

The Release of Heavy Metals in Stabilized MSW by Oxidation

Final Report

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1. Introduction

Many substances in municipal solid waste (MSW) are not stable under natural conditions and especially not in contact with water. During the stabilisation process, reactive substances will be broken down or dissolved. Mobile reaction products will be removed by erosion or synthesised into new more stable solid phases. In natural soil systems, secondary minerals such as clay minerals, carbonates, oxyhydroxides and sulphides are formed together with new organic molecules. Stabilised waste would hence contain a mixture of resistant primary substances, degradation products and synthesised solid phases of organic and inorganic matter. Secondary minerals are often reactive, amorphous and metastable phases and therefore sensitive to changing environmental conditions, such as pH and the redox potential. They often cover other particles together with organic matter and are considered as powerful adsorbents due to a large specific surface area (m^2/kg) and active adsorption sites on their surface. Heavy metals are also affected by the stabilisation process and secondary solid phases often act as scavengers of heavy metals released. Important scavenging reactions are precipitation, co-precipitation and adsorption.

During the stabilisation of MSW under reduced conditions, only a small proportion of the content of heavy metals in the waste is removed by erosion (leaching). However, results presented by Flyhammar (1997) indicate that heavy metals are transformed to oxidizable solid phases, such as sulphides and organic matter, which are stable under the prevailing conditions. However, the solubility of these phases and associated heavy metal can increase due to changing redox conditions.

During the oxidation of anaerobically stabilised waste, reactive secondary solid phases can be expected to degrade or dissolve while heavy metals are released. A high solubility of the metals can be maintained under acid conditions or by the formation of complexing ligands such as organic compounds resulting from redox reactions. The impact of acid conditions on the solubility of heavy metals during oxidation experiments carried out on sediments from anoxic environments is demonstrated by Calmano et al. (1993). However, during acid conditions, the formation of anionic complexes could decrease the solubility due to adsorption. Under certain conditions, the oxidation of waste can trigger a chemical time bomb (CTB), which is considered to be “a chain of events resulting in the delayed and sudden occurrence of harmful effects due to mobilisation of chemicals stored in soils and sediments in response to slow alterations of the environment” (Stigliani, 1991).

The aim of this study was to study the effects on heavy metals in partly anaerobically stabilised MSW during the exposure to air. Two experiments were carried out during 7 and 15 days, respectively. It was assumed that oxygen would react with at least the most reactive phases of the sulphides and the organic matter. Therefore, the experiment will simulate the most rapid reactions following the exposure of partly stabilised MSW to air, which might be of interest in connection with human action, such as landfill mining.

2. Solubility of heavy metals

The leaching of heavy metals can be controlled by the solubility or by rate limiting dissolution and diffusion processes. The solubility of heavy metals is mainly controlled by pH, the redox conditions and the concentration of salts and complexing agents in the leachate (i.e. Förstner and Salomons, 1991). However, the mineralogy of the waste is also important for the leaching, since different mineral phases have different solubilities and reaction kinetics (Bäverman, 1997). If the transport of an element away from the reaction or mixing zone is larger than the release from the porous solid waste, the leaching process will be controlled by dissolution processes and the diffusion in micropores.

In the absence of major interactions between metals and organic matter, low pH and moderate to high redox conditions are most favourable for the solubilization of many heavy metals in systems containing sufficient supply of sulphur. However, if the content of sulphur is low, anaerobic conditions tend to induce high solubility (Bourg and Loch, 1995). In waste containing large quantities of organic matter, such as MSW, organic substances also have to be considered. The interaction of metals with organic compounds can both increase and decrease the solubility depending on if the compounds are mobile or not.

Anaerobic and neutral conditions that prevail in organic waste (MSW) during the methanogenic degradation phase would not induce high solubility of cationic heavy metals. Exceptions can be found among anionic ions and molecules such as As^- , CrO_4^{2-} , etc. However, deviations from expected concentrations can occur due to complexation with dissolved agents, binding to colloids or particles (no filtered samples). The concentrations of heavy metals in leachate from Swedish municipal landfills (Öman et al., 1998; Flyhammar, 1995) are often found within one order of magnitude above the lower level for increased concentrations in natural surface waters (SNV, 1993). There are also indications of that anaerobic stabilisation processes will induce changes of heavy metal binding forms in deposited MSW (Flyhammar, 1997). During this transformation, the heavy metals become less sensitive to acid conditions due to associations with sulphides and organic matter, but they might be released by oxidation reactions. However, secondary minerals such as acid volatile sulphides (AVS) are dissolved by weak acids. Aulin et al. (1997) assumes that heavy metals in MSW will be retained by sulphides and humic substances (HS) during anaerobic conditions. It was estimated that the binding capacity of humic substances is one tenth of all HS binding metals and about five times that of all toxic metals (Cd, Cr, Zn, Pb and Hg) if 30 % of the organic waste remained as humic substances. Sulphides, on the other hand, can only bind twice the amount of all toxic metal even if all sulphur in the waste is reduced and precipitated as sulphide. The binding capacity of hydrous ferric oxides, which can be formed by oxidation reactions during the humic phase succeeding the methanogenic degradation phase, is estimated to be three times the total content of metals that are assumed to be sorbed on hydrous ferric oxides. However, sorbed metals can be released during the crystallisation of ferric iron hydroxides (Aulin et al., 1997).

Processes that control the proton balance and pH are (Bourg and Loch, 1995)

- processes that supply protons
- processes that consume protons
- amphoteric processes
- production of biomass/respiration of biomass

Protons can be supplied by atmospheric depositions and oxidation reactions (Table 1). Alkalinity and pH tend to increase during reduction and decrease during oxidation, since oxidised components are more acidic or less basic than their reduced counterparts (Bourg and Loch, 1995). Most oxidations of organic carbon result in a net release of CO₂, which will force the pH to decrease in a system that is not in equilibrium with the atmosphere (Förstner, 1995). All acid generating processes will contribute to the acid production capacity (APC) of the system.

Table 1. Acid producing redox reactions (Calmano et al., 1993).

