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Waste Materials in Construction: Putting Theory into Practice

Immobilisation of heavy metals in contaminated soils by thermal treatment at intermediate temperatures

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Abstract

Thermal treatment at intermediate temperatures is widely considered as an effective technology to remove organic contaminants from soil by volatilization and/or destruction. Average operating temperatures of commercial soil treatment systems generally vary between 500 and 650°C. Thermal treatment also alters the physical and chemical properties of the soil, and thus affects the leachability of co-contaminants such as heavy metals. In the present study the effects of thermal treatment on heavy metal leaching from soil have been examined. The results presented in this paper and other work suggest that thermal technologies in the intermediate temperature range offer an opportunity to destroy simultaneously organic contaminants and to immobilize heavy metals in soil in one unit operation. However, further work is necessary to determine the capabilities and limitations of these technologies for soils contaminated with both heavy metals and organic pollutants. The results of this study seem to justify emphasis on the role of iron and clay minerals in thermally treated soil and on the conditions of thermal treatment which affect the behaviour of these constituents in soils.

1. INTRODUCTION

Thermal treatment in a rotary kiln at intermediate temperatures is widely considered as an effective technology to remove organic contaminants from soils by volatilization and/or destruction. In the Netherlands about 1,000,000 tonnes/year of contaminated soil is thermally treated. Thermal treatment also alters the physical and chemical properties of the soil and thus may affect the leachability of co-contaminants like heavy metals. At present, there is a lack of knowledge on heavy metal leaching from thermally treated soil and its relation with soil characteristics and operating conditions.

Average operating temperatures of thermal soil treatment plants vary between 500 and 650°C. At these temperatures heavy metals remain in the soil except for mercury. This heavy metal is removed from the soil during thermal treatment by volatilization (Van Hasselt, pers. comm.). Modern thermal soil treatment plants are equipped with flue gas treatment to meet stringent air pollution standards (Van Hasselt, 1996). In the kiln the soil is usually directly heated by a gas burner. The atmosphere in the kiln is generally reducing (Van Hasselt, pers. comm.). Once the pre-selected temperature has been reached, it is held only a few minutes and then drops to a temperature just below 100°C. In this cooling step the hot treated soil is quenched either with water or indirect with water and air. The treated soil is kept in storage in a stockpile during several days to several weeks. During storage the temperature may increase slightly due to exothermic weathering reactions.

Recent research has indicated that heavy metals exhibit a lower leachability in soils after thermal treatment at intermediate temperatures than the original untreated materials. Eddings and co-workers (1994) have revealed that a significant fraction of cadmium, chromium, and lead reacts with the glassy aluminosilicates during thermal treatment of montmorillonite clay at a temperature of 650 to 980°C to form compounds that are extractable only by HF digestion techniques. At lower temperatures (150 to 500°C) Wei (1995) has demonstrated that soils spiked with cadmium and lead after treatment in bench-scale thermal experiments generate lower TCLP leachate concentrations than the untreated soil. They also observed that an increase in thermal treatment temperature enhanced immobilisation of these metals.

In the present experimental study the effects of thermal treatment at intermediate temperatures on heavy metal leaching from soils have been examined using petrographical and chemical techniques, electron microscopy, and leaching tests. Essential features of the thermal alteration products are emphasized, along with their effect on the soil leaching properties. For comparison, leaching data derived from soils before and after treatment in Dutch thermal soil treatment plants are reported. These data have been accumulated by the authors in the last three years as part of a larger study on the leaching behaviour of contaminated soils, which is reported elsewhere (Heynen *et al.*, 1997).

2. MATERIALS AND METHODS

A series of laboratory experiments were performed in which three different soil types were heated with different residence times and temperatures, ranging from respectively 10 to 30 min. and from 550 to 750°C (abbreviated hereafter as min/°C). Differential thermal analysis (DTA), X-ray diffraction (XRD), selective extractions, and electron microscopy were used to obtain information on thermal alteration products and heavy metal distribution. Other important properties as allophane content and cation exchange capacity (CEC) of the untreated and treated materials were included as well. Heavy metal leaching was determined using a column test (Dutch standard NEN 7343). The experimental results were compared with data derived from full-scale treatments.

Materials

Three (air-dried) soil samples were used in the experimental study: (i) a residue from wet soil treatment (sample I), (ii) a clayey soil sample (sample II), and (iii) a fine loamy soil sample (sample III). The residue from wet soil treatment used in this study comprises the <63 μm fraction of a contaminated soil separated by means of a wet mechanical separation method in a soil washing plant. The soil samples were selected to cover a wide range of physical and chemical properties. Physical and chemical properties of the soil samples are listed in Table 1.

Thermal experiments

The thermal experiments were carried out in an electrically heated ceramic laboratory furnace. The temperature of the furnace was adjusted using a thermocouple which was placed in the centre of the furnace. When the test temperature was reached, crucibles filled with about 2 kg of air-dried material were introduced into the centre of the hot furnace. No attempt was made to determine the amount of metal volatilization during the treatment. Loss of heavy metals by volatilization for all thermal experiments was expected to be less than 5% (Wei, 1995). The heated material was subsequently quenched with air. After cooling the treated samples were rewetted to approximately their original moisture content. Finally, the samples were cured in a climate room at 28°C during three weeks to simulate the weathering conditions during storage in a stockpile. The samples lost about 6 to 13% of their original total weight due to the thermal treatment.

DTA, XRD, CEC, and allophane content

Differential thermal analysis (DTA) was used to study under controlled conditions the thermal changes and reactions in the samples which occur in the temperature range between 80 and 750°C. The untreated samples were heated at a rate of 10°C/min together with thermally inert alumina. The temperature differentials between the sample and the alumina indicate physical and chemical processes occurring in the soil. The reactions are typically graphed from an arbitrary base line as a function of the temperature. Exothermic reactions show upward curves and endothermic reactions downward curves from the baseline. Mineralogical properties of the clay minerals in the < 2 μm fraction of the untreated and thermally treated samples were studied by (well-oriented) X-ray diffraction (XRD). Cation exchange capacity and allophane content of the untreated and thermally treated samples were determined according to Mizota and Van Reeuwijk (1989).

Table 1. Physical and chemical properties of the untreated samples (in % (w/w)).

	sample I	sample II	sample III
SiO_2	53.75	56.13	82.88
TiO_2	0.7	0.84	0.31
Al_2O_3	11.05	13.3	4.17
Fe_2O_3	5.75	6.03	2.14
MnO	0.11	0.1	0.02
MgO	1.76	2.26	0.35
CaO	6.87	5.58	1.49
Na_2O	0.7	0.49	0.38
K_2O	1.95	2.4	1.18
P_2O_5	0.29	0.22	0.07
BaO	0.05	0.03	0.04
LOI	16.9	12.00	5.6
sum	99.88	99.39	98.63
As*	23	12	5.4
Cd*	2.2	<0.1	3.5
Cr*	51	35	24
Cu*	120	13	1,700
Pb*	870	24	2,000
Ni*	41	25	26
Zn*	750	93	2,300
fraction <63 μm	29	55	3.3
organic matter	12	10	3.9
$CaCO_3$	11	<0.1	1.9
dry matter	52.3	67.5	84.3

LOI loss on ignition
* in mg/kg

Electron microscopy

Advanced electron microscopy equipped with a solid state X-ray detector provides detailed information on alteration features and the distribution of heavy metals in soil and soil-like materials (Bates *et al.*, 1992; Zevenbergen *et al.*, 1996). The untreated and treated sample III (10 min/650°C) were examined using an analytical (transmission) electron microscope (AEM) (JEOL 2010). Sample III was selected for its relatively high heavy metal content (see Table 1). Size-fractionated samples of dried and disaggregated soil were embedded in epoxy and thin-sectioned using an ultramicrotome. The thin sections (>100 nm thick) were examined using brightfield/darkfield imaging, lattice fringe, and surface area electron diffraction (SAED). Compositional trends were determined using energy dispersive x-ray spectroscopy (EDS).

Selective dissolution with oxalate and dithionite

Both oxalate and dithionate dissolution procedures for the extraction of Al and Fe have widely found application in soil classification and in studying soil genesis (Mizota and Van Reeuwijk, 1989). Acid oxalate extraction was used to determine the heavy metal fraction that is associated with the 'active Al' and 'active Fe' components. This includes allophane (amorphous hydrous aluminosilicate), Al- and Fe-humus complexes, and amorphous or poorly ordered oxides such as ferrihydrite (Mizota and Van Reeuwijk,1989). The extraction with dithionite was used to determine the heavy metal fraction that is associated with the so-called 'free iron oxide'. This fraction consists of ferrihydrite and crystalline Fe, such as goethite, hematite, and magnetite particles up to about 50 μm in diameter. The extraction procedures were carried out on sample III.

Leaching test

Column tests were carried out according to NEN 7343. This test is considered to simulate leaching in the short- and medium-term by relating the emission (expressed in mg/kg) to the liquid to solid (L/S in l/kg) ratio and is adopted in Dutch legislation.

3. RESULTS AND DISCUSSION

DTA

The DTA analysis of the three samples shows a first change at temperatures up to 200°C which reflects the loss of pore water, adsorbed water and part of the interlayer and lattice water of the clay minerals. These reactions are endothermic. A large exothermic peak between 200 and 400°C arises in all samples from the oxidation of organic material. As the temperature rises, the chemically combined water within the clay minerals begins to be lost (dehydroxylation). The clay minerals remain intact until a temperature of 450 to 600°C is reached, and then break down into an amorphous mass. All the samples show a continuous loss of water due to dehydration and dehydroxylation of the clay minerals upon heating. As a consequence a distinct endothermic peak cannot be discerned in this temperature range. The small endothermic peak around 570°C marks the inversion of alpha-quartz to beta-quartz. Sample III exhibits an endothermic peak at 740°C presumably due to the dissociation of calcium carbonate in CaO and CO_2 (see Fig. 1).

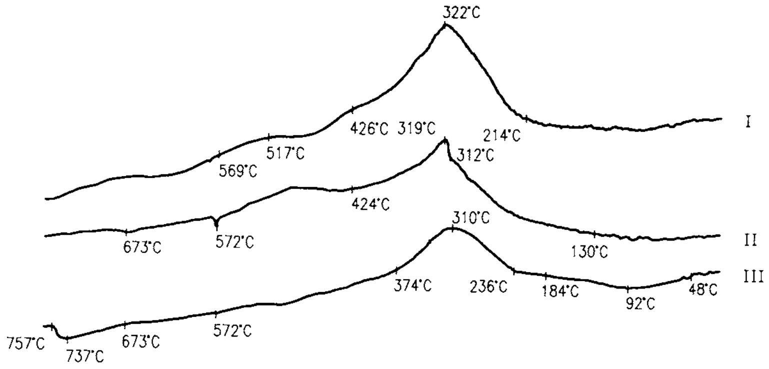

Figure 1. DTA curves for the untreated samples.

Electron microscopy

Comparison of the untreated and treated sample III shows that a significant fraction of the clay minerals has melted (vitrified) during the thermal treatment (see Fig. 2). The melted particles have a porous appearance and Fe appears depleted in these particles. Some of the particles have conserved their original structure, which indicates that they have not been subjected to the pre-set temperature (see Fig. 3). In both samples, the heavy metal content in the clay structures is very low. In the untreated sample the heavy metals are found as major elements in discrete, submicrometer metal, alloys, and primary oxide grains. Occasionally they are found as major constituents in coatings on silicate grains like quartz and clays. The untreated sample also contains abundant grains rich in Fe and O. The major elements in all these grains are O en Fe and their crystal structures range from poorly crystalline to well-ordered polycrystalline grains. The poorly crystalline grains consist of ferrihydrite while the well-ordered grains are hematite. Admixtures of these two minerals are common and both contain heavy metals (see Fig. 4). Unlike the untreated sample, discrete metal alloys and primary oxide grains are rare in the treated sample. Virtually all the heavy metals found in the treated sample are associated to the Fe and O rich grains. However, the grains are no longer ferrihydrite or hematite but rather magnetite and hematite. Heavy metals are sometimes present as major constituents of Fe-rich grains with the magnetite structure (see Fig. 5). The magnetite is presumably formed during the thermal treatment both from ferrihydrite and from Fe released by the clay minerals, and appears to have incorporated most of the heavy metals into its spinel structure.

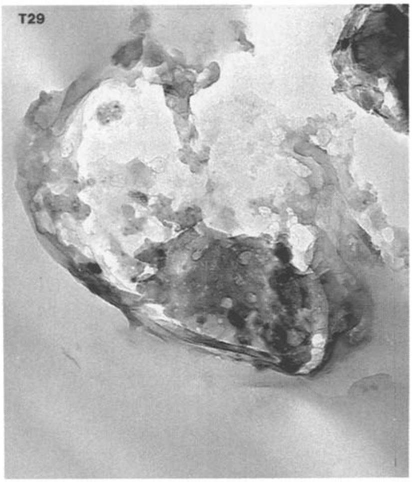

Figure 2. Vesicular melted clay particle clay in the thermally treated sample III (10 min/650°C) (1 cm = 150 nm).

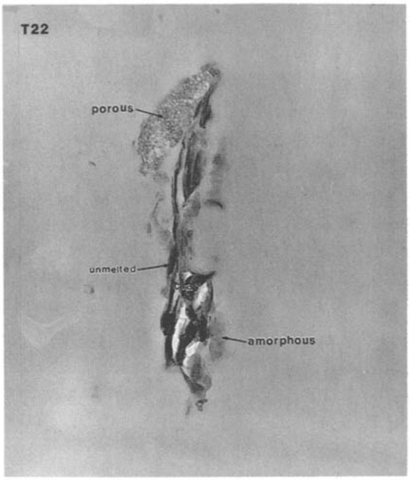

Figure 3. Partially melted clay particle clay in the thermally treated sample III (10 min/650°C) (1 cm = 300 nm).

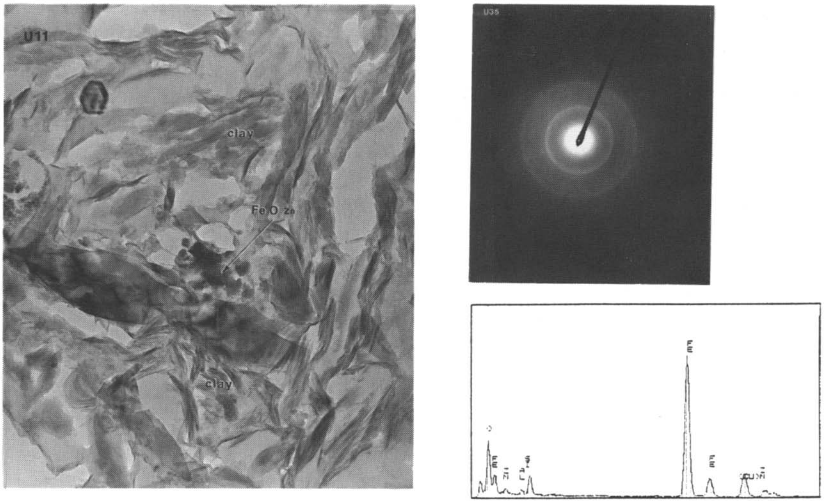

Figure 4. Fe-rich grain embedded in a clay matrix of the untreated sample III. EDS spectrum from the Fe-rich grain indicating that this phase contains Zn (1 cm = 300 nm). Selected area diffraction pattern (SAED) from the Fe-rich grain showing classic ferrihydrite diffraction characteristics.

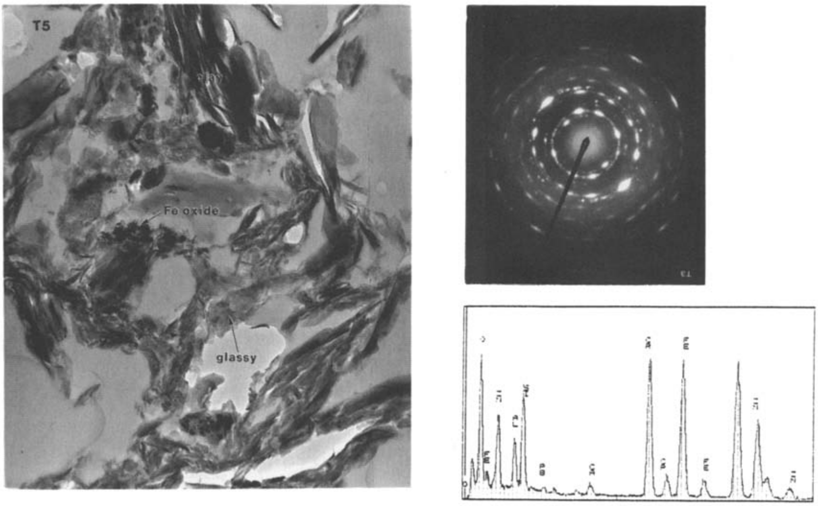

Figure 5. Well-ordered clay and partly 'vitrified' clay in the thermally treated sample III (10 min/650°C) (1 cm = 300 nm). The SAED pattern from the Fe-rich grain is consistent with the lattice spacings of magnetite. The EDS spectrum reveals that this Fe-rich grain is enriched with heavy metals.

Mineralogy, cation exchange capacity and allophane content

Results of the X-ray diffraction analysis, cation exchange capacity and allophane content determination are summarized in Table 2. The X-ray diffraction results suggest that during the thermal treatment the bulk of the clay minerals are decomposed resulting in the formation of more poorly ordered structures. In general the allophane content increases as the temperature and/or residence time increases, which indicates that the decomposition of the clay minerals is not yet fully completed under the prevailing experimental conditions as mentioned above. This suggestion is consistent with the earlier noted TEM observations. The CEC decrease is mainly a result of the destruction of organic matter.

Table 2. Relative abundance of the clay minerals ($< 2\ \mu m$ fraction), CEC, and allophane content of the untreated and treated samples.

sample	treatment	relative abundance of the clay minerals	CEC (meq/100g)	allophane content (% (w/w))
sample I	untreated	++	29	1.3
	10 min/550°C	+	17	1.2
	30 min/550°C	+/-	13	2.0
	10 min/650°C	-	15	1.5
sample II	untreated	++	48	1.8
	30 min/650°C	-	16	1.2
	10 min/750°C	-	18	1.8
	30 min/750°C	-	12	3.8
sample III	untreated	++	6	0.6
	10 min/650°C	-	2	1.2
	30 min/650°C	-	2	1.5
	30 min/750°C	-	2	3.0

++ = abundant (> 10%); + = moderate (5-10 %); +/- = traces (5%); - = non detectable (< 5%)

Selective dissolution with oxalate and dithionite

The results of the selective dissolution experiments are given in Figure 6. The results indicate that the dithionite extractable heavy metals fraction and to a lesser extent the oxalate extractable fraction are affected by the thermal treatment. The dithionite extractable heavy metal fraction is in general significantly higher in the thermally treated samples than in the untreated sample. Moreover, the dithionite extractable heavy metal fraction generally increases when the samples are treated at longer residence times. With the exception of Cu, a relatively small amount of the heavy metals, compared to the amount released in the dithionite extraction, is extracted in the oxalate extraction. The increase of the dithionite extractable heavy metal fraction after thermal treatment most likely results from the transformation of amorphous iron hydroxides to more crystalline forms. This conclusion is consistent with the earlier noted TEM-observations that during the thermal treatment a significant fraction of these metals is scavenged by magnetite structures. In addition, the results reveal that Cu and to a lesser extent Cd, Pb, and Zn are also retained by thermal decomposition products of the clay minerals (allophane-like materials). Along similar lines, compositional mapping using electron microscopy recently indicated that these heavy metals were incorporated into newly formed hydrous aluminosilicate rims on glassy grains of weathered municipal solid waste incinerator ash (Zevenbergen *et al.*, 1996 and references therein). In conclusion, the formation of magnetite and allophane-like materials may significantly reduce leaching of those metals from thermally treated soil.

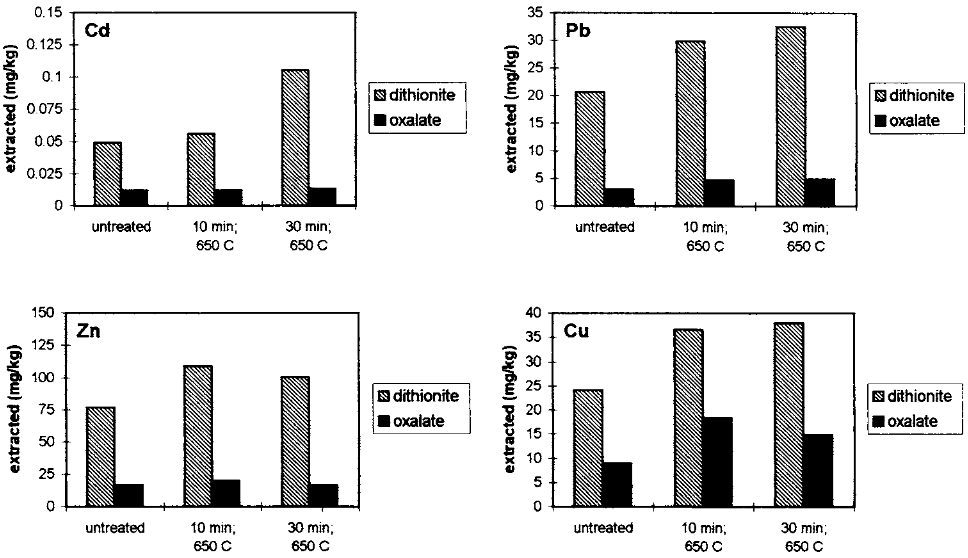

Figure 6. Amount of dithionite and oxalate extractable heavy metals (in mg/kg) from the untreated and the thermally treated sample III (10 min/650°C).

Leach testing

Figure 7 summarizes the column test results derived form the untreated and treated samples. The results are presented as cumulative emission (mg/kg) at a L/S ratio of 10. As the temperature and/or residence time increase, the emission of the heavy metals generally decreases. This effect is most obvious for Cd, Cu, Pb, Ni, and Zn. As exhibits no systematic trend. In sample I a longer treatment time seems to enhance the leachability of this oxyanion, while the reverse is observed in samples II and III. The leachability of Cr appears to be slightly affected by the thermal treatment with the exception of the sample which has been treated at the highest temperature and longest residence time (sample II, 30 min/750°C). In this sample the leachability of Cr is significantly higher than in the untreated sample.

For comparison, CEC, pH, and leaching data of As, Cr, Cu, Ni, Pb, and Zn derived from different soils before and after treatment in thermal soil cleaning plants (closed symbols) are plotted together with the experimental results (open symbols) in Figure 8. These results reveal that the pH generally increases from values around 8 to values around 10, while the CEC decreases after thermal treatment. Both alterations are probably a result of the removal of organic matter by thermal destruction. The leaching data derived from the samples which have been treated in the thermal treatment plants are consistent with the above reported experimental leaching data.

Recent studies have revealed that the leachability of heavy metals like Zn, Cd, Pb, and Cu from thermal residues (e.g. coal fly ash and MSWI ashes) and contaminated soils typically attains a minimum value in the pH range between 7 and 10 (Van der Sloot, 1996; Meima and Comans, 1997). Since the pH of both untreated and thermally treated soils roughly coincides with this pH-range, it is not likely to assume that the observed decrease in leachability of these contaminants after thermal treatment is exclusively due to a pH-effect.

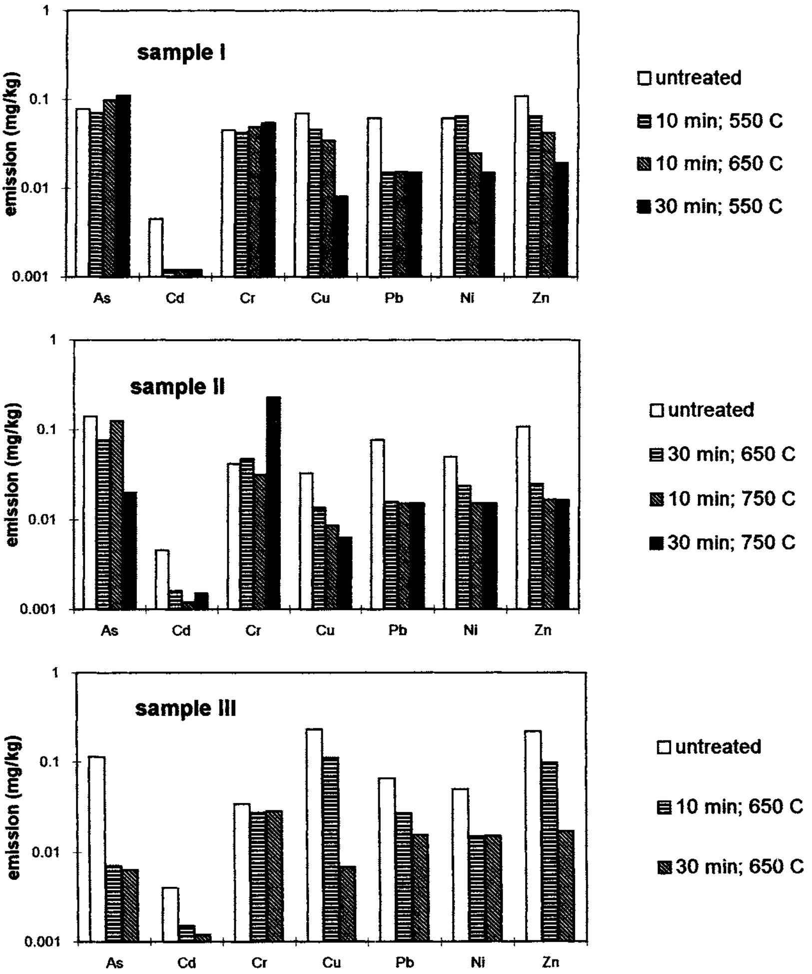

Figure 7. Leachability (cumulative emission at L/S = 10 in mg/kg) of heavy metals from the untreated and thermally treated samples.

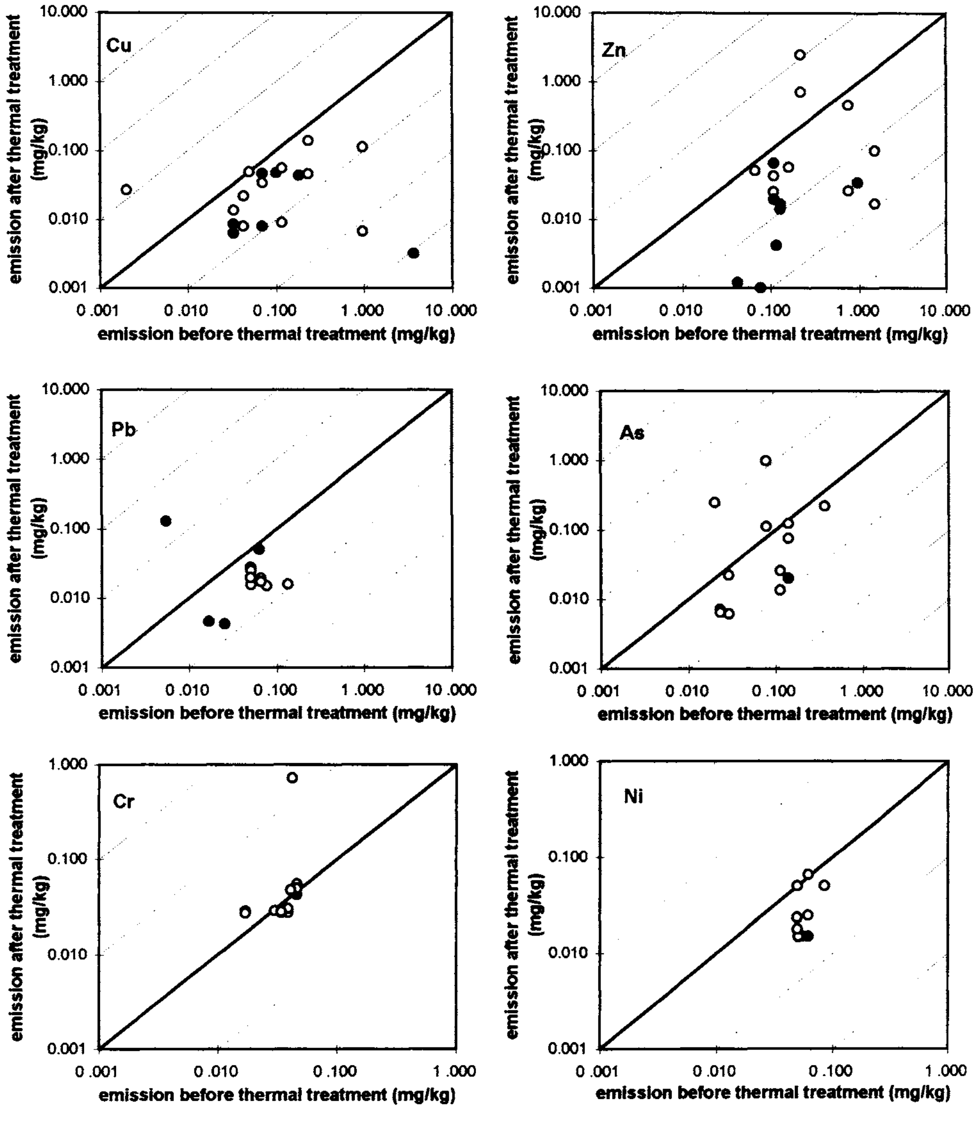

Figure 8. CEC (meq/100g), pH and leachability of As, Cd, Cr, Cu, Ni, and Zn (cumulative emission at L/S = 10 in mg/kg) before and after thermal treatment (open symbols = thermal experiments; closed symbols = soil thermal treatment plants).

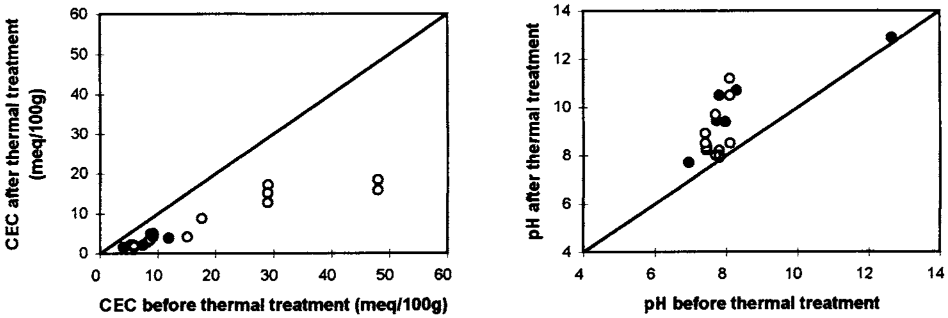

Figure 8. Continued

4. CONCLUSIONS

Recent research has revealed that heavy metals exhibit a lower leachability in soils after thermal treatment at intermediate (550 to 750°C) temperatures than the original materials. Our experimental data are consistent with these observations. However, we also observed that thermal treatment had little or even an inverse effect on the leachability of As and Cr.

The experimental data reveal that thermal treatment results in a drastic change of the mineralogical an chemical nature of the soil. The thermal alterations which may contribute to the observed decrease in leachability of these heavy metals are:

- an increase of the pH;
- formation of crystalline magnetite structures from ferrihydrite and from Fe expelled by the clay minerals during the treatment. These magnetite structures appear to have scavenged heavy metals during the treatment;
- formation of reactive, amorphous aluminosilicates from clays.

It should be noted that the pH of thermally treated soil will gradually decrease to approximately its original pH due to weathering and accumulation of organic matter. At present, it is unknown to what extent these processes will affect the leachability of these heavy metals. Further study is needed to assess the effects of weathering on leaching behaviour of thermally treated soils on the longer term.

The results presented in this paper and other work suggest that thermal technologies in the intermediate temperature range (500 - 650°C) offer an opportunity to simultaneously destroy organic contaminants and to immobilize heavy metals in soils in one unit operation. However, further work is necessary to determine the capabilities and limitations of these technologies for soils contaminated with both heavy metals and organic pollutants. The results of this study seem to justify emphasis on the role of iron and clay minerals in thermally treated soil and on the conditions of thermal treatment which affect the behaviour of these constituents in soils.

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