organisms in and on the soil are not determined by the total level of heavy metals as such, but mainly by the concentration of these metals in the soil solution. As a result plants in a clay soil in which most of the heavy metals are bound to the clay, take up less heavy metals than plants in a sandy soil with the same amounts of heavy metals present. This has resulted in the present-day differentiation of soil standards: soils with a lot of clay and organic matter are allowed to contain more heavy metals than soils with low amounts of these binding substances. In addition to the levels of clay and organic matter also the pH of the soil is important for the availability of heavy metals; in an acid environment metals dissolve more easily than in an alkaline environment. Figure 2 shows a number of *in situ* immobilization approaches that can be applied to contaminated soils in order to fix or immobilize heavy metals.
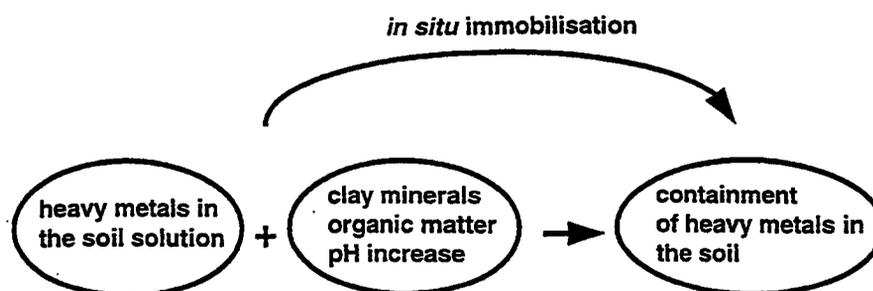

Figure 2.   *In situ* immobilization of heavy metals.

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1.3.2 Remediation

Remediation by means of immobilization implies that contaminants are not removed but rather are fixed in the soil in an innocuous form, or immobilized. This method does not have to be inferior to removal and replacement of the soil. This is because the immobilizing agent will also catch contaminants that will be deposited later through the atmosphere. An additional advantage of immobilizing agents is that they often improve the soil structure, thus stimulating plant growth. Remediation by means of immobilizing agents is a relatively new, little applied technique, and there are no standard recipes available, also because of the importance of location specific factors, such as the nature of the contamination, the soil type and the soil use. Responsible application of immobilizing agents therefore requires a coupling between research and application, in which:

- soil and vegetation are analyzed for (available) heavy metals;
- to what extent and at what rate soil flora and fauna and the soil ecosystem recover;
- to what extent heavy metals still wash out;
- information is collected with which it will be possible to optimize the technique in the course of the remediation process (if necessary).

1.3.3 Philosophy

Immobilization of heavy metals in contaminated soils is a new technique without a proven track record. Its recognition as a sustainable method has to await the availability and evaluation of data obtained from its application in the field with special emphasis on the durability of the immobilization effect. The availability of a durable immobilization method will of course not imply that the soil thus can be filled up to the limit, or that such limits may be extended, just as the present-day policy is not that one can fill up the soil with heavy metals to its presently known ecological or legal limits.

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2. Applicability of immobilizing agents in The Netherlands

2.1 Introduction

A number of cases of soil pollution with heavy metals in The Netherlands will be evaluated for their possibilities to be remediated by means of *in situ* immobilizing techniques. The following questions are of importance:

- which immobilizing techniques are known from the literature?
- what is the nature and the degree of the contamination: what are the contaminant levels especially in the soil solution?
- what is the pH of the soil?
- are the plant cover conditions such that the immobilizing agent can be applied in the required amounts?
- what are the objectives of the clean-up; what is the (future) use of the soil; is immobilization of heavy metals in the top layer of the soil sufficient to eliminate urgent risks?

2.2 Immobilization techniques

From the literature (see: appendix) it is clear that there are presently a number of promising immobilization techniques available. None of these techniques however has been tested in the field. The promising techniques are beringite with compost, Al- or Al_{13}-montmorillonite, and Mn-oxide. A single ideal immobilization technique does not (yet?) exist. The choice for a technique will depend on the location (especially the local pH of the soil) and the nature of the contamination, as not all metals in the soil behave in a similar way. Ni, Zn, Cd and Pb for example are sparingly soluble at high pH and do not or only to a very low degree sorb to Dissolved Organic Carbon (DOC) in the soil solution. The concentrations of these heavy metals in the soil solution can under acid conditions thus be diminished by increasing the pH. Cu on the other hand has a high affinity for DOC in the soil solution. Organic carbon has a tendency to go into solution at pH values above 6. Thus in the case of Cu increasing the pH of the soil results in mobilization rather than immobilization of the metal.

The choice of a technique depends on the acidity of the soil: acid (pH 3-6), neutral (pH 6-8) or alkaline (pH >8) conditions. Beringite can be used under both acid and alkaline conditions, because it increases both the pH and the binding capacity of the soil. Aluminum and Al_{13}-montmorillonite and Mn-oxide can only be used under neutral and alkaline conditions, since these techniques only increase the binding capacity of the soil, and not the pH, unless lime is also added to increase the pH. Aluminum- or Al_{13}-montmorillonite and Mn-oxide can be used to immobilize Ni and Cu. The effect of

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beringite on Ni has not been described in the literature. Cu has to be immobilized under acid conditions, i.e. at pH 4.5 to 6, because Cu is mobilized by DOC in the soil solution at pH > 6. Both beringite with compost, and Al- or Al_{13}-montmorillonite, and Mn-oxide can be used to immobilize Zn, Cd and Pb. This is summarized in table 1.

Table 1. Applicability of immobilization techniques for the remediation of heavy metal contaminated soils.

metal	pH	technique
Ni	3-6	Al- of Al_{13}-montmorillonite with lime Mn-oxide with lime
Ni	>6	Al- of Al_{13}-montmorillonite Mn-oxide
Cu	4.5-6	Al- of Al_{13}-montmorillonite Mn-oxide
Zn, Cd and Pb	3-6	beringite with compost Al- of Al_{13}-montmorillonite with lime Mn-oxide with lime
Zn, Cd and Pb	>6	beringite with lime Al- of Al_{13}-montmorillonite Mn-oxide

2.3 Examples of polluted locations in The Netherlands

Figure 3 shows five locations in The Netherlands that are polluted with heavy metals. Both the total levels and the concentrations of the heavy metals in the soil solution have been measured for these locations. Table 2 shows the ratios between the heavy metal levels in these soils and the levels at which the Dutch law requires immediate action (the "intervention values"). Also given are the ratios between the concentrations in the soil solution and the concentrations at which the law would have required remedial action if the soil solution had been groundwater, i.e. the intervention values for the Maximum Acceptable Risk (MAR). This concerns values where 50% of the species in the soil ecosystem is no longer protected. Exceeding the intervention value should be cause for immediate action.

At two locations the heavy metal levels in the soil exceed the intervention values, namely Valkenswaard (for Zn and Cd) and Callantsoog (for Pb). An evaluation based on the concentrations of heavy metals in the soil solution however yields a different picture. At all five locations the concentrations of one or more of the metals exceed the intervention values,

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Figure 3.   Examples of heavy metal contaminated sites in The Netherlands.

varying from 1.1 times the intervention value for Cu in Valkenswaard to 25 times the intervention value for Zn in Budel. These results beg the question whether in the future the evaluation of soil quality should be based on concentrations (of heavy metals) in the soil solution rather than on total contents.

Table 2.   Ratios between total contents of heavy metals and intervention values for soils (left) and ratios between concentrations of heavy metals in the soil solution and intervention values for groundwater (right) at five typical sites in The Netherlands (sampling depth 0-20 cm, except for Budel 0-5 cm; Janssen *et al.*, 1996; AB-DLO, unpublished results).

location	Ni	Cu	Zn	Cd	Pb	Ni	Cu	Zn	Cd	Pb
Budel	n.m.	n.m.	0.4	0.2	n.m.	n.m.	n.m.	**25**	**15**	n.m.
Woerden	<0.01	0.1	0.1	0.02	0.2	0.3	**3.3**	0.2	0.1	0.8
Valkenswaard	0.2	0.7	**1.8**	**5.8**	0.6	0.8	**1.1**	**9.5**	**15**	0.5
Callantsoog	0.02	0.02	0.01	0.01	**1.0**	0.01	0.4	0.2	0.2	**5.2**
Mook	0.1	0.03	0.05	n.d.	0.3	n.a.	0.4	**6.3**	n.a.	n.a.

Bold numbers: value exceeds the intervention value; n.a.: not available; n.d.: not detectable; n.m.: not measured.

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Table 3 lists the metals that exceed the intervention values for groundwater in the aforementioned five locations together with their source. Cu, Zn, Cd and Pb are the problem compounds. At these locations remediation by means of immobilizing agents would be worthwhile. An other advantage of the use of immobilizing agents is that heavy metals that may be deposited in the future from sources that remain active will also be immobilized. The zinc smelter and the galvanizing facility at Mook are still active. The heavy metals emissions from these works have undoubtedly been lowered due to environmental measures but whether they have been reduced to zero is unknown.

Table 3.   Sites of heavy metal polluted groundwater and sources (Janssen et al., 1996).

location	metal	source
Budel	Zn, Cd	zinc smelter (+/-)
Woerden	Cu	motorway A12 (+)
Valkenswaard	Cu, Zn, Cd	source upstream (+)
Callantsoog	Pb	military target practice (-)
Mook	Zn	galvanizing facility (+/-)

+: active; -: not active; +/-: activity status unknown.

2.3.1 Acidity, vegetation and usage of the soil

Table 4 lists the soil type, soil pH and type of vegetation of the five locations. Four of them consist of a humic sandy soil, with a pH of 4.4 to 5.5. The fifth location has a humic clay soil with a pH of 5.5. At these pH values Zn, Cd, and Pb are quite soluble, so the pH of the soil has to be raised.

Table 4.   Soil type, pH and vegetation conditions of the contaminated sites (Janssen et al., 1996).

location	soil type	pH H₂O	vegetation
Budel	humic sand	4.8	drifting sand
Woerden	humic rich clay	5.8	grass
Valkenswaard	humic sand	5.5	grass at a river bank (The Dommel)
Callantsoog	humic sand	4.8	dunes with marram grass
Mook	humic sand	4.4	grass

Sand: <8% clay; light clay: 8% < clay <35%; heavy clay: >35% clay; humic poor: <2.5% organic matter; humic: 2.5% < organic matter <15%; humic rich >15% organic matter; after Kuipers, 1984.

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The type of vegetation is of importance, because not all types of vegetation will allow the practical application of immobilizing agents. In for example a thick forest the application of immobilizing agents will be very troublesome. The type of vegetation in these five locations does not impede the use of immobilizing agents. The development of a vegetation cover on the sand dunes at Budel and Callantsoog after the application of immobilizing agents will preclude further drifting and lateral dispersion of heavy metals by means of wind erosion.

At contaminated locations with a function allowing direct contact between contaminants and humans significant health risks will exist. Such risks will probably not be reduced sufficiently by the application of immobilizing agents to the contaminated soil. At e.g. a contaminated site in a residential area people can be exposed to elevated concentrations of heavy metals after ingestion of soil particles. Ingestion of soil particles is one of the most important routes by which humans, especially children, are exposed to contaminated soil. Heavy metals immobilized in soil particles can be remobilized in the stomach at low pH, thus causing health risks. The health risks of contaminated areas in residential areas must be assessed explicitly, before it can be evaluated whether the use of immobilizing agents at such locations is prudent. Table 5 lists the functions of the five locations, which vary between military training ground to traffic shoulder and nature area. For these functions it is to be expected that direct contact between humans and contaminants is minimal.

Table 5.   Land use at the contaminated sites.

location	land use
Budel	military target practice
Woerden	roadside motorway A12
Valkenswaard	nature area
Callantsoog	nature area
Mook	nature area

2.3.2 Applicability of immobilizing agents at contaminated sites

In table 6 immobilization techniques are selected for the remediation of the five heavy metal contaminated locations. The objective of remediation is the achievement of risk reduction for the soil ecosystem and/or the reduction of the risk that the metals will spread to the (ground)water. The expectation is that the application of the right immobilization technique results in a lower concentration of the heavy metals in the soil solution, and hence in risk reduction. Based on a literature survey of heavy metal immobilizing techniques, and knowledge of the behavior of heavy metals in the soil (see: appendix), the best choice would be to use beringite in combination with compost,

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or Al- or Al_{13}-montmorillonite or Mn-oxide in combination with lime for the locations Budel, Callantsoog, and Mook with pH values around 4.5.

Table 6. *In situ* immobilization techniques for the remediation of the sites.

location	technique
Budel	beringite with compost Al- of Al_{13}-montmorillonite with lime Mn-oxide with lime
Woerden	Al- of Al_{13}-montmorillonite Mn-oxide
Valkenswaard	beringite with compost Al- of Al_{13}-montmorillonite with lime
Callantsoog	beringite with compost Al- of Al_{13}-montmorillonite with lime Mn-oxide with lime
Mook	beringite with compost Al- of Al_{13}-montmorillonite with lime Mn-oxide with lime

For the location Valkenswaard it is proposed to use beringite in combination with compost, or Al-montmorillonite in combination with lime. The resulting pH increase can however cause mobilization of Cu by dissolved organic carbon. Considering the Zn and Cd concentrations, exceeding the current intervention values by 9.5 and 15 times respectively, versus Cu by only 1.1, it is prudent to focus on Zn and Cd. On this location sampling was at a river bank, so there is a risk that the contaminated soil will be flooded. This may cause reducing conditions. Reducing conditions will cause dissolution of Mn-oxide, thereby mobilizing heavy metals sorbed by Mn-oxide. Thus Mn-oxide should not be used at this site. At the location in Woerden, with pH 5.8, Al- or Al_{13}-montmorillonite or Mn-oxide are the best choice to immobilize Cu.

Table 7 gives the amounts of the various immobilizing agents ha^{-1} necessary to remediate the upper 30 cm of a contaminated soil. Immobilizing agents are applied by means of a rotary cultivator reaching a depth of about 30 to 35 cm. This limits the applicability of immobilizing agents thus to the upper soil layers. For all contaminated areas more than one immobilization technique is proposed. The choice between the techniques will have to be made on the basis of their effectiveness and of the durability of the effects, but the costs also play a role. To give an indication of the costs of beringite: the price amounts to Hfl 300,= 1000 kg^{-1}, so an amount of 110 ton ha^{-1} (table 7) amounts to

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Hfl 33,000, = ha^{-1}. These costs are an order of magnitude lower than the costs of removing the contaminants by excavating the polluted soil. There is a need for additional research in order to test the effectiveness and durability of proposed immobilization techniques in the field. Additional research will yield knowledge and insight that can contribute to a successful application of these techniques for the remediation of contaminated soils. In The Netherlands such research is being carried out at the DLO-Research Institute for Agrobiology and Soil Fertility (AB-DLO) and at the Agricultural University in Wageningen.

Table 7. Immobilizing agents and amounts to be added to the upper 30 cm of the soil (Lothenbach *et al.*, 1998; Mench *et al.*, 1994; Vangronsveld *et al.*, 1995b).

technique	% (weight based)	ton ha^{-1}
beringite	2	110
compost	1.5	80
Al- or Al$_{13}$-montmorillonite	6	330
Mn-oxide	1	55
lime	0.1	6

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Appendix: **Review of recent literature on heavy metal immobilization in soils**

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1. Introduction

1.1 Heavy metals in soil

Heavy metals, such as Ni, Cu, Zn, Cd and Pb, are ubiquitous natural soil constituents. Table 1.1 shows an indication of background levels of heavy metals in Dutch soil, which range between 0.1-100 mg kg^{-1}.

Table 1.1. Indication of natural background levels of heavy metals in Dutch soil (mg kg^{-1} on dry weight basis) (Lagas & Groot, 1996).

soil type	Ni	Cu	Zn	Cd	Pb
sand	6	2	7	0.1	2.9
sea clay	28	12	69	0.2	23
river clay	35	24	87	0.3	29

Because of anthropogenic activities (metalliferous industries, traffic, etc.), heavy metals are emitted to the atmosphere and may end up in the soil by atmospheric deposition exceeding the natural background level. As an example the Zn content may become as high as 5000 mg kg^{-1} as measured at the site of a metalliferous smelting industry (Slooff et al., 1989). Besides atmospheric deposition, other diffuse sources such as fertilizer, manure and sewage sludge amendements and point sources such as industrial and municipal waste dumping grounds contribute to the heavy metal load of soil. Obviously, not all of these sources contribute a similar amount of heavy metals to all soils. Pollution of soil with heavy metals is a general point of concern, because heavy metals may adversely affect soil ecology, agricultural production or product quality and (ground)water quality, and because of a lack of realistic and cost-effective techniques for the remediation of such soils. Normally, the mobility of heavy metals in soil is low. Heavy metals are removed only slowly by leaching, plant uptake or erosion. In contrast to organic micro-pollutants, heavy metals can not be biodegraded. Therefore, pollution of soil with heavy metals appears to be persistent (Kabata-Pendias & Pendias, 1992).

Adverse effects of heavy metals in soil are related to their bioavailability and mobility, which are controlled by the speciation. The chemical form of heavy metals is determined by the physico-chemical soil conditions such as soil type, pH and cation exchange capacity: CEC) (figure 1.1). Due to changes in land use, the physico-chemical conditions may be altered: e.g. nature development on former agricultural land will result in a lower pH

(Hesterberg, 1993; Japenga et al., 1997). A low pH may increase the bioavailability and mobility of heavy metals in soil. Thus, pollution of soil with heavy metals exhibits risks to the soil ecology, agriculture and (ground)water quality, and poses the question of remediation. The answer to this question depends upon the extent of the pollution problem and the technical and financial means available.
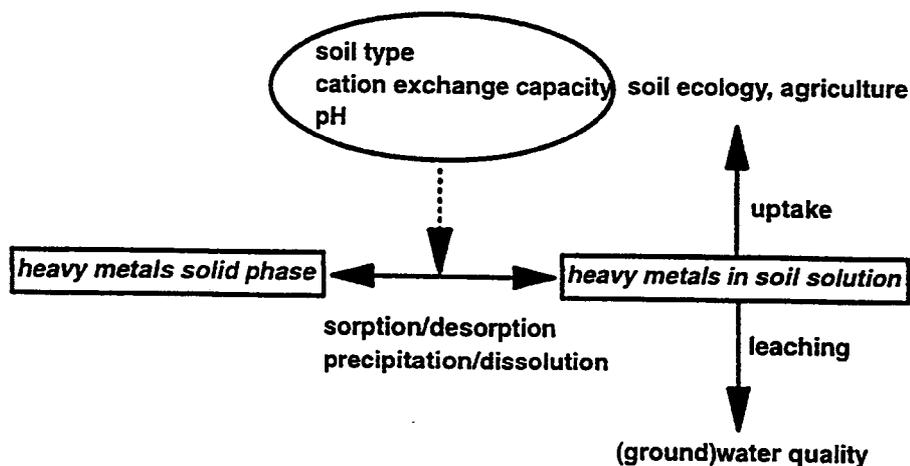
Figure 1.1.   Heavy metals in the soil.

1.2   Traditional soil remediation techniques

The most comprehensive remediation technique is to excavate polluted soil and replace it by unpolluted material. On a large scale, however, this is not feasible due to the high costs involved, the problems related to the safe disposal of the polluted material and the limited availability of clean soil for replacement. Other remediation techniques are in situ or ex situ clean-up of polluted soil by chemical or physico-chemical techniques, which extract or remove the heavy metals from the soil. The clean soil can be reintroduced at the original site or disposed elsewhere (Vangronsveld et al., 1994a). However, new problems can arise such as an increase of the bioavailability and mobility of the remaining heavy metals in the treated soil, the disposal of polluted process agents or rests (resins, sludges, etc.) and changes in the physico-chemical conditions of the soil decreasing its potential to be used as normal soil (Van Gestel et al., 1988). An alternative technique is the in situ immobilization of pollution by using heavy metal immobilizing additives.

1.3   *In situ* immobilization

In situ immobilization can be an economically realistic and cost-effective technique for the reduction of risks imposed by heavy metal polluted soil. *In situ* immobilization means that heavy metals are not extracted from the polluted soil, but remain immobilized in the soil so that the heavy metals impose no risks to the soil ecology, agriculture and (ground)water quality. Immobilization of heavy metals can be achieved by decreasing the concentration in the soil solution or by increasing the soil sorption capacity (Krebs, 1996). Several immobilization techniques have been reported in literature (e.g. Lothenbach *et al.*, 1997; Vangronsveld *et al.*, 1995a). Lime, phosphate and olivine decrease the heavy metal concentration in the soil solution due to an increasing pH and/or the formation of slightly soluble precipitates, whereas clay minerals, manganese oxides and organic matter increase the sorption capacity. Figure 1.2 shows the *in situ* immobilization techniques, which may be useful for reducing the risks posed by soil polluted with heavy metals.

pH, precipitation

lime
phosphate
olivine

heavy metals in soil solution   in situ immobilization

clay mineral
Mn-oxide
organic matter

sorption capacity
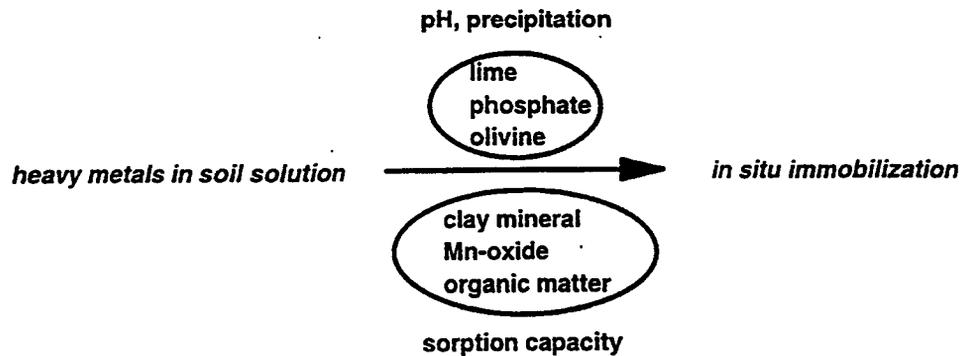
Figure 1.2.   *In situ* immobilization techniques for the treatment of soil polluted with heavy metals.

2.   Soil chemistry of heavy metals

2.1   Speciation of heavy metals

The speciation of heavy metals can be defined as the chemical forms in which they can exist. Figure 2.1 shows an overview of the main forms of heavy metals in soil. Heavy metals are distributed among several phases and fractions depending on the physico-chemical conditions of the soil. Two soil phases of major importance are the solid and the solution phase.

```
┌─────────────────────────────────────────────┐   ┌──────────────────────────────┐
│ solid phase                                  │   │ solution phase               │
│                                              │   │                              │
│ • sorbed fraction (clay, oxides, organic matter) │ • free heavy metals          │
│ • secondary precipitates              ◀┈┈▶   │   │ • inorganic complexes        │
│ • primary minerals                           │   │ • organic complexes          │
└─────────────────────────────────────────────┘   └──────────────────────────────┘
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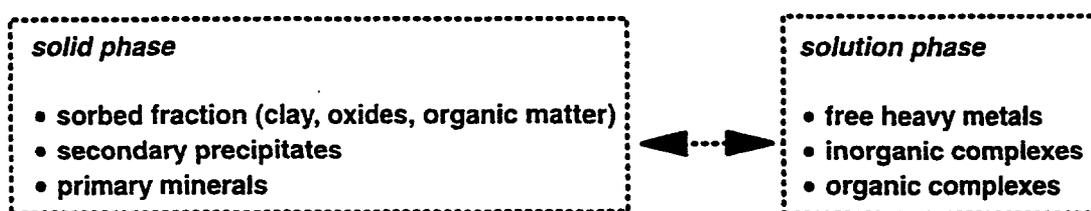
Figure 2.1.   Distribution of heavy metals in soil (after Römkens *et al.*, 1993).

Solid phase

Three main fractions of heavy metals are distinguished within the solid phase (Shuman, 1991a; Stevenson, 1994):

- sorbed;
- as secondary precipitates (precipitates of dissolved minerals, e.g. $PbCO_3$);
- in primary soil minerals.

Sorption can be defined as all interactions between dissolved heavy metals and the solid phase causing an accumulation of heavy metals at the surface of the soil particles. Sorption does not include precipitation. Usually the sorbed fraction is the smallest. Nevertheless, it is considered to be the most reactive. Dissolution of heavy metals from secondary precipitates and primary minerals is slow compared to sorption and desorption. Therefore, the equilibrium between heavy metals in the solid and the solution phase is hardly affected by these fractions (Shuman, 1991b). The main sorbents are clay minerals, oxides and organic matter. Clay minerals and other inorganic surfaces can be coated and intercalated with organic matter and oxides, forming additional sorption sites (Sposito, 1989).

Solution phase

The solution phase is the most important one in the soil, although it contains only a small fraction of the total heavy metal content. It is the main determinant of plant availability and the amounts of heavy metals which can be leached to lower soil horizons and the

groundwater. The speciation of heavy metals in the solution phase is important, because it affects toxicity. The toxicity of heavy metals generally decreases with an increasing degree of complexation. Plants predominantly take up heavy metals in the free ionic form (Pain, 1995). Three main fractions are distinguished within the solution phase (Shuman, 1991a; Stevenson, 1994):

- free heavy metal ions;
- complexes with inorganic ligands;
- complexes with organic ligands (both dissolved and colloidal).

Important ligands forming stable complexes in the soil solution are: Cl^-, OH^-, PO_4^{3-}, CO_3^{2-} and Dissolved Organic Carbon (DOC).

2.2 Soil parameters

The distribution of heavy metals among the several phases distinguished within the soil is determined by physico-chemical soil parameters affecting processes such as sorption and desorption, complexation and precipitation and dissolution of heavy metals. Important physico-chemical soil parameters in this respect are the pH and the CEC.

2.2.1 pH

Buffering capacity
The pH mainly depends on the prevailing pH buffering mechanism in the soil. The buffering capacity is an expression of the ability of the soil to resist chemically to a varying pH. Table 2.1 shows the pH buffering mechanisms in soil. The clay mineral and organic matter content are of major importance for determining the buffering capacity. Non-calcareous sandy soils with a low clay mineral and organic matter content have a low buffering capacity. When there is a net input of H^+ due to acidic atmospheric deposition, these soils can acidify rapidly. Changes in land use may cause the soil to acidify. Johnston *et al.* (1986) measured a decrease of the pH from 7 to 4.2 over a period of 100 years when formerly limed agricultural land was changed into deciduous forest.

Table 2.1.   pH buffering mechanisms in soil (after Robarge & Johnson, 1992).

pH range	buffer mechanism
2.4-3.8	Fe buffer
3.0-4.8	Al/Fe buffer
4.2-5.0	cation exchange
>5.0	silicate buffer
6.5-8.3	CaCO₃ dissolution

Proton exchange on variable charge sorption sites

Hydroxyl groups (R-OH) and carboxylic (R-COOH) and phenolic hydroxyl groups (R-OH) of organic matter can be protonated or deprotonated by sorption or desorption of H^+, as shown for a hydroxyl group by:

$$R\text{-OH} + H^+ \leftrightarrow R\text{-OH}_2^+$$
$$R\text{-OH} \quad\quad \leftrightarrow R\text{-O}^- + H^+$$
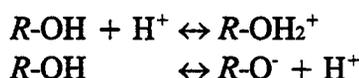
After deprotonation, positively charged free heavy metal ions or partially complexed heavy metals can sorb to the negatively charged sites. Sorption of heavy metals involving proton exchange on variable charge sites is dependent on pH. Several studies (e.g. McKenzie, 1980) indeed demonstrated that sorption of heavy metals decreased at lower pH values. Figure 2.2 shows the influence of pH on sorption of Ni, Cu, Zn and Pb to the iron oxide goethite.
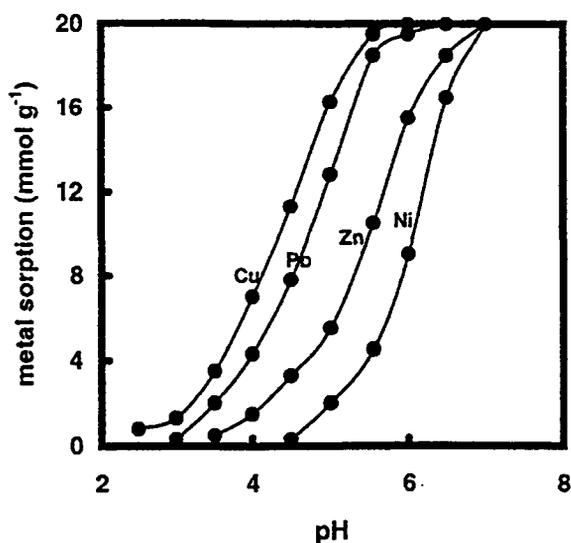
Figure 2.2. Sorption of heavy metals on the iron oxide goethite (after McKenzie, 1980).

Sorption of cations on variable charge sites can be due to either cation exchange or covalent binding. Cation exchange involves electrostatic forces causing attraction between the distinct negatively charged sites and the positively charged heavy metal ions (R-O$^-$...K$^+$, R-COO$^-$ ...Na$^+$). The sorbed cations are readily exchangeable. Covalent binding involves a chemically specific interaction (R-O-Cu-O-R). The sorbed cations are hardly exchangeable and specific sorption sites do, therefore, not contribute to the CEC of soil or soil constituent. Cations all have a different affinity for the formation of a covalent binding. Based on electronegativity (Pauling), the predicted affinity order of divalent cations for oxides is: $Cu^{2+} > Ni^{2+} > Pb^{2+} > Cd^{2+} > Zn^{2+}$ (McBride, 1994).

2.2.2 Cation exchange capacity

The CEC is defined as the sum of exchangeable cations that a soil or a soil constituent can sorb at a specific pH (Sparks, 1995). The CEC of a soil is mainly determined by the clay mineral, oxide, and organic matter content. An increase in either of these soil constituents results in an increase of the CEC (Sposito, 1989).

Clay minerals

Clay minerals of major importance in soil are montmorillonites, vermiculites, illites and kaolinites. They exhibit a varying composition and structure, but all are aluminosilicates. Table 2.2 shows some physico-chemical characteristics of these clay minerals. The specific surface area and CEC decrease in the order montmorillonite, vermiculite> illite> kaolinite (Stevenson, 1994).

Table 2.2. Specific surface area (m^2 g^{-1}) and CEC ($cmol_c$ kg^{-1}) of important clay minerals (Stevenson, 1994).

clay mineral	area	CEC
montmorillonite	600-800	100-150
vermiculite	600-800	80-150
illite	65-100	10-40
kaolinite	7-30	3-15

Clay minerals exhibit a negative surface charge; part of this negative charge is variable depending on pH and part of it is permanent resulting from isomorphous substitution. The variable negative charge is located at the edge-sites of the clay minerals, where hydroxyl groups are protonated or deprotonated depending on pH. The CEC of clay minerals increases with pH because of deprotonation of hydroxyl groups. Due to the permanent negative charge, electrostatic forces cause attraction of positively charged heavy metal ions resulting in a layer at the boundary of the clay mineral surface and the solution phase from which negative ions are expelled and positive ions are accumulated, i.e. the diffuse double layer. The sorbed cations are readily exchanged by other cations such as Mg^{2+} or Ca^{2+} (Van Bladel *et al.*, 1993), but also H^+ may compete for the cation exchange sites resulting in a further pH dependency of heavy metal sorption in soil. Figure 2.3 shows Co sorption by various soil constituents. Montmorillonite sorbs a larger amount of Co (on weight basis) than illite does. Furthermore, figure 2.3 shows that birnessite (a Mn-oxide) and humic acid sorb a larger amount of Co from solution than montmorillonite does.
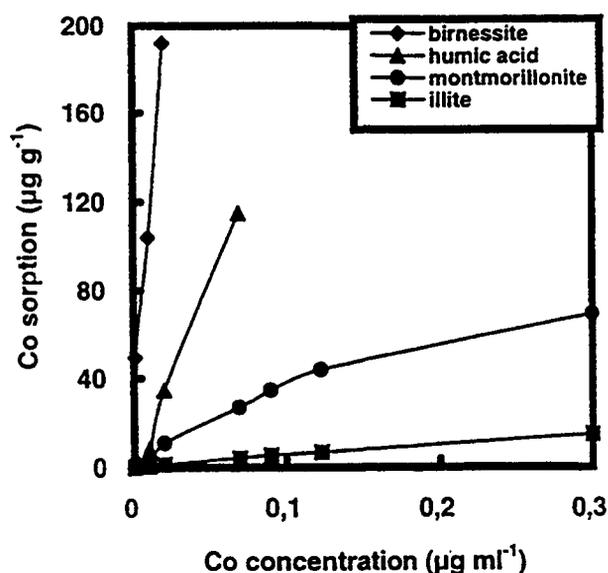
Figure 2.3. Sorption of Co on birnessite, humic acid, montmorillonite and illite at pH 6 (after McLaren, 1986).

Oxides

Al-, Mn- and Fe-oxides are important in the chemistry of the soil. Although oxides are not present in large amounts, they have a significant effect on various soil chemical processes, because of their high specific surface area and reactivity. The general term oxides refers to hydroxides, oxyhydroxides and hydrous oxides (where non-stoichiometric water is in the structure). Oxides are commonly present in the soil as minerals or as surface coatings on other (in)organic surfaces, and have a low solubility in the normal pH range of the soil. Generally heavy metals are sorbed either by cation exchange or by covalent binding, but isomorphous substitution may also contribute to immobilization of heavy metals by oxides.

Organic matter

In sandy soil with a low clay content (<5% clay), up to 90% of the CEC may be attributed to organic matter (Sposito, 1989; Stevenson, 1994). Soil organic matter mainly occurs as non-soluble and stable humic substances sorbed to the solid phase. The most important functional groups for heavy metal sorption are carboxylic and phenolic hydroxyl groups. The CEC increases at higher pH values resulting from the formation of additional sorption sites. The proton dissociation constants (pK$_i$) for carboxylic and phenolic hydroxyl groups range between respectively 4.4-4.9 and 8.1-8.9 (Römkens et al., 1996), i.e. 50% of the respective functional groups exists in the dissociated form at pH 4.4-4.9 and 8.1-8.9. Multivalent cations (Cu^{2+}, Zn^{2+}, etc.) have the potential to form covalent bindings with the functional groups (Stevenson, 1994). Table 2.3 shows the order of affinity of divalent cations for soil organic matter related to electronegativity.

Table 2.3.   Measured order of affinity of divalent cations for soil organic matter related to electronegativity (McBride, 1994).

affinity order	$Cu^{2+} > Ni^{2+} > Pb^{2+} > Co^{2+} > Zn^{2+} > Mn^{2+} > Mg^{2+}$						
electronegativity (Pauling)	2.0	1.91	1.87	1.88	1.65	1.55	1.31

Dissolved organic carbon

The amount of DOC in the soil solution is determined by physico-chemical parameters such as pH and the Ca^{2+} concentration and may range from 0-100 mg l^{-1} (Römkens et al., 1996). Several studies (e.g. Davis, 1984) demonstrated that DOC can increase the solubility and mobility of heavy metals. The DOC competes with the solid phase for heavy metal complexation. This may cause a mobilization of heavy metals such as Cu, exhibiting a high affinity for sorbing to DOC. From the Cu concentration in the soil solution 70 to almost 100 per cent can be in the organically complexed form (Hodgson et al., 1965). Due to complexation to DOC, the net positive charge of a heavy metal decreases compared to the free ionic form. Thereby, the electrostatic attraction between the complexed heavy metal and the predominantly negatively charged soil surface decreases. This causes the heavy metal to become increasingly mobile in soil. The complexed heavy metal can be transported to the lower soil horizons and groundwater. Whether the complexed heavy metal remains in solution or is sorbed by the solid phase depends on the local pH and organic matter content.

Thus, solid organic matter can decrease the mobility of heavy metals in soil. By DOC in the contrary it can be increased.

3. *In situ* immobilization

In situ immobilization of heavy metals in the soil can be achieved by decreasing the concentration in the soil solution or by increasing the sorption capacity (Krebs, 1996). Reported techniques aiming to decrease the solution concentration by increasing pH and/or causing precipitation are the addition of lime, phosphate and olivine, whereas techniques aiming to increase the sorption capacity are the addition of beringite, montmorillonite, Mn-oxide, gravel sludge, and brown coal.

3.1 Techniques aiming to increase pH and/or cause precipitation

3.1.1 Lime

Liming (CaO) of slightly acidic soils is a common practice in agriculture to compensate for acidification resulting from the amendment of fertilizers and the natural process of leaching, in order to maintain a pH of about 4.5-6.0 for an optimal crop growth. Lime can react chemically to compensate for a high concentration of H^+, as is shown by the following reactions:

$$CaO \text{ (s)} + H_2O \rightarrow Ca(OH)_2$$

$$Ca(OH)_2 + 2H^+ \rightarrow 2H_2O + Ca^{2+}$$
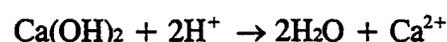
Liming may cause immobilization of heavy metals in soil, because of the formation of additional sorption sites and precipitation of heavy metals as hydroxides at higher pH values.

Hydroxylation
The use of lime to increase pH causing dissolved heavy metals to precipitate as slightly soluble hydroxides is a common clean-up technology in waste-water treatment (De Boodt, 1991). The hydroxylation of a hydrated heavy metal in water at neutral pH values can be described by:

$$Zn^{2+} \bullet (H_2O)_6 \leftrightarrow Zn(OH)^+ \bullet (H_2O)_5 + H^+$$

The equilibrium of the hydroxylation reaction can be described by the dissociation constant log K_{dc}, of which the negative logarithm is the pK_{dc}. Table 3.1 shows the pK_{dc} values of Ni, Cu, Zn, Cd and Pb. The pK_{dc} value of a heavy metal is the pH level at which 50% of the concentration is present as a hydrated cation and the other 50% as a cation hydroxide complex. The lower the pK_{dc} value of a heavy metal, the lower the pH will be at which it precipitates.

Table 3.1.   Dissociation constants (pK$_{dc}$) of heavy metals in water (De Boodt, 1991).

heavy metal	pK$_{dc}$
Ni	8.9
Cu	6.7
Zn	7.6
Cd	8.7
Pb	7.3

In waste-water treatment, the pH must increase 1-2 units above the pK$_{dc}$ value before precipitation of heavy metals occurs (De Boodt, 1991). Thus, for precipitation, the pH would have to increase to a minimum value of 7.7-8.7 for Cu and a maximum value of 9.9-10.9 for Ni. Liming of soil may increase pH to above 7. Hydroxylation may not be able to remove sufficient heavy metals from the soil solution to reach the reference or intervention values for dissolved heavy metals in groundwater in The Netherlands, shown in table 3.2. These values are based on ecotoxicological risk assessment (Ministry of Housing, Spatial Planning and the Environment, 1991). There are no reference and intervention values for heavy metals in the soil solution.

Table 3.2.   Reference and intervention values of dissolved heavy metals in groundwater (mg l^{-1}) (Ministry of Housing, Spatial Planning and the Environment, 1991).

metal	reference value	intervention value
Ni	0.015	0.075
Cu	0.015	0.075
Zn	0.065	0.8
Cd	0.0004	0.006
Pb	0.015	0.075

At equilibrium, the heavy metal concentration maintained by the dissolution of the hydroxide may still be significantly high. The equilibrium of the dissolution reaction of a solid phase can be described by the solubility product log K$_{sp}$, of which the negative logarithm is the pK$_{sp}$. Table 3.3 shows the equilibrium reactions of the dissolution of the hydroxides and the respective pK$_{sp}$ values and heavy metal concentrations in equilibrium with the hydroxides calculated at pH 8. At this pH, the concentrations of Ni, Zn, Cd and Pb are still significantly

higher than the intervention values. Therefore, hydroxylation by liming is not of importance for heavy metal immobilization in soil. Only the concentration of Cu is lower than the reference value. The actual Cu concentration in the soil solution, however, will be higher, due to the presence of DOC exhibiting a high affinity for the formation of soluble Cu-DOC complexes.

Table 3.3.   Equilibrium reactions of the dissolution of hydroxides and the respective solubility products (pK_{sp}) and heavy metal concentrations (mg l^{-1}) in water at pH 8 (De Boodt, 1991).

hydroxide dissolution	pK_{sp}	concentration	intervention value
$Ni(OH)_2$ (c) $\leftrightarrow Ni^{2+} + 2OH^-$	14.0	587	0.075
$Cu(OH)_2$ (c) $\leftrightarrow Cu^{2+} + 2OH^-$	19.0	0.003	0.075
$Zn(OH)_2$ (c) $\leftrightarrow Zn^{2+} + 2OH^-$	16.1	5.19	0.8
$Cd(OH)_2$ (c) $\leftrightarrow Cd^{2+} + 2OH^-$	13.5	3555	0.006
$Pb(OH)_2$ (c) $\leftrightarrow Pb^{2+} + 2OH^-$	15.0	207	0.075

Plant uptake of heavy metals

Liming of a sewage sludge amended soil, resulting in a pH increase from 6 to 7.1, significantly decreased the accumulation of heavy metals in carrot roots, wheat and spinach leaves (Hooda & Alloway, 1996; Hooda *et al.*, 1997). Table 3.4 shows average heavy metal contents of spinach leaves grown in (un)limed soil. Liming decreased the heavy metal contents by about 40% for Ni, Zn and Cd, by 27% for Cu, and by only 19% for Pb.

Table 3.4.   Heavy metal contents of spinach leaves grown in (un)limed soil and phytotoxic contents in mature leave tissue generalized for various plant species (mg kg^{-1} on dry weight basis) (Kabata-Pendias & Pendias, 1992; Hooda & Alloway, 1996).

metal	unlimed	limed	phytotoxicity
Ni	12.0	7.0	10-100
Cu	19.3	14.2	20-100
Zn	502.0	297.5	100-400
Cd	12.4	7.6	5-30
Pb	1.3	1.0	30-300

The effect of liming was not sufficient to reach normal Zn and Cd contents in spinach leaves, because the contents still exceeded the values considered as phytotoxic (Kabata-Pendias & Pendias, 1992). Thus, liming only partially decreased the risks of causing environmental effects of heavy metals.

Heavy metal solubility

Marschner *et al.* (1995) added 0.3% lime (on weight basis) to a sewage sludge amended humic sandy soil polluted with Cu, Zn and Cd. By liming the pH increased from 5.3 to 6.3. Table 3.5 shows the water-extractable heavy metal contents of the (un)limed soil. Liming decreased the Zn and Cd contents by about 60-80%, whereas the Cu content only decreased by 30%. Immobilization of Zn and Cd was probably due to the increased sorption capacity of the soil.

Table 3.5.   Water-extractable heavy metal contents (mg kg^{-1} on dry weight basis) of (un)limed soil (sampling depth 0-20 cm) (Marschner *et al.*, 1995).

metal	unlimed	limed
Cu	0.16	0.11
Zn	5.16	0.94
Cd	0.08	0.032

In situ *immobilization*

Krebs *et al.* (1998) limed a sandy soil low in organic matter, either amended with sewage sludge or pig manure, *in situ* with about 10 tons of lime ha^{-1}. Liming increased the total heavy metal content by <40%, because the lime was contaminated with heavy metals (5 mg Ni, 28 mg Cu, 51 mg Zn and 0.3 mg Cd kg^{-1}). The pH increased from 5-5.4 to 6.1-6.3. Table 3.6 shows the (0.1 M) NaNO$_3$-extractable Cu, Zn and Cd contents in the upper 20 cm of the (un)limed soil. The Zn and Cd contents decreased to below 0.1 mg kg^{-1}, whereas Cu was hardly affected. The Zn and Cd contents in the subsoil (20-40 cm) also decreased, but the Cu content increased from 0.05 to 0.07 mg kg^{-1}. This slight increase can be caused by the elevated organic matter content of the limed soil, which may function as a source for dissolved/colloidal organic ligands with the increased pH, resulting in the formation of soluble Cu-DOC complexes. Thus, liming effectively immobilized Zn and Cd in soil, but mobilized rather than immobilized Cu by DOC complexation.

Table 3.6.   NaNO$_3$-extractable heavy metal content (mg kg^{-1} on dry weight basis) of (un)limed soil (sampling depth 0-20 cm) (Krebs *et al.*, 1998).

metal	unlimed	limed
Cu	0.1	0.1
Zn	1.8	<0.1
Cd	0.01	<0.002

Liming does not increase the total number of sorption sites, but only increases the affinity of the sorption sites. This effect may not be sufficient for sorbing all heavy metals in the soil solution of a polluted soil. Therefore, other techniques increasing the total sorption capacity may have more potential for treating polluted soil. The effect of liming on heavy metal immobilization will only be temporary. When there is a net input of H^+, the lime dissolves, counteracting the acidification of the soil. Therefore, depending on soil type and external acid input, liming has to be repeated every year or every 5 years. This should not be a problem when the costs of liming are sufficiently low.

3.1.2 Phosphate

The interest in the use of phosphate minerals for treating soils polluted with heavy metals mainly exists in urban environments in the United States of America (USA). The research group of Q.Y. Ma (University of Florida, Gainesville, USA) conducted several studies on the use of phosphate minerals for the immobilization of heavy metals. These studies concentrated on Pb, because of the Pb toxicity to the ecosystem and human beings and the numerous Pb polluted sites, resulting from large scale use of Pb in paints and the widespread Pb emission by traffic.

Precipitation

Precipitation is a chemical reaction affecting the speciation of inorganic minerals in soil, because it removes solutes from the soil solution through the formation of new solid phases. Precipitation only occurs when supersaturation exists in the soil solution; i.e. the soil solution contains more solutes than should be present at equilibrium. At undersaturation the solid phases will dissolve. In non-polluted soils solutions are usually undersaturated and precipitation of dissolved heavy metals is not likely to occur (McBride, 1994). However, in soils polluted with heavy metals, the soil solution may become saturated to a level supporting precipitation of new solid phases. Phosphate can be added to remove the heavy metals from the soil solution. Slightly soluble phosphate minerals of heavy metals may form, thereby immobilizing the pollutants and decreasing bioavailability. Precipitation may, however, not be able to remove enough of the heavy metals from the soil solution to restore the natural background concentrations and reference values. At equilibrium, the heavy metal concentrations maintained by the dissolution of the phosphate minerals may still be significantly high. The equilibrium of a dissolution reaction of a solid phase is described by the reaction product log K_{rp}, of which the negative logarithm is the pK_{rp}. Table 3.7 shows the equilibrium reactions of the dissolution of phosphate minerals, the respective pK_{rp} values, and the heavy metal equilibrium concentrations. The heavy metal concentrations were calculated at a $H_2PO_4^-$ concentration of 0.4 mg l^{-1} and pH 5. The value 0.4 mg l^{-1} is the reference value for total inorganic phosphate in groundwater of sandy soil in the Netherlands; the reference value of clay and peat soil is 3 mg l^{-1} (Ministry of Housing, Spatial Planning and the Environment, 1991). There are no reference values for total

inorganic phosphate in the soil solution. At these conditions, the concentrations of Pb in equilibrium with hydroxypyromorphite ($Pb_5(PO_4)_3OH$) and fluoropyromorphite ($Pb_5(PO_4)_3F$) and of Ni, Cu, Zn and Cd in equilibrium with their phosphate minerals are significantly higher than the intervention values. Therefore, the formation of these heavy metal phosphate minerals does not have potential for treating polluted soil at the given reference values in The Netherlands. Only the concentration of Pb in equilibrium with chloropyromorphite ($Pb_5(PO_4)_3Cl$) is lower than the reference value.

Table 3.7. Equilibrium reactions of the dissolution of phosphate minerals and the respective reaction products (pK_{rp}) and equilibrium concentrations of heavy metals (mg l^{-1}) in water at pH 5.

phosphate mineral dissolution	pK_{rp}	concentration
$Ni_3(PO_4)_2$ (c) + 4H$^+$ ↔ 3Ni^{2+} + 2H$_2$PO$_4^-$	-8.8*	42838
$Cu_3(PO_4)_2$ (c) + 4H$^+$ ↔ 3Cu^{2+} + 2H$_2$PO$_4^-$	-2.2	297
	-7.1*	12356
$Zn_3(PO_4)_2$ (c) + 4H$^+$ ↔ 3Cu^{2+} + 2H$_2$PO$_4^-$	-3.8	1012
$Zn_3(PO_4)_2 \bullet 4H_2O$ (c) + 4H$^+$ ↔ 3Zn^{2+} + 2H$_2$PO$_4^-$ + 4H$_2$O	-1	203
$Cd_3(PO_4)_2$ (c) + 4H$^+$ ↔ 3Cd^{2+} + 2H$_2$PO$_4^-$	4.1	5.2
	25.1	0.014
$Pb_5(PO_4)_3OH$ (c) + 7H$^+$ ↔ 5Pb^{2+} + 3H$_2$PO$_4^-$ + H$_2$O	13	5.9
$Pb_5(PO_4)_3Cl$ (c) + 6H$^+$ ↔ 5Pb^{2+} + 3H$_2$PO$_4^-$ + Cl$^-$		
$Pb_5(PO_4)_3F$ (c) + 5Pb^{2+} + 3H$_2$PO$_4^-$ + F$^-$		

Data from Lindsay (1979) unless noted; * data from Vieillard & Tardy (1984). Concentrations of heavy metals calculated at a Cl$^-$ concentration of 25 mg l^{-1} and a F$^-$ concentration of 1.5 mg l^{-1} (Walworth, 1992).

Table 3.8 shows the heavy metal concentrations in the solution of a sewage sludge amended soil, which all exceed the intervention values. The concentrations of Pb in equilibrium with hydroxypyromorphite and fluoropyromorphite and of Ni, Cu, Zn and Cd in equilibrium with their phosphate minerals are even significantly higher than these elevated solution concentrations of heavy metals.

Table 3.8. Heavy metal concentrations (mg l^{-1}) in the soil solution of a sewage sludge treated soil at pH 5 (Behel et al., 1983).

metal	concentration
Ni	0.4
Cu	0.4
Zn	23.7
Cd	0.16
Pb	0.21

Thus, the formation of these phosphate minerals does not have potential for treatment of this sewage sludge amended soil. Only the formation of chloropyromorphite could have potential to treat Pb polluted soil, when the theoretical value of the equilibrium concentration would apply also to the soil solution. The actual Pb concentration in the soil solution could, however, be higher, due to the presence of dissolved/colloidal (in)organic ligands/chelates competing with phosphate for Pb complexation.

Lead solubility

Apatite ($Ca_5(PO_4)_3OH$) effectively immobilized Pb in a laboratory experiment as was demonstrated by Ma *et al.* (1993). Pb immobilization was due to the dissolution of apatite, providing phosphate to the solution, after which phosphate precipitated with dissolved Pb as hydroxypyromorphite ($Pb_5(PO_4)_3OH$), removing Pb from the solution, as is shown by the following reactions:

$$Ca_5(PO_4)_3OH \text{ (s)} + 6H^+ \rightarrow 5Ca^{2+} \text{ (aq)} + 3H_2PO_4^- \text{ (aq)} + OH^-$$

$$5Pb^{2+} \text{ (aq)} + 3H_2PO_4^- \text{ (aq)} \rightarrow Pb_5(PO_4)_3OH \text{ (s)} + 6H^+$$
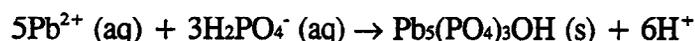
Table 3.9 shows the Pb concentration after reaction of apatite with dissolved Pb. The Pb concentration is even lower than the reference value. Thus, according to the results of Ma *et al.* (1993), apatite has potential for treating Pb polluted soil. If the formation of hydroxypyromorphite determined both the Pb and phosphate concentrations in the solution, the $H_2PO_4^-$ concentration in equilibrium with hydroxypyromorphite must have been about 100 mg l^{-1} at pH 6.4 and about 300 mg l^{-1} at pH 5.9 according to our calculations. These concentrations would significantly exceed the reference value for total inorganic phosphate in groundwater.

Table 3.9. Pb concentrations after reaction of apatite with dissolved Pb in aqueous solutions (mg l^{-1}) (Ma *et al.*, 1993).

pH	initial Pb	final Pb
6.4	50	0.002
5.9	100	0.005

Lead immobilization and phosphate

Figure 3.1 shows the Pb and $H_2PO_4^-$ concentrations in equilibrium with the dissolution of hydroxypyromorphite at pH 4, 5 and 6. At the reference value of 0.4 mg total inorganic phosphate l^{-1} and pH 6, the Pb concentration is more than 10 times higher than the Pb reference value. Only at a $H_2PO_4^-$ concentration >25 mg l^{-1} and pH 6, the Pb concentration

is lower than this value. At pH values higher than 6, the $H_2PO_4^-$ concentration in solution would be lower. However, at pH 6, the $H_2PO_4^-$ concentration at which the Pb concentration is sufficiently low would significantly exceed the Dutch reference value for total inorganic phosphate in groundwater. In The Netherlands, this would be unacceptable for policy makers. To provide an indication of the amounts of phosphate being used for *in situ* Pb remediation, Yang *et al.* (1997) added as much as 1% H_3PO_4 (on weight basis) to a Pb polluted soil. This amount is about 15 times higher than the average total phosphate content of a Dutch agricultural soil. A high phosphate concentration in the soil solution can support transport of phosphate by lateral (sub)surface runoff and/or drainage tiles to surface waters, where it may cause eutrophication. This should be avoided, because it causes effects in various aquatic ecosystems: e.g. mass algal growth and dominance of cyanobacteria in lakes, increase of algal biomass in ditches, increased occurrence of nuisance algae and oxygen depletion in the North Sea (Boers *et al.*, 1995). Therefore, the use of phosphate for treating Pb polluted soil does not have much potential in The Netherlands.
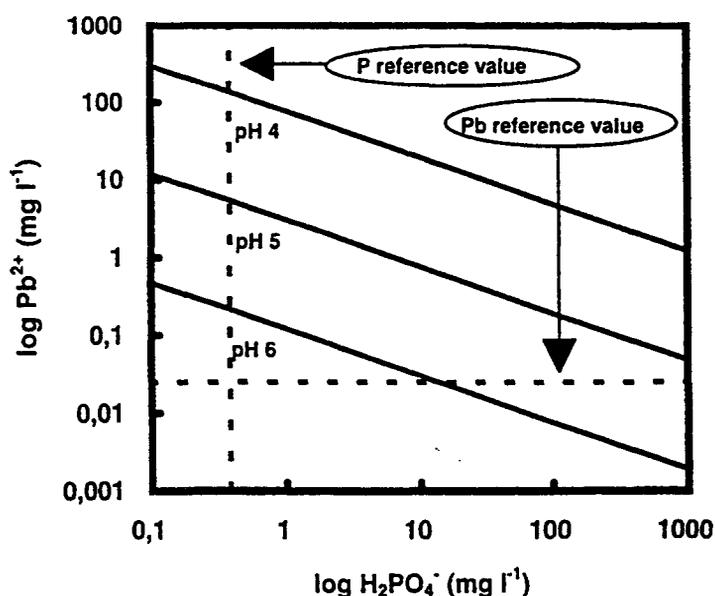
Figure 3.1.   Pb   and $H_2PO_4^-$ concentrations   in   equilibrium   with   the   dissolution   of hydroxypyromorphite at pH 4, 5 and 6.

The use of phosphate in the USA

In the USA, the technique of immobilizing Pb using phosphate is being further developed for remediating urban soils, as an alternative for excavation of the soil (Pierzynski, 1997). The local authorities do not accept a techniques, which only increase the sorption capacity. Instead, Pb has to be converted into another binding form, for which Pb phosphate minerals

were selected. In feeding studies with pigs, it was found that Pb-phosphate minerals were taken up to a lesser extent than Pb in soil samples. It is assumed that the same will occur after ingestion of soil by humans. It is accepted by the authorities that the Pb concentration of the soil solution can be even higher after addition of phosphates.

3.1.3 Olivine

Olivine is a magnesium-iron silicate, which is known as the most rapidly weathering primary mineral thereby consuming H^+. It can be added to highly acidic soils to reach a less acidic pH. The chemical composition of olivine is $[Mg_2, Fe_2]SiO_4$, whereby Mg dominates over Fe. Olivine is able to react chemically consuming H^+, as is shown by the following reactions (X denotes Mg or Fe):

$$X_2SiO_4 + 4H^+ \rightarrow 2X^{2+} + SiO_2 + 2H_2O$$

$$2Mg_2SiO_4 + 2H^+ + H_2O \rightarrow Mg_3Si_2O_5(OH)_4 + Mg^{2+}$$

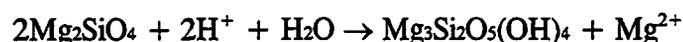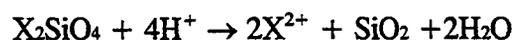The costs of the use of olivine will be low. It is mined in Norway and the northern part of Spain. Olivine is used in the steel industry. It is slightly contaminated with Ni, i.e. 3 mg kg^{-1} (Del Castilho, 1997).

Dissolution rate

The dissolution rate of olivine mainly depends on the pH and pCO_2, and the presence of microcracks on the grains (Wogelius & Walther, 1990; 1992). Obviously, the dissolution rate increases at lower pH values. The pCO_2 affects the dissolution rate, as is shown by the reaction (X denotes Mg or Fe):

$$2X_2SiO_4 + CO_2 + 2H_2O \rightarrow X_3Si_2O_5(OH)_4 + XCO_3$$
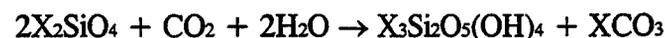
The dissolution rate is also promoted by small grain sizes and the presence of micro-cracks on the grains because of the higher specific surface area.

pH Buffering

The pH buffering effect of olivine in soil is as yet not well investigated. It is expected that an addition of a ton of olivine ha^{-1} to a highly acidic soil with pH 3 will increase the pH to about 4 (Del Castilho, 1997). According to calculations of Jonckbloedt (unpublished), a soil of pH 3 will be buffered for a considerable period of time. Table 3.10 shows maximum pH buffering periods for different scenarios by varying grainsize, rainwater pH and dosage. The results are tentative, because the parameter pCO_2 was not taken into account.

Appendix: Review of recent literature on heavy metal immobilization in soils

Table 3.10. Maximum pH buffering period (years) based on different scenarios including the parameters grainsize (μm), rainwater pH and dosage (kg ha^{-1}); annual rainfall 760 mm (Jonckbloedt, unpublished); data after Wogelius & Walther (1992).

diameter	rainwater pH	dosage		
		500	1000	1500
1-250	4	13	30	>45
	5	>45	>45	>45
1-2000	4	8	22	37
	5	>45	>45	>45

Usefulness

Olivine may be useful for forest and nature areas for maintaining a slightly acidic pH. In The Netherlands, large forest and nature areas consist of non-calcareous soil with a low clay and organic matter content and, thus, having a low pH buffering capacity. Due to a net input of H$^+$, the pH of these soils can decrease to 3-4. In this pH range, Al phytotoxicity and leaching to the groundwater can become a problem. Buffering of pH at about 4 by olivine is expected to prevent the Al problem. In this case, lime is not an alternative to olivine. In nature areas consisting of acidic and poor sandy soils, a vegetation adapted to these conditions has developed, and liming would cause this natural vegetation to disappear, because of a higher nutrient availability resulting from the increased rate of mineralization of organic matter at higher pH.

Another potential application of olivine is in the preventive treatment of poor, generally sandy, agricultural soils. A substantial part of these soils is in the process of being converted into nature areas. Here, stopping the normal agricultural practice of liming will result in a decrease in the pH of the soil, and thus in solubilization of a large fraction of the heavy metals present in these soils as a result of past applications of manure and fertilizers. Addition of olivine can help to maintain the pH of these soils at values that are high enough to preclude solubilization and mobilization of heavy metals. Field experiments to test this scenario are presently being discussed (Del Castilho, 1997).

Olivine does not have potential for treating heavy metal polluted soil. It buffers the pH in the acid range, limiting the risks associated with Al, but without sufficiently decreasing the risks of heavy metal toxicity and leaching. However, laboratory and field experiments with olivine are necessary for testing its ability to limit Al phytotoxicity and leaching.

3.2 Techniques aiming to increase the sorption capacity of the soil

3.2.1 Beringite

The aluminosilicate beringite is a coal mining residue. It is a product of the fluidized bed burning of mine pile material (mainly schists and coal) originating from a former coal mine at Beringen in Belgium. The minerals present in the schists are quartz, phyllosilicates (illite, kaolinite and chlorite), calcite ($CaCO_3$), dolomite ($[Ca, Mg]CO_3$), anhydrite ($CaSO_4$), siderite ($FeCO_3$) and pyrite (FeS_2). The schists are pulverized by heating in an electrically guided fluidized bed oven at about 800°C. During the heating process, the schists are partly broken down and partly recrystalized resulting in the modified clay mineral beringite. The element composition is similar to the original schists. Particles with a medium diameter of 0.02-0.2 mm are separated by air suction (De Boodt, 1991). Table 3.11 shows the average chemical composition of beringite in which SiO_2 and Al_2O_3 are the main fractions. Beringite is contaminated with heavy metals from the coal mining residue, which may decrease its acceptance by policy makers when used for treatment of polluted soil. However, the contaminants are strongly sorbed by beringite as indicated by a solubility experiment of De Boodt (1991).

Table 3.11. Chemical composition of beringite (De Boodt, 1991).

compound	content (%)	element	content (mg kg^{-1})
SiO2	52	Cr	950
Al2O3	30	Mn	1100
CaO	3.45	Co	98
MgO	1.48	Ni	123
K2O	2.65	Cu	120
Na2O	0.58	Zn	630
Fe2O3	4.72	Cd	9.1
loss at ignition	5.12	Pb	203

Mechanism of formation

The mechanism of formation of beringite is well understood. There is a method to produce a less polluted product by heating calcareous marine clay with fly ash at a ratio of 9:1 (on weight basis) up to 800-850°C. Fly ash is added because of the high FeO and Fe_2O_3 content providing specific sorption sites. The minimum CaO content will amount to about 4.3%, which is higher than in beringite. Additional calcite can be added to increase

the CaO content. Thus, the production of a comparable, but less polluted agent is not really a problem.

Mechanism of immobilization

Beringite has a high potential for heavy metal immobilization in soil, although the mechanism is not yet completely understood. It may affect the soil pH, the CEC and specific sorption capacity (e.g. SiOH, AlOH), but also lead to (co-)precipitation of heavy metals. The specific surface area and CEC of beringite are respectively 20 m^2 g^{-1} and 16-22 cmol$_c$ kg^{-1} (at pH 7) (De Boodt, 1991). These values may be considered as low. Beringite induces a strong alkaline reaction. The pH can become as high as 12.5. The high pH is due to the presence of MgO and CaO formed during the heating of $CaCO_3$ and $[Ca, Mg]CO_3$. CaO and MgO will dissolve when reacting with H_2O forming their hydroxides $Mg(OH)_2$ and $Ca(OH)_2$. The dissolution of $Mg(OH)_2$ and $Ca(OH)_2$ will produce OH^- and consume H^+. It leads to an increase of the soil pH.

Leaching of heavy metals in a pot experiment

The research group of J. Vangronsveld (University of Limburg, Diepenbeek, Belgium) has conducted several studies on the effectiveness of beringite for the immobilization of heavy metals in the soil.

Vangronsveld et al. (1995a) studied the effect on heavy metal leaching of the addition of 5% beringite (on weight basis) to a bare soil, the effect of a plant cover of the heavy metal tolerant grasses Agrostis capillaris and Festuca rubra without beringite addition, and the effect of 5% beringite addition together with a plant cover. The soil was sampled from the site of a former metallurgical zinc smelter in Belgium, and was characterized as an acidic sandy soil low in organic matter and heavily polluted with Cu, Zn, Cd and Pb. Table 3.12 shows the effects of the treatments on the Zn and Cd concentrations in the water leached through the soil profile and the total amounts of Zn and Cd transported. Beringite reduces the Zn and Cd concentrations in the leachate by 70-75%, the plant cover alone only by 50%. However, beringite significantly increased the amount of water leached out of the soil, which caused the total amounts of Zn and Cd moved to decrease only by 40-50%. The plant cover on the other hand restricted the amount of water leached, reducing the total amounts of Zn and Cd moved by about 85%. Thus revegetation as such already strongly decreased leaching of heavy metals out of the soil. Revegetation also reduces lateral transport of heavy metal containing topsoil by wind erosion.

Nevertheless, Vangronsveld et al. (1995a) concluded that to decrease the heavy metal problem in these soils, beringite may be helpful for reducing phytotoxicity when necessary for a successful revegetation, because beringite lowers the concentration of heavy metals like Zn and Cd in the soil solution.

Table 3.12. Effect of the addition of beringite with or without a plant cover on heavy metal concentrations (mg l⁻¹) of the leachates, the total amounts of water leached (l) and total amounts of heavy metals (mg) leached from the soil sampled at a former zinc smelter site in Belgium (after Vangronsveld *et al.*, 1995a).

treatment	concentration		water	total amount	
	Zn	Cd		Zn	Cd
control	2.15	0.171	96	206.4	16.4
plant cover	1.12	0.090	26	29.1	2.3
beringite	0.53	0.052	187	99.1	9.7
beringite with plant cover	0.68	0.056	96	65.3	5.4

Phytotoxicity

The soil sampled from the above zinc smelter was highly phytotoxic. The results of a biological investigation by Van Assche & Clijsters (1990) demonstrated that the phytotoxicity of the soil decreased after the addition of 5% beringite (on weight basis) (Vangronsveld *et al.*, 1995b). It is based on the analysis of some morphological (shoot length, weight, leaf area) and biochemical (induction of stress-enzyme capacity and modification of iso-enzyme patterns) parameters of test plants grown in soil under controlled conditions in the laboratory. Morphological and biochemical parameters of non-tolerant test plants (*Phaseolus vulgaris*) grown in untreated soil were highly affected. Beringite prevented morphological and biochemical damages and decreased the Zn and Cd contents by about 80% (table 3.13). However, the Zn content of the plants grown in treated soil still exceeds the value considered as phytotoxic by Kabata-Pendias & Pendias (1992).

Table 3.13. Effect of a 5 % beringite addition on heavy metal contents of primary leaves of non-tolerant test plants (*Phaseolus vulgaris*) (mg kg⁻¹ on dry weight basis) grown in soil from the site of a former metallurgical zinc smelter in Belgium (Vangronsveld *et al.*, 1995b).

heavy metal	untreated	treated
Zn	738	157
Cd	8.5	<2.0

In situ *detoxification*

Vangronsveld *et al.* (1995b) treated the heavily polluted site of the former zinc smelter (table 3.14) *in situ* with beringite to decrease the soil phytotoxicity for restoring

the vegetation cover. Because of soil phytotoxicity, the natural heather and grass vegetation had completely disappeared from this area. About 120 tons of beringite and 100 tons of compost ha⁻¹ (respectively 2 and 1.5% on weight basis) were added to the upper 35 cm of the soil. Compost can help to overcome the plant nutrient deficiency, to improve the water retention capacity of the soil, and to increase the total sorption capacity. The tests with *P. vulgaris* demonstrated that the phytotoxicity of the treated soil decreased after 4 weeks of equilibration. Typical features of phytotoxicity such as extreme growth inhibition and induction of stress (iso-enzymes) as observed in *P. vulgaris* grown in untreated soil did not show up any more and heavy metal contents in plants decreased significantly. After the treatment a seed mixture of commercially available cultivars of heavy metal and drought tolerant *A. capillaris* (10%) and *F. rubra* (65%) supplemented with non-tolerant *Lolium perenne* (25%) was sown. Because of the amendements phytotoxicity of the soil was limited as indicated by the fruitful development of a vegetation cover immediately after sowing. The vegetation cover became fully established after 16 weeks.

Table 3.14. Total heavy metal contents (mg kg⁻¹ soil on dry weight basis) at the site of a former metallurgical zinc smelter in Belgium (sampling depth 0-20 cm) (Vangronsveld *et al.*, 1995b).

metal	range
Cu	408-1650
Zn	2850-10450
Cd	10-67
Pb	710-1710

Durability of in situ *immobilization by beringite*

To be a useful technique, *in situ* immobilization of heavy metals in soil has to last for a considerable period of time. Wessolek & Fahrenhorst (1994) calculated long-term leaching of Zn and Cd with a numerical simulation model after the addition of beringite. The simulation indicated an effective immobilization of Zn and Cd by the solid phase during 80 years.

Vangronsveld *et al.* (1996) studied *in situ* the physico-chemical soil conditions, phytotoxicity, floristic and fungal diversity and mycorrhizal infection of the plant community five years after the application of beringite and compost at the site already discussed. Table 3.15 shows the pH, organic matter content, CEC and water-extractable Zn concentration before and after the treatment. The untreated soil exhibited an acidic pH, a low organic matter content and CEC, a high water-soluble Zn content and a high phytotoxicity. Five years after

the treatment, the pH, organic matter content and CEC had increased significantly. The water-extractable Zn content had decreased by >98%. The phytotoxicity was still comparable to the level measured 4 weeks after the treatment as demonstrated by the biological tests. The vegetation was still healthy and regenerating by vegetative means and seed. The floristic and fungal diversity of the treated soil was higher than that of the untreated soil. The ubiquity of the mycorrhizal fungi in plant roots demonstrated that a functioning ecosystem was establishing.

Vangronsveld et al. (1996) did not provide results of the water-extractable Cu, Cd and Pb contents and DOC concentration. The increased organic matter content may function as a source for DOC. Cu exhibits a high affinity for complexation with DOC. Cu may be mobilized by DOC in the pH range of the treated soil, due to the formation of soluble Cu-DOC complexes (Römkens et al., 1996). However, Farnworth et al. (1996) demonstrated that beringite is able to sorb DOC. Therefore, beringite may immobilize soluble heavy metal-DOC complexes, although its sorption capacity for DOC is low.

Table 3.15.   Organic matter content (%), pH, CEC (cmol$_c$ kg^{-1}) and water-extractable Zn content (mg kg^{-1} on dry weight basis) before and five years after treating the site of a former zinc smelter in Belgium (Vangronsveld et al., 1996).

parameter	before treatment	after treatment
pH	4.5-6.0	7.3-7.9
organic matter	<2	3.1-5.2
CEC	<2	4.9-10
Zn	130-152	2.0-2.4

3.2.2 Montmorillonite

Montmorillonite may have potential for heavy metal immobilization in soil, because it has a large specific surface area and a high CEC. Heavy metals mainly sorb on montmorillonite by electrostatic attraction. They can, therefore, be readily exchanged for other cations such as Mg^{2+} and Ca^{2+} (Van Bladel et al., 1993). Sorption of heavy metals can be improved by the addition of Al. The Al-hydroxide groups compensate part of the permanent negative charge of the clay mineral. Thus, the sorption of heavy metals due to CEC is smaller than on the untreated montmorillonite. The loss of CEC is, however, more than offset by the formation of surface hydroxyl groups providing specific sorption sites located at the surface of the Al-hydroxide coatings (Lothenbach et al., 1997). Specific sorption sites can also

be provided by the polynuclear aluminum complex $AlO_4Al_{12}(OH)_{24}(H_2O)_{12}^{7+}$ referred to as Al_{13}. Deprotonation of the Al_{13}-H_2O ligands forms hydroxyl groups with a high affinity for heavy metal complexation (Janssen, 1995). The sorbent Al_{13}-montmorillonite can be formed from the addition of Al_{13} to montmorillonite. Table 3.16 shows the specific surface area and CEC of the sorbents.

Table 3.16.   Specific surface area (m^2 g^{-1}) and CEC (cmol$_c$ kg^{-1}) of montmorillonite and Al- and Al_{13}-montmorillonite (Lothenbach et al. 1997).

clay mineral	area	CEC
montmorillonite	20	86
Al-montmorillonite	60	14
Al_{13}-montmorillonite	220	4

Montmorillonite

Lothenbach et al. (1997) added montmorillonite to aqueous solutions of Ni, Cu, Zn, Cd and Pb. In the pH range 4-7, montmorillonite sorbed only 20% of the heavy metals. Sorption further increased at pH >7, due to a decrease of the competition effect between heavy metals and H^+, and the increasing importance of hydroxylation at a pH of about the pK$_{dc}$ values of the heavy metals. All heavy metals sorbed were considerably remobilized after the addition of an excess of Ba indicating that these heavy metals were readily exchangeable. Because of the risks of remobilization, montmorillonite may have less potential for the immobilization of heavy metals in soil.

Al_{13} and Al- and Al_{13}-montmorillonite

Lothenbach et al. (1997) added Al_{13} and Al- and Al_{13}-montmorillonite to aqueous solutions of Ni, Cu, Zn, Cd and Pb. Heavy metal sorption by Al_{13} and Al- and Al_{13}-montmorillonite was pH dependent. Sorption increased to 100% at pH values above 6, due to the formation of additional sorption sites resulting from the deprotonation of hydroxyl groups and Al_{13}-H_2O ligands. The polynuclear aluminum complex Al_{13} formed soluble complexes with Ni, Cu, Zn and Pb in the pH range 5.8-6.1. Thus, Al_{13} may cause mobilization of heavy metals rather than immobilization and does, therefore, not have potential for soil remediation. Table 3.17 shows the pH ranges in which Al- and Al_{13}-montmorillonite sorbed heavy metals. Ni, Cu and Zn were sorbed by specific sites, because the addition of Ba did not show significant remobilization. Thus, other cations in the soil solution would hardly affect sorption, because these heavy metals are not exchangeable. In contrast, Cd was readily exchanged, whereas Pb was partially remobilized.

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Table 3.17. pH ranges and heavy metal sorption by Al- and Al13-montmorillonite (Lothenbach *et al.*, 1997).

clay mineral	Ni	Cu	Zn	Cd	Pb
Al-montmorillonite	6-8	4-6	6-8	7-9	5-7
Al13-montmorillonite	6-8	5-6	7-8	8-9	5-7

Figure 3.2 shows the influence of pH on the sorption of heavy metals to montmorillonite and Al- and Al13-montmorillonite.

Pot experiment

Lothenbach *et al.* (1998) added 0.5 and 6% (on weight basis) montmorillonite and Al-montmorillonite to a sewage sludge amended sandy soil low in organic matter with pH 6.7. Table 3.18 shows the (0.1 M) $NaNO_3$-extractable Zn and Cd contents of (un)treated soil. Al-montmorillonite appeared to be more effective for immobilizing Zn and Cd. A dosage of 60 g Al-montmorillonite kg^{-1} soil decreased the amount of $NaNO_3$-extractable Zn and Cd by >70%, whereas a similar dosage of montmorillonite decreased the amount only by about 30-40%.
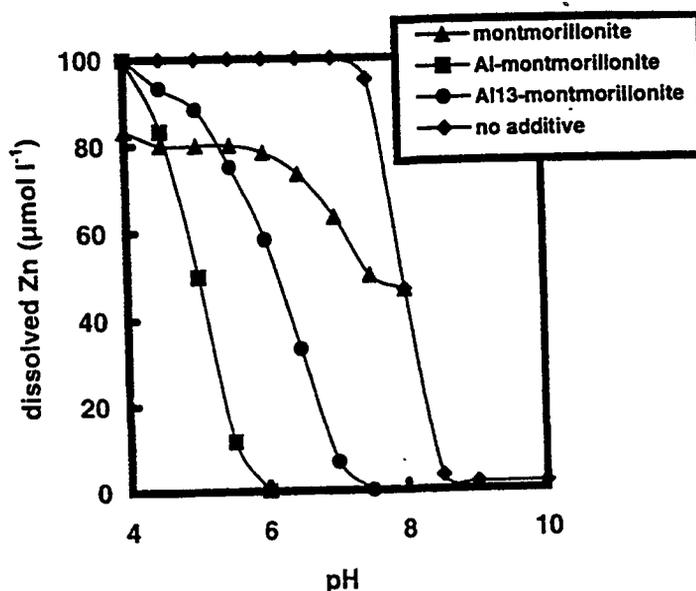

Figure 3.2. Sorption of Zn on montmorillonite and Al- and Al13-montmorillonite (after Lothenbach *et al.*, 1997).

Aluminum toxicity

In using Al-montmorillonite for soil remediation, the question of Al toxicity becomes important. The most toxic aluminum species are $Al(OH)^{2+}$ and $Al(OH)_2^+$ (Marschner, 1995). A solubility experiment of Al-montmorillonite in water by Lothenbach *et al.* (1998) demonstrated that the dissolved Al concentration was below 0.5 mg l^{-1} in the pH range 5-8.5. The solubility of Al in soil mainly is determined by pH. At pH values above 5.5, the soil solution contains an Al concentration of about 0.4 mg l^{-1} which is not considered as toxic for plants (Kabata-Pendias & Pendias, 1992; Marschner, 1995). Thus, the addition of Al-montmorillonite to soil in the pH range of 5.5 and 8.5 is not likely to be toxic. High toxicity is also attributed to the polynuclear cation Al_{13}^{7+} (Parker *et al.*, 1989). However, results on the solubility of Al_{13}-montmorillonite are lacking.

Table 3.18. NaNO₃-extractable heavy metal contents (mg kg^{-1} on dry weight basis) in untreated soil and in soil treated with 5 or 60 g montmorillonite or Al-montmorillonite kg^{-1} soil (Lothenbach *et al.*, 1998).

additive and metal		untreated	treatment	
			5	60
montmorillonite Zn		4.8	4.6	2.9
	Cd	0.007	0.006	0.005
Al-montmorillonite	Zn	4.8	3.5	<1.0
	Cd	0.007	0.005	<0.002

Usefulness

Montmorillonite and Al- and Al_{13}-montmorillonite effectively immobilized Ni, Cu, Zn, Cd and Pb. Because the heavy metals sorbed by montmorillonite were readily exchangeable this mineral it may have less potential for soil remediation though. Al- and Al_{13}-montmorillonite hardly have cation exchange sites. Thus, sorption of heavy metals would not be affected by other cations in the soil solution, and they probably would not affect nutrient availability for plants in soil. Also, the sorption capacity of Al-montmorillonite was higher than that of montmorillonite at higher pH. Therefore, Al- and Al_{13}-montmorillonite can be effective for heavy metal immobilization in neutral or alkaline soil with a high pH buffering capacity. In acidic soil, the solution concentration of heavy metals can hardly be decreased without increasing the pH (Krebs, 1996). Thus, in these soils, Al- or Al_{13}-montmorillonite should be used with lime. Field experiments have as yet not been conducted to test the effectiveness and durability of immobilization by these substances.

3.2.3 Manganese oxide

Manganese oxides are common in soil. They provide a source of Mn, an essential element for plants. Manganese oxides occur in soil as coatings on other (in)organic surfaces, in micro-cracks and as nodules as large as 2 cm in diameter. Birnessite is the most prevalent Mn-oxide in soil (Sposito, 1989). Manganese oxides are known to decrease the mobility of heavy metals in soil (McKenzie, 1980). Heavy metals may be sorbed either by cation exchange or by covalent binding, but isomorphous substitution may also contribute to immobilization.

Plant uptake of heavy metals
Mench *et al.* (1994) added 1% Mn-oxide (on weight basis) to three soils with a low organic matter content and polluted with Cd and Pb in a pot experiment (i.e. a sandy soil with pH 7.4, a clay soil with pH 7.8, and a sandy soil with pH 4.2). Table 3.19 shows the Cd and Pb contents of ryegrass grown in the (un)treated soil. The Cd contents of ryegrass grown in the sandy soil with pH 7.4 and clay soil decreased by about 60-75%. The Pb contents of ryegrass grown in the clay soil and sandy soil with pH 4.2 decreased by about 70-95%. However, the effect of Mn-oxide was not sufficient, because the Cd and Pb contents still partially exceeded the normal contents of grasses, i.e. respectively 0.6 and 1.2 mg kg^{-1} (on dry weight basis) (Kabata-Pendias & Pendias, 1992).

Table 3.19. Heavy metal contents of ryegrass (mg kg^{-1} on dry weight basis) grown in (un)treated soil (Mench *et al.*, 1994).

soil type and pH		metal	untreated	treated
sand	7.4	Cd	16.2	6.9
clay	7.8	Cd	4.9	1.2
		Pb	13.3	3.9
sand	4.2	Pb	4.9	0.2

Heavy metal solubility
McKenzie (1980) measured sorption of heavy metals on synthetic Mn-oxide in an aqueous solution. Figure 3.3 shows the influence of pH on sorption of Ni, Cu, Zn and Pb to Mn-oxide. Sorption was dependent on pH. In the pH range 2-8, sorption of Cu, Zn and Pb increased to 100%, whereas sorption of Ni increased to 80%.
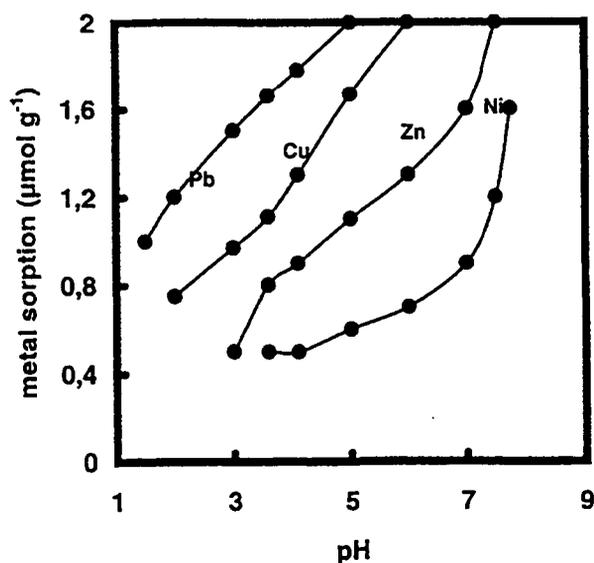
Figure 3.3. Sorption of heavy metals on the manganese oxide birnessite (after McKenzie, 1980).

Table 3.20 shows the results of Mench *et al.* (1994) on water-extractable Cd and Pb contents of untreated and 1% Mn-oxide (on weight basis) treated soil in a pot experiment. Manganese oxide effectively immobilized Cd and Pb. The Cd and Pb contents decreased by about 65-90%. The Point Zero Charge (PZC) of Mn-oxide lies between 1.5-2.0. The PZC can be defined as the pH at which the surface of soil or soil constituent has a net charge of zero. When the pH is lower than the PZC, the net charge of the surface is positive; when the pH is > PZC, the net charge of the surface is negative. Because of the low PZC, Mn-oxide can sorb heavy metals in acidic soil. Manganese oxide can, however, only be used in aerated soils, because it dissolves under reducing conditions. Field experiments to test the effectiveness and durability of immobilization have not yet been conducted, and are, therefore, necessary.

Table 3.20. Water-extractable heavy metal contents (mg kg^{-1} on dry weight basis) in (un)treated soil (sampling depth 0-20 cm) (Mench *et al.*, 1994).

soil type	pH	metal	untreated	treated
sand	7.4	Cd	0.648	0.216
clay	7.8	Cd	0.144	0.018
sand	4.2	Pb	0.625	0.1

Due to precipitation of oxides, a hardpan (impermeable layer) may form at the interface of the aerated and non-aerated zones if the water table perches at a particular position in

the soil profile (McBride, 1994). A hardpan may decrease the potential of a soil for plant growth. Therefore, additional experiments should be conducted to test if Mn-oxide may form a hardpan in soil, and thus, whether its use involves a risk of decreasing the quality of soil.

3.2.4 Gravel sludge

Gravel sludge is a waste product of the gravel industry. Its composition depends on its origin. A typical example taken from the Swiss literature (Krebs et al., submitted) contained 41% clay minerals (mainly illites, chlorites and montmorillonites), 30% $CaCO_3$, 18% quartz, 7% plagioclase, 2% dolomite and 2% organic matter. Table 3.21 shows the average chemical composition of gravel sludge.

Gravel sludge may have potential for the immobilization of heavy metals in soil, because of its high CEC of 156 $cmol_c$ kg^{-1}, and its ability to increase the pH (Krebs et al., submitted). The latter can be attributed to its high $CaCO_3$ content. The specific surface area was 8 m^2 g^{-1}, which may be considered as low (Krebs et al., submitted). Gravel sludge is available, at least in Switzerland, in large amounts and at low cost. However, it contains considerable quantities of heavy metals such as Cd, Cu, Zn and Pb (i.e. 15.0 mg Cu, 53.5 mg Zn, 0.13 mg Cd and 10.6 mg Pb kg^{-1} gravel sludge). This may reduce its acceptance by policy makers, when used for the treatment of polluted soil.

Table 3.21.   Average chemical composition of gravel sludge (Krebs et al., submitted).

compound	amount (%)	compound	amount (%)
SiO_2	38.1	CaO	23.4
TiO_2	0.4	Na_2O	1.0
Al_2O_3	8.3	K_2O	1.5
Fe_2O_3	3.8	P_2O_5	0.1
MnO	0.1	loss on ignition	21.7
MgO	1.6		

Plant uptake of heavy metals

Gravel sludge treatment moderately decreased the accumulation of heavy metals in the above-ground parts of ryegrass (Krebs et al., submitted). Table 3.22 shows the heavy metal contents of ryegrass grown in (un)treated soil. In the presence of gravel sludge the Cu, Zn and Cd contents decreased by about 20-60%. The effect of gravel sludge was not sufficient,

because Cu and Zn still exceed the normal contents in grasses of 4.2 mg Cu and 59 mg Zn kg^{-1} (on dry weight basis) (Kabata-Pendias & Pendias, 1992).

Table 3.22. Heavy metal contents in the above-ground plant parts of ryegrass (mg kg^{-1} on dry weight basis) grown in untreated (pH 6.2-6.9) and treated soil (pH 6.8-7.2) (Krebs et al., submitted).

metal	untreated	treated
Cu	16-47	13-31
Zn	86-502	66-236
Cd	0.13-0.68	0.07-0.33

In situ *immobilization*

Krebs et al. (submitted) added 3.7 tons of gravel sludge ha^{-1} *in situ* to the upper 20 cm of three sewage sludge amended sandy soils low in organic matter and polluted with Cu and Zn. The pH increased from 6.2-6.9 to 6.8-7.2. The CEC was hardly affected. Table 3.23 shows the (0.1 M) NaNO$_3$-extractable Cu and Zn contents of the (un)treated soils. The treatment caused the extractable Cu and Zn contents to decrease to below respectively 1.24 and 2.0 mg kg^{-1}. The treatment was not effective for Cu in all soils. In one soil, the extractable Cu amount slightly increased from 0.01-0.24 to 0.02-0.26 mg kg^{-1}. The pH increase with soil organic matter functioning as a source for dissolved/colloidal DOC may have caused this slight increase. A higher dosage of 110 tons of gravel sludge ha^{-1} did not further decrease extractable Zn and Cu contents. According to Krebs et al. (submitted), at least part of the immobilization of Cu and Zn was a pH effect. Therefore, other techniques increasing the total sorption capacity of the soil have more potential for the treatment of heavy metal polluted soil.

Table 3.23. NaNO$_3$-extractable heavy metal contents (mg kg^{-1} on dry weight basis) in (un)treated soil (Krebs et al., submitted).

metal	untreated	treated
Cu	0.01-2.07	0.02-1.24
Zn	0.54-8.04	0.03-2.0

3.2.5 Brown coal

Brown coal mainly consists of non-soluble and stable humic substances. Humic substances contain carboxylic and phenolic hydroxides and other oxygen-containing groups, which are important for heavy metal sorption. Brown coal may be used for *in situ* heavy metal

immobilization in the soil because of its high specific surface area of 180 m^2 g^{-1} and low water-solubility. The stated CEC of brown coal was 37-43 cmol$_c$ kg^{-1} (at pH 7), which may be considered as moderate (Karczewska et al., 1996).

Heavy metal solubility

Marschner et al. (1995) added 3% brown coal (on weight basis), 3% brown coal in combination with 3% lime and 3% lime to a sewage sludge amended humic sandy soil in a pot experiment. The soil was polluted with Cu, Zn and Cd. Table 3.24 shows the effects of the treatments on pH, CEC and organic matter content, and the water-extractable Cu, Zn and Cd contents. Brown coal without lime slightly decreased pH, due to its low pH of 4.9 (Karczewska et al., 1996). Brown coal in combination with lime increased both the pH and CEC. The organic matter content of the brown coal treated soils only increased by about 14-17%. Brown coal with lime lowered the water extractable Zn and Cd contents by about 55-80%, the water extractable Cu content by 30%. Zn and Cd immobilization was at least partly due to a pH effect, because the organic matter content only slightly increased, and liming decreased the water extractable Zn and Cd contents to a similar extent. Additional laboratory and field experiments should be conducted to test whether a higher dosage of brown coal would be more effective for immobilizing heavy metals in soil. However, based on the results of Marschner et al. (1995), other techniques increasing the total sorption capacity of soil may have more potential for treating heavy metal polluted soils.

Table 3.24.   Effects of treatments on pH, CEC (cmol$_c$ kg^{-1}), organic matter (o.m.) content (%), and water-extractable heavy metal contents (mg kg^{-1} on dry weight basis) (Marschner et al., 1995).

treatment	pH	CEC	o.m.	Cu	Zn	Cd
control	5.3	16	4.2	0.165	0.16	0.08
brown coal	5.2	16	4.9	0.164	0.76	0.083
brown coal with lime	6.0	18	4.8	0.111	0.07	0.035
lime	6.2	17	4.2	0.110	0.94	0.032

4. Summary

Several *in situ* techniques have been developed for immobilizing heavy metals in soil. Only a few of these techniques significantly decreased the water- and $NaNO_3$-extractable heavy metal contents, and therefore, the relative risks of heavy metal toxicity and leaching. Whether this decrease is considered sufficient depends on the total heavy metal content of a soil, and the concentration in the soil solution. Thus, a few techniques can have potential for reducing the risks imposed by soil polluted with heavy metals. The majority of the techniques outlined here only have been tested in laboratory experiments. Results of heavy metal concentrations in the solutions of polluted soils under field conditions are virtually lacking. Beringite has been used for the remediation of a bare industrial site heavily polluted with Cu, Zn, Cd and Pb. The addition of beringite with compost successfully restored a vegetation cover, thereby decreasing the risks of heavy metal transport to the surrounding ecosystem. Al- or Al_{13}-montmorillonite and Mn-oxide effectively immobilized Ni, Cu, Zn, Cd and Pb in laboratory experiments. Here field experiments have not yet been conducted, which can provide the knowledge necessary for a successful application in practice.

Techniques, which aim at an increase of the total sorption capacity of the soil, can have potential for *in situ* treatment of heavy metal polluted soil. They are summarized in table 4.1. However, additional laboratory and field experiments should be conducted to test the effectiveness and durability of immobilization.

Table 4.1.   *In situ* immobilization techniques exhibiting potential for the treatment of soil polluted with heavy metals in The Netherlands.

technique	metal	pH
Al- or Al_{13}-montmorillonite with lime Mn-oxide with lime	Ni	3-6
Al- or Al_{13}-montmorillonite Mn-oxide	Ni	>6
Al- or Al_{13}-montmorillonite Mn-oxide	Cu	4.5-6
beringite with compost Al- or Al_{13}-montmorillonite with lime Mn-oxide with lime	Zn, Cd and Pb	3-6
beringite with compost Al- or Al_{13}-montmorillonite Mn-oxide	Zn, Cd and Pb	>6

Appendix: Review of recent literature on heavy metal immobilization in soils

Al- or Al13-montmorillonite and Mn-oxide can be used for immobilizing Ni. At pH <6, they should to be used together with lime. In acidic soils, the solution concentrations of heavy metals can hardly be decreased without increasing the pH. Al- or Al13-montmorillonite and Mn-oxide can be used for immobilizing Cu. However, Cu has to be immobilized at pH 4.5-6. At higher pH values, Cu may be mobilized by complexation to DOC. Beringite with compost, Al- or Al13-montmorillonite and Mn-oxide can be used for immobilizing Zn, Cd and Pb. In acidic soil, the latter two techniques would have to be used together with lime. Manganese oxide can only be used in aerated soil, because it dissolves under reducing conditions.

Techniques such as gravel sludge and brown coal, and techniques aiming to decrease the heavy metal concentration in the soil solution by increasing pH and/or causing precipitation, such as lime, phosphate and olivine, have less potential. Gravel sludge and brown coal only moderately decreased the extractable heavy metal contents in soil. Gravel sludge contained by itself already considerable amounts of heavy metals, which reduces its acceptance as an additive. Additional experiments should be conducted with brown coal in order to find out whether a higher dosage of brown coal would be more effective for the immobilization of heavy metals in the soil. Liming only increases the affinity of sorption sites, which may not always be sufficient for immobilizing all heavy metals in the soil solution. The addition of phosphate to Pb polluted sites for forming slightly soluble Pb phosphate minerals would result in a high phosphate concentration in the soil solution. A high phosphate concentration in the soil solution may increase the risk of eutrophication of surface waters by leaching.

This would be unacceptable in The Netherlands. Olivine buffers the pH only in the acid range, not decreasing the risks of heavy metal toxicity and leaching sufficiently. However, the potential of olivine to stabilize the natural acidity in sandy nature areas, preventing Al phytotoxicity and leaching, should be further studied.

Thus, the most promising immobilizing additives for remediating soils polluted with heavy metals are beringite together with compost, Al- or Al13-montmorillonite and Mn-oxide (in acidic soil, the latter two techniques together with lime) (table 4.1).