Elements		Reactions
Inorganic	S	$\text{H}_2\text{S} + 2 \text{O}_2 = \text{SO}_4^{2-} + 2 \text{H}^+$
	S	$\text{S} + 3/2 \text{O}_2 + \text{H}_2\text{O} = \text{SO}_4^{2-} + 2 \text{H}^+$
	S,Fe	$\text{FeS} + 9/4 \text{O}_2 + 3/2 \text{H}_2\text{O} = \text{FeOOH} + \text{SO}_4^{2-} + 2 \text{H}^+$
	S,Fe	$\text{FeS}_2 + 15/4 \text{O}_2 + 5/2 \text{H}_2\text{O} = \text{FeOOH} + 2 \text{SO}_4^{2-} + 4 \text{H}^+$
	Fe	$\text{Fe}^{2+} + 1/4 \text{O}_2 + 5/2 \text{H}_2\text{O} = \text{Fe}(\text{OH})_3 + 2 \text{H}^+$
	N	$\text{NH}_4^+ + 2 \text{O}_2 = \text{NO}_3^- + \text{H}_2\text{O} + 2 \text{H}^+$
Organic	N	$\text{NO}_x + 1/4(5-2x) \text{O}_2 + 1/2 \text{H}_2\text{O} = \text{NO}_3^- + \text{H}^+$
	N	$\text{R-NH}_2 + 2 \text{O}_2 = \text{R-OH} + \text{NO}_3^- + \text{H}^+$
	S	$\text{R-SH} + \text{H}_2\text{O} + 2 \text{O}_2 = \text{R-OH} + \text{SO}_4^{2-} + 2 \text{H}^+$

Several heterogeneous reactions (Table 2) consume protons and efficiently buffer the pH of natural water systems. Other proton consuming reactions are reduction reactions, such as denitrification, sulphate reduction and iron oxide reduction (Bourg and Loch, 1995; Heron et al., 1993). Initially the pH in a solution decreases when protons are added. After the dissolution of the buffering substance a new equilibrium is established, which reduces the pH shift which would take place in absence of the buffering substance. Carbonate solids are efficient buffers in the neutral to basic pH range (pH > 6.2) and they will buffer the system as long as carbonate solids are available for dissolution. When a buffer substance is depleted, added protons decrease the pH until the dissolution of a new solid phase start to consume the protons added, which will prevent a further drop of the pH. Dissolved hydrogen ions can also be removed from the solution by ion exchange reactions.

Table 2. Acid buffering reactions in natural systems (Calmano et al., 1993, Bourg and Loch, 1995; Förstner, 1995).

Reaction
$\text{CaCO}_3 + 2 \text{H}^+ \rightarrow \text{Ca}^{2+} + \text{H}_2\text{O} + \text{CO}_2$
$\text{primary rock mineral} + 2 \text{H}^+ + \text{H}_2\text{O} \rightarrow \text{cations} + \text{H}_4\text{SiO}_4 + \text{secondary minerals}$
$\text{Al}_2\text{O}_3 + 6 \text{H}^+ \rightarrow 2 \text{Al}^{3+} + 3 \text{H}_2\text{O}$
$\text{Fe}_2\text{O}_3 + 6 \text{H}^+ \rightarrow 2 \text{Fe}^{3+} + 3 \text{H}_2\text{O}$
$\text{SO}=\text{Me} + \text{H}^+ \rightarrow \text{SO}=\text{H}_2 + \text{Me}^{2+}$

The oxidants will be used in a predictable sequence (Figure 1) which is based on their ease of reduction which can be represented by the free energy of their reduction (Reddy et al., 1987). However, if oxygen is supplied to the system, the degradation returns to aerobic respiration. Other effects of redox reactions under oxic conditions are the production of protons (Table 1) and potential to produce soluble organic complexing agents.

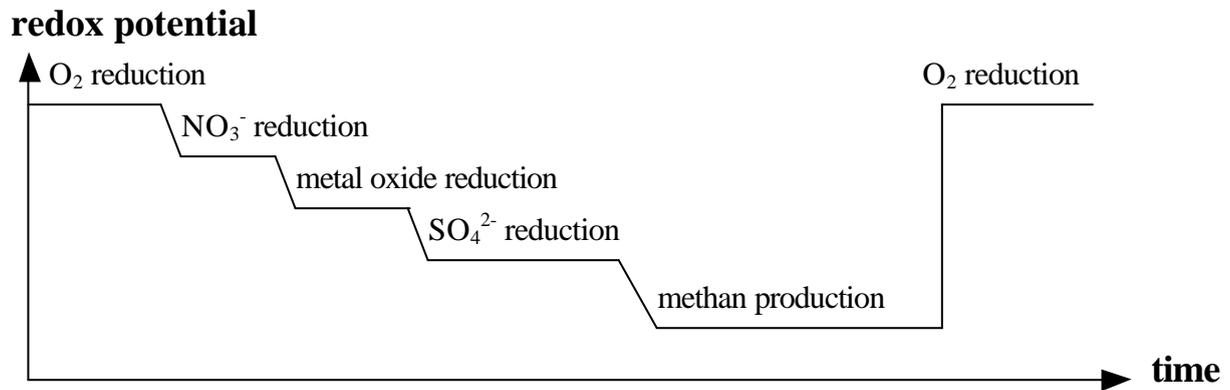


Figure 1. Redox reactions (Förstner, 1995; Meyer et al., 1994).

3. Material and analysing methods

The waste used in our experiments has earlier been extensively described in Flyhammar et al. (1998). In 1973 the waste, consisting of a mixture of shredded MSW and sewage sludge (5 % dry substance), was deposited in a testcell (approximately 145 tons dry substance). The cell was used in leachate recycling experiments during 1974-75. In the late 1970s, the cell and the surrounding landfill area were covered by 1 m of clay. As a result, the water table rises and the movements of water within the cell become much lower and the waste was water saturated during long periods of time. Solid samples were collected at two occasions between 1993 and 1995. Each samples (approximately 0.1 - 1.0 kg wet substance) was collected and transported with minimum exposure to air and then stored frozen until the time for analysis (Persson and Rylander, 1977; Flyhammar et al., 1998). Some of these samples have been used in the experiments.

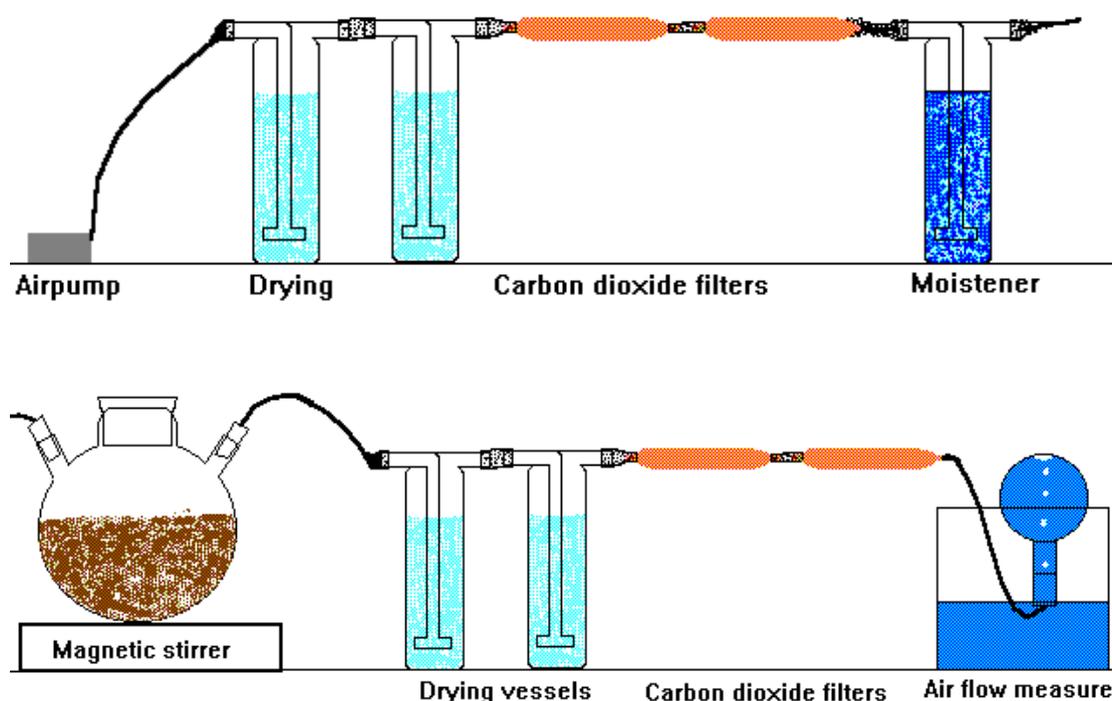


Figure 2. Configuration of the experiments.

The configuration of the experiments is presented in figure 2. Air containing oxygen was pumped into the system with an aquarium pump. The air first passed through two bottles filled with bluegel to dry the air. Then it passed two filters filled with ascarite (sodium hydroxide) to adsorb carbon dioxide in the air. The air was then bubbled through deionised water, in order to moisten the air to minimize evaporation from the samples. The sample was put in a retort with three openings. The sample was continuously stirred with a magnetic stirrer and the air above the sample was continuously exchanged with the carbon dioxide free air stream. The air passing the retort then flowed through two tubes filled with ascarite that would absorb the carbon dioxide evolved in the sample retort. After passage a tentative measurement of airflow was done.

When the experiment started the sample consisted of 400 ml of deionised water and approximately 40 g of moist waste material, corresponding to 20 g of dry substance. At different points of time, the airflow was stopped and pH was measured, magnetic stirring was stopped and redox potential was measured. A portion of the water in the sample retort (200 ml) was taken from the retort and replaced with the same amount of fresh deionised water. The sampled water was filtered through acid washed filters (0,45 μm) with an acid washed Teflon filtering device. The solid material obtained on the filter was put back into the retort. The weight of the carbon dioxide traps was registered. The bluegel was exchanged and dried when it was needed, about twice a day. One sample bottle was saved for analysis of sulfate, TOC (total organic carbon), TC (total carbon) and total nitrogen. One bottle was preserved with HNO_3 for analysis of metals.

Table 3. Data (accumulated L/S ratio and leaching time) from Ex. 1 and Ex. 2.

Time (hour and days)											
Ex. 1	0.5 h	3 h	6 h	1 day	2 days	3 days	5 days	6 days	8 days	10 days	15 days
Ex. 2	0.5 h	6 h	1 day	2 days	3 days	4 days	7 days				
L/S (kg water/kg dry waste)											
Ex. 1	24	35	47	59	71	83	94	106	118	130	141
Ex. 2	23		35	47	58	70	77	93			

Two experiments (referred to Ex. 1 and Ex.2 in the following text) were carried out in this study for 7 and 15 days (Table 3), respectively. Water samples were taken out and analyzed at different points and L/S (leachate used (kg)/kg dry waste). The samples were analyzed for pH, Eh, NH_4^+ , TOC, TC, SO_4^{2-} , Ca, Fe(tot), K, Mg, Na, S, Al, As, Ba, Cd, Co, Cr, Cu, Hg, Mn, Ni, Pb and Zn. PH and redox were measured with PHM201 portable pH-meter from MeterLab Radiometer. A standard method was used (SIS 028134) to analyze NH_4^+ , and the other elements were measured by SGAB with ICP-MS, ICP-AES or atomic fluorescens.

Ex. 2 was carried in the same way as Ex. 1 and with the same material, but a small amount of the leachate from Ex. 1, 2 ml from the last subsample, was added to the sample. It was believed that a more efficient oxidative microbial activity thus should develop much faster in this experiment. After sample number 8 was taken out during Ex. 1 the airflow was set to a much lower level. This would still allow atmospheric oxygen pressure to be maintained in the air above the samples, while the removal of water and carbon dioxide would be more efficient. A low airflow was also kept during Ex. 2. Chemical equilibrium or near equilibrium conditions between the leachate and solid waste might not be expected during each leaching steps due to the high L/S ratio and the short leaching time used.

The “total” content of elements in the waste has been measured by chemical extraction with HNO_3 and HCl. The heavy metal binding forms in the solid phase were analysed by using a sequential extraction method (Table 4). This method is based on the method developed by Tessier and co-workers (Tessier et al., 1979), but later modified by Calmano and Förstner (1983) and Calmano (1989). The accuracy of sequential extraction procedures has been

questioned mainly for two reasons, redistribution of metals in the course of the extractions and the poor selectivity of the extraction steps (Kim and Fergusson, 1991). Despite these problems, the method used will give some information of the heavy metals binding forms, since successively stronger reagents are used in sequence. The solvents have also been designed to simulate extreme environmental conditions (Förstner and Salomons, 1991). The non-residual extraction steps used are assumed to dissolve reactive heavy metal binding forms which are susceptible to early diagenetic transformations (Calmano et al., 1993). Sequential extractions were carried on the waste before and after the oxidation experiments and metals in the extraction solutions were analysed by ICP-MS, ICP-AES or atomic fluorescens.

Table 4. Sequential extraction scheme used.

Step	Solvent	Fraction	Target forms
1	(1 M NH ₄ Ac) †	exchangeable and	exchangeable cations
	1 M NaAc (pH 5)	acid soluble	carbonates
			AVS
2	0.01 M NH ₂ OH +	easily reducible	hydroxides of Mn
	0.01 M HNO ₃ (pH 2)		
3	0.1 oxalate buffer (pH 3)	moderately reducible	hydroxides of Fe
4	30 % H ₂ O ₂	Oxidizable	organic matter and sulphides
5	Hot conc. HNO ₂	Residual	less reactive species

†Step 1 in Flyhammar (1997)

4. Results

4.1 Fractions of heavy metals in the solid waste

Tables 5 and 6 show three fractions of heavy metals and other elements in the solid waste; “total” content (dissolved by HNO₃+HCl or by the whole extraction sequence (Σ step 1-5) in Table 4), reactive heavy metal binding forms (Σ step 1-4) and the proportion of the “total” content which was leached during the experiment. The results imply that most heavy metals released by wet chemical extractions can be considered as reactive binding forms. The proportion of heavy metals which are released by the leaching experiments is low (a few percent or less), except for Ni, Co and As. The leachability of elements in tables 5 and 6 decrease in the following order; K,Na > S > Mg > Ca ≥ As ≥ Ni,Co > Mn,Cu,Zn,Cr > Fe,Pb,Cd,Al.

4.2 Leaching experiments

Accumulated leached amounts (mg/kg waste dry substance) of different elements and the concentration (mg/L) of different elements during different leaching steps are presented in figures 3 and 4. The continuous removal of CO₂ produced during the experiments, due to the carbon oxide free air stream, will probably affect the carbonate buffering system and factors such as pH, the concentration of dissolved inorganic carbon and the dissolution of carbonate solids.

During the initial stages (step 1-2, from start until 3-6 hours) soluble species (ions and complexes) and perhaps colloidal fractions were rapidly leached out of the waste. The concentrations of heavy metals may be enhanced by complexation reactions with dissolved organic substances, indicated by TOC, and salts. High values of pH (8.8 - 9.0) were maintained in the solution during this initial stage and the high concentration of inorganic carbon (IC) might be explained by continues dissolution of CO₂ in a buffer solution (1). A possible process controlling the pH might be ion exchange of Na⁺ and K⁺ (2).



(SO: = reaction groups on the solid phase, Me = metal ions)

Between 5 to 6 hours and 1 day after the start of the experiment, the decrease of pH was almost one unity and the concentration of Ca, Mg, Mn and SO₄²⁻ increase several times. During the experiments, it is assumed that the increased leaching of SO₄²⁻ emanates from the oxidation of reactive sulphide phases, such as acid volatile sulphides (AVS) (3). The simultaneous decreasing pH (from approximately 9.0 to approximately 8.0) and increasing concentrations of Ca, Mg and Mn, seem to indicate the dissolution of carbonate solids and neutralisation of protons added (4).





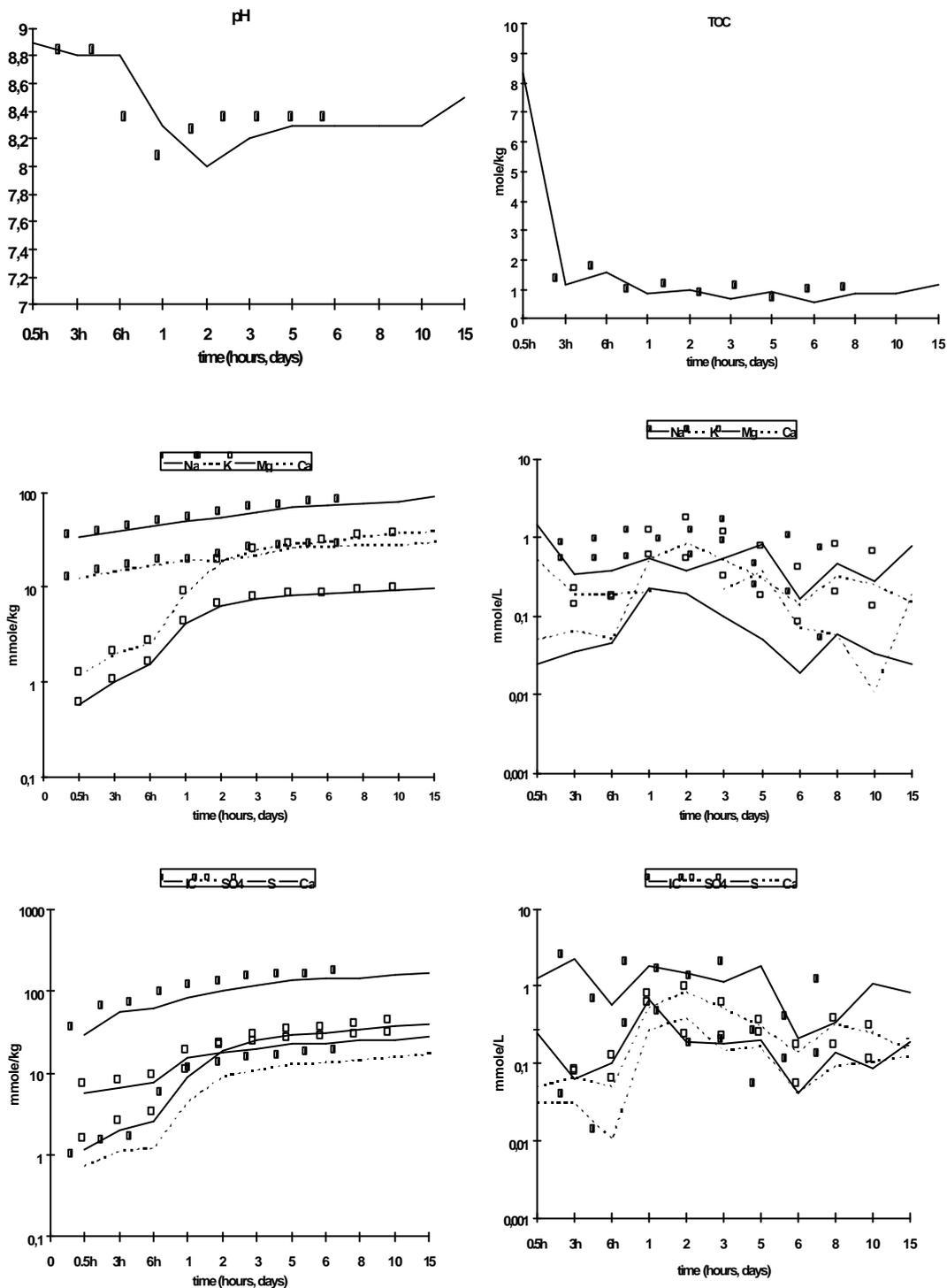


Figure 3. The accumulated leached amount (mole/kg dry substance) and the concentration (mole/L; mg/L (TOC)) in the leachate during different leaching steps of pH, TOC, Na, K, Mg, Ca, inorganic carbon (IC), SO_4^{2-} , S and Ca (Ex. 1).

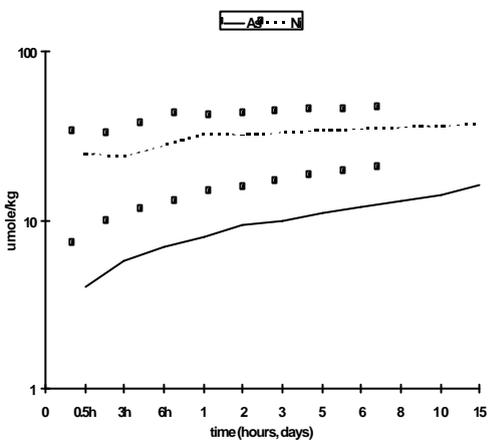
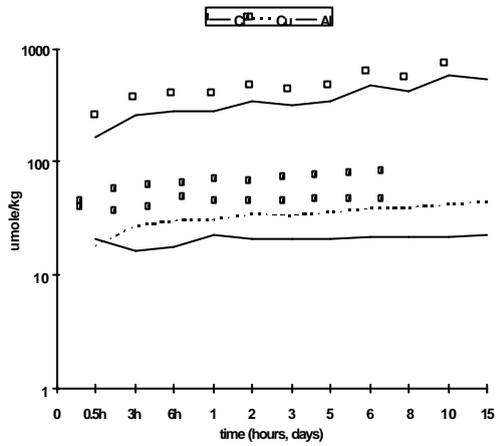
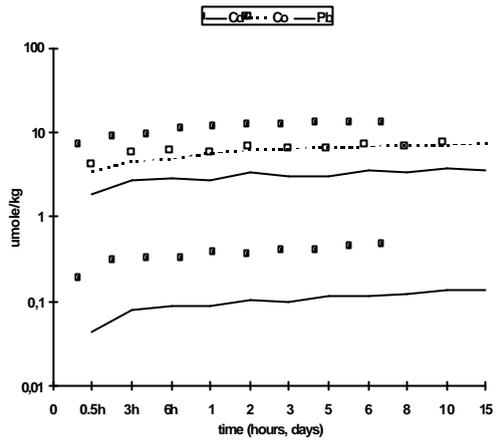
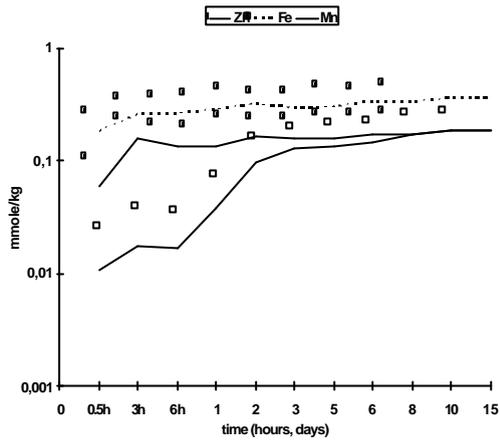


Figure 3. (continue) The accumulated leached amount (mole/kg dry substance) of Zn Fe, Mn, Cd, Co, Cr, Cu, Al, As and Ni (Ex.1).

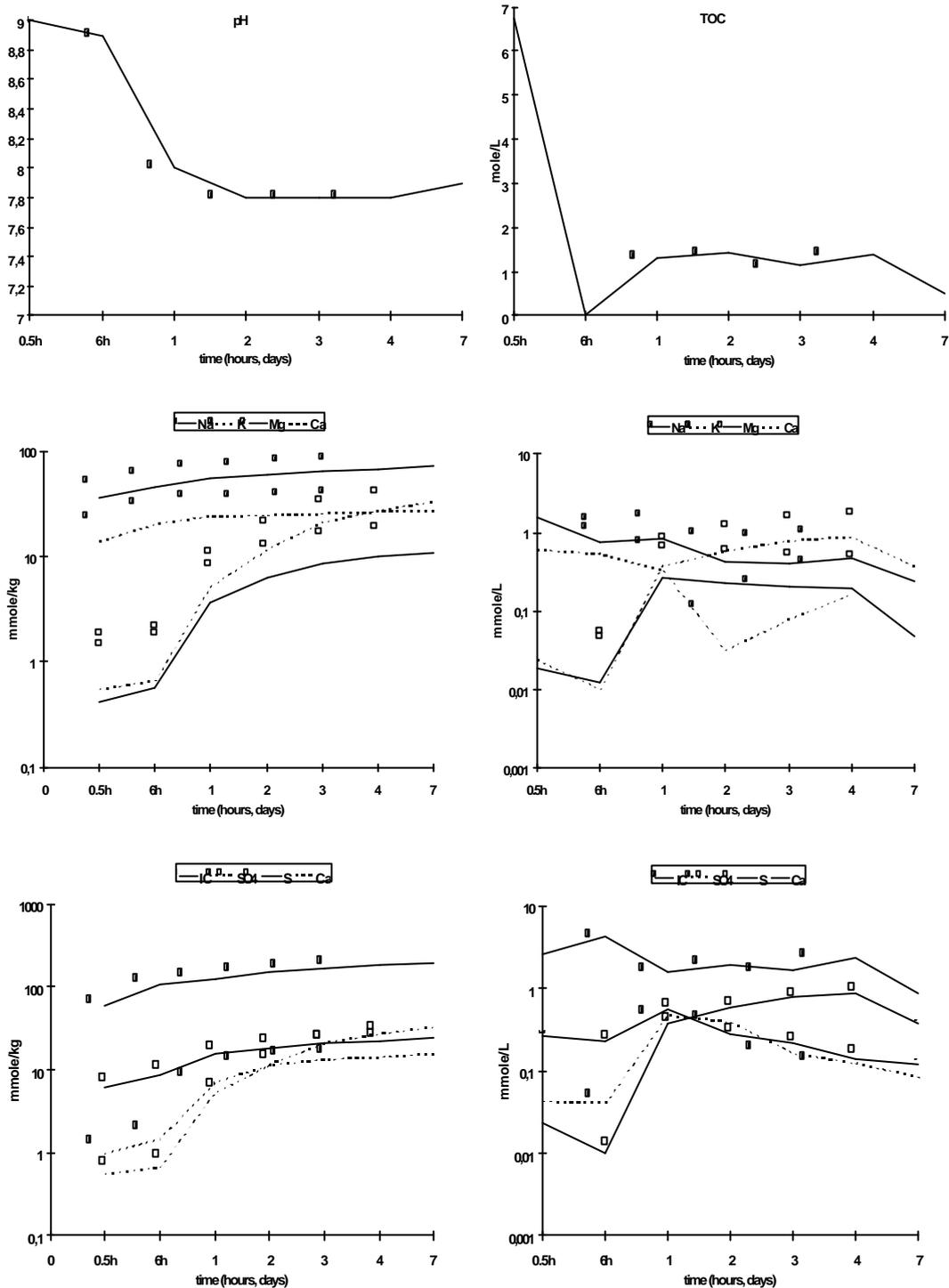


Figure 4. The accumulated leached amount (mole/kg dry substance) and the concentration (mole/L; mg/L (TOC)) in the leachate during different leaching steps of pH, TOC, Na, K, Mg, Ca, inorganic carbon (IC), SO_4^{2-} , S and Ca (Ex. 2).

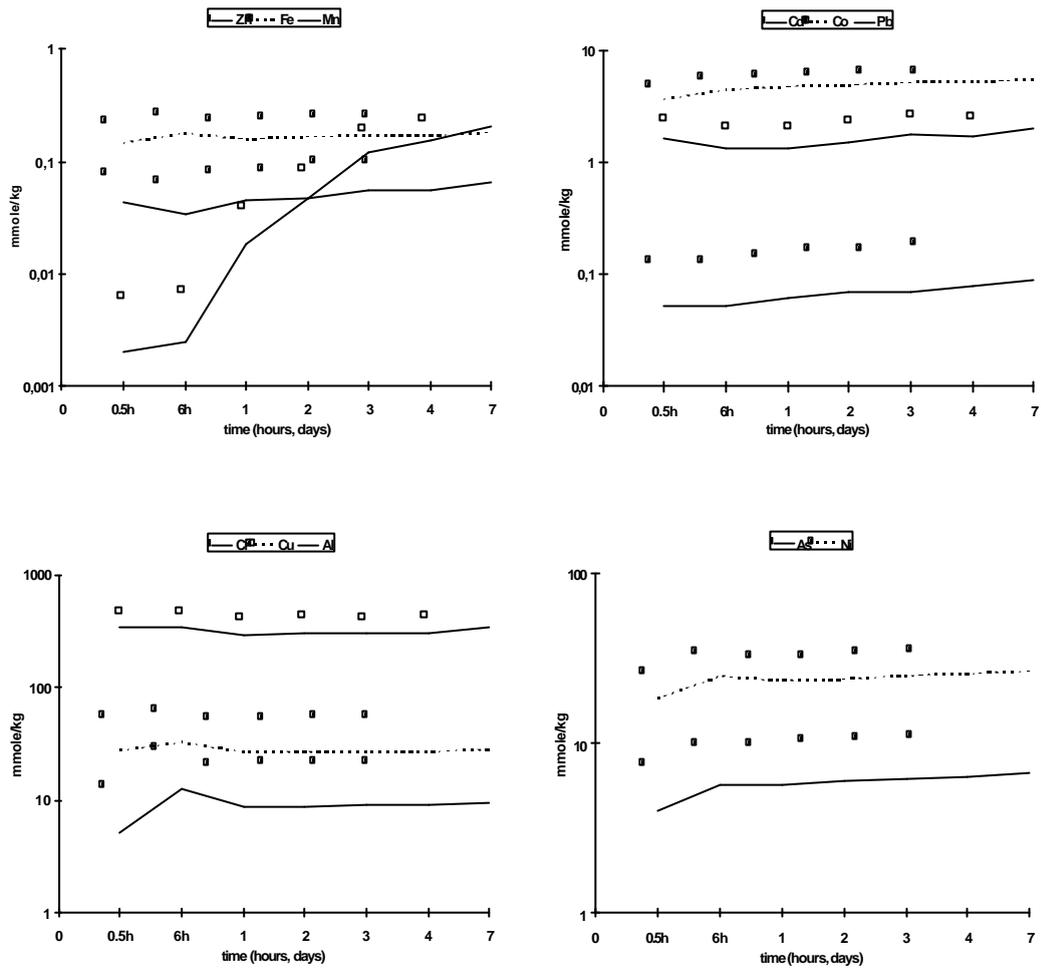


Figure 4. (continue) The accumulated leached amount (mole/kg dry substance) of Zn Fe, Mn, Cd, Co, Cr, Cu, Al, As and Ni (Ex.2).



Both the sulphide oxidation and the carbonate dissolution seem to vanish after five days during Ex 1, while high concentrations of potential carbonate cat ions remain during Ex 2. An additional supplier of protons during Ex. 2 can be organic acids (5). According to Figures 3 and 4, the sulphur released during the most intensive oxidation phase is between 10 and 12 mmole S/kg TS, which should be compared with the amount of sulphur bound as AVS (mean = 6.7, range : 0.1 - 15 mmole S/kg TS) in the degraded waste (Flyhammar, 1998). The major cations in these phases seem to be iron and zinc. However, the concentrations of Fe and/or Zn in the leachates during both experiments do not support the assumption of (Fe, Zn)S dissolution.

The accumulated amount of carbon released during Ex. 2 was 12.5 g/kg dry substance (19 % inorganic carbon (IC) in the leachates, 21 % organic carbon (TOC) in the leachates and 61 % CO₂ released to the air stream) (Håkansson, 1995). If the content of organic carbon is assumed to be 127 g/kg (Mårtensson et al. (1998) in partly degraded MSW, the released amount of organic carbon would be less than 10 %.

4.3 Solid phase transformations

The transformations of heavy metals between different binding forms are shown in Figure 5. The importance of different binding forms and developing trends are illustrated by triangle diagrams showing extraction fraction 1 (exchangeable, adsorbed and/or bound to acid soluble forms such as carbonates and AVS), extraction fraction 2+3 (bound to Mn/Fe oxides/hydroxides and/or strongly adsorbed to organic matter) and extraction fraction 4 (very strongly bound to organic matter and or other oxidizable species, such as sulphides) (see Flyhammar, 1997). The effects of the leaching tests on heavy metal binding forms seem to be limited (Figure 4), except for Pb, Cd, Zn and Fe. One explanation can be that the amount of heavy metals leached during the tests only constitutes a small proportion (a few percent or less) of the amount identified as reactive binding forms (Tables 5 and 6), except for Ni, As and Co. The changes proposed for Cd and Pb are difficult to evaluate since both elements show extremely variable fractions patterns in the partly stabilised waste (Flyhammar, 1997). The changes of iron (toward fraction 3 and 4) and zinc (towards fraction 1) can be explained by the dissolution of AVS phases (containing Zn and Fe) and the precipitation of Fe oxyhydroxides. These secondary phases (or other scavenging phases such as organic matter) could act as powerful scavengers of the zinc ions released during the sulphide oxidation. This would explain the lack of Fe and Zn ions in the leachates, which was mentioned above.

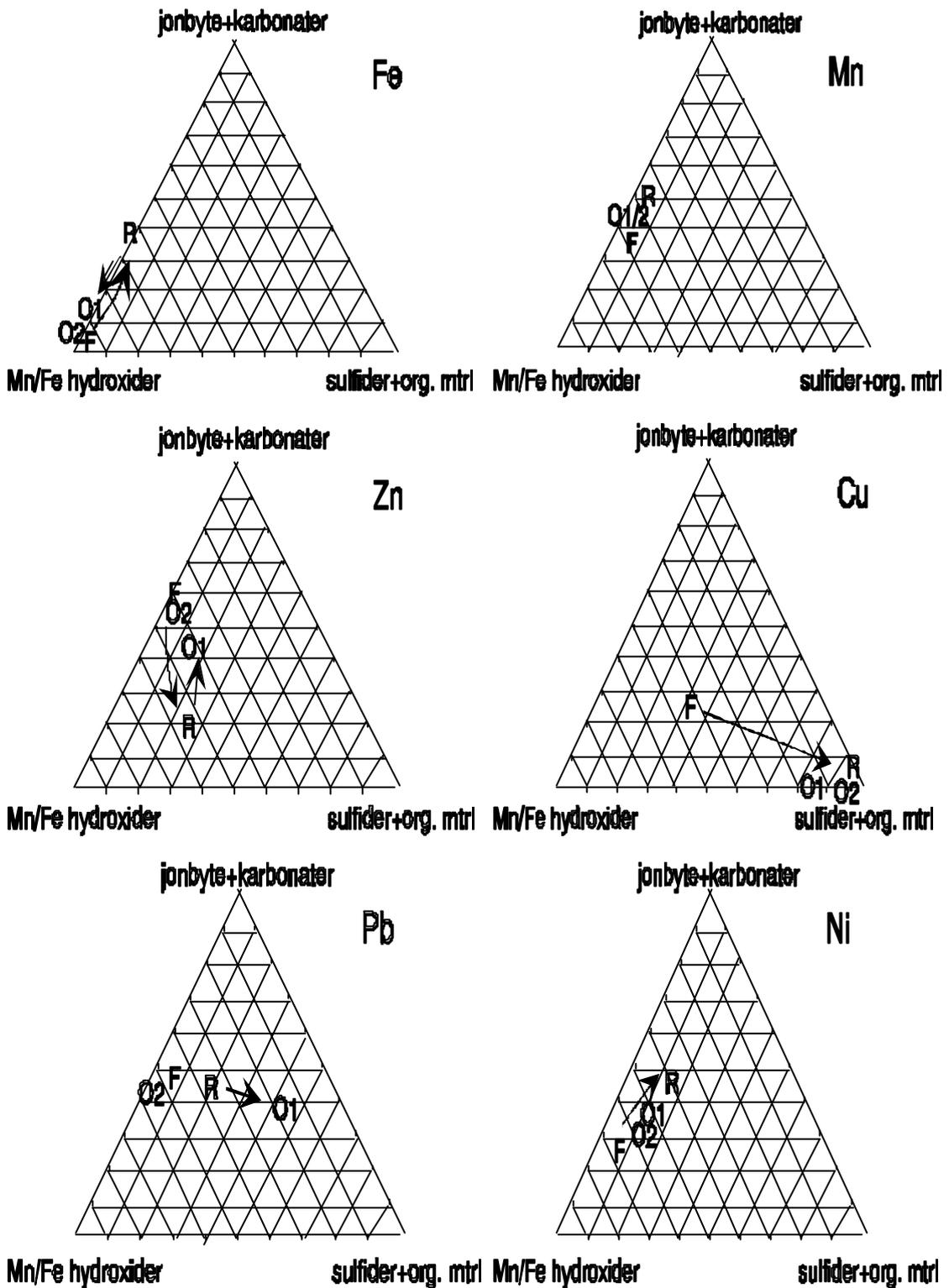


Figure 5. Development of the reactive heavy metal binding forms due to oxidation of anoxic waste samples (R @ O1/2). F @ R shows the development of the forms during the proceeding anaerobic waste degradation (from Flyhammar, 1997) (F) fresh MSW, (R) stabilized waste and (O1 and O2) oxidized stabilized waste.

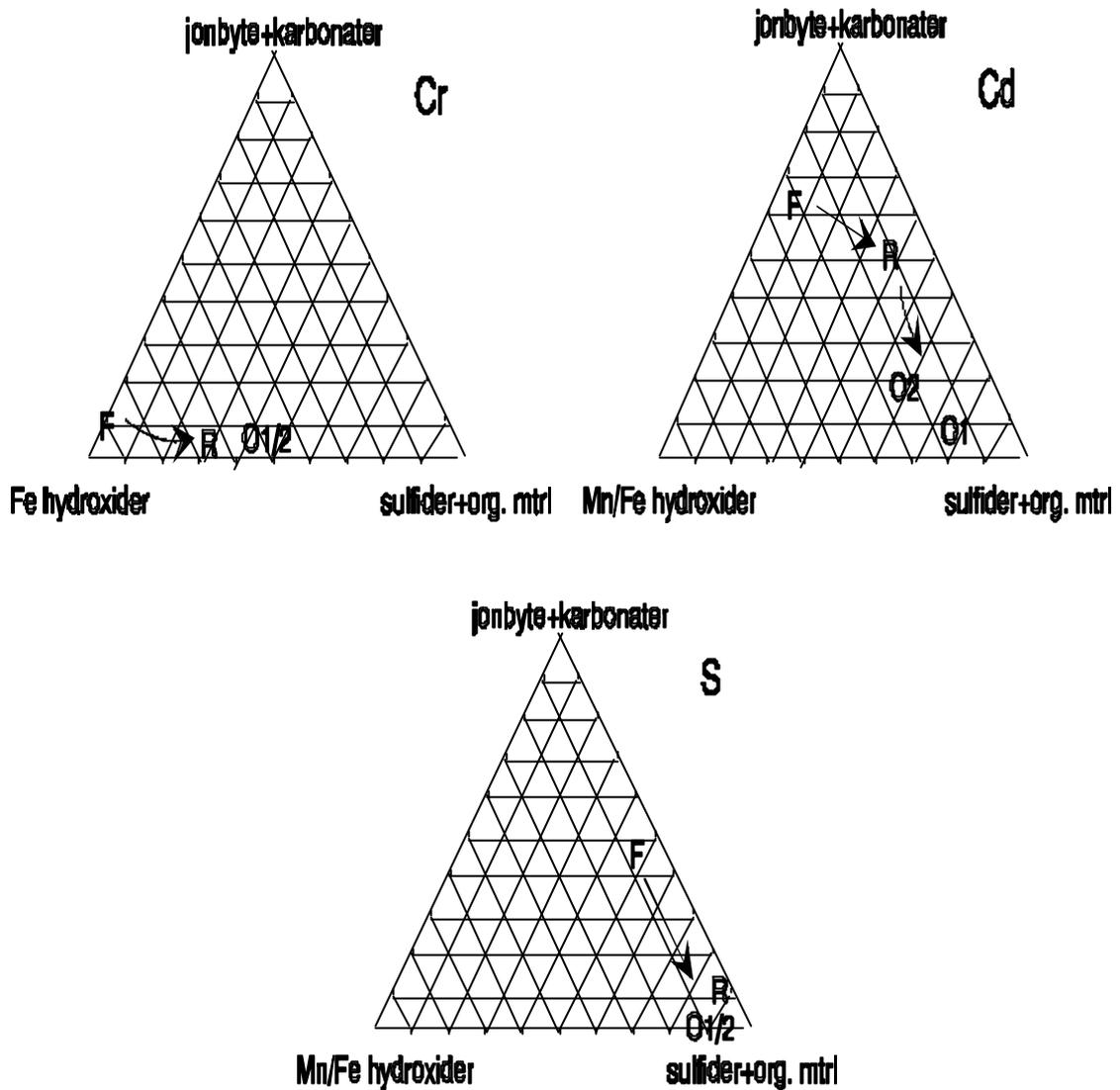


Figure 5. (continue) Development of the reactive heavy metal binding forms due to oxidation of anoxic waste samples (R @ O1/2). F @ R shows the development of the forms during the proceeding anaerobic waste degradation (from Flyhammar, 1997). (F) fresh MSW, (R) stabilized waste and (O1 and O2) oxidized stabilized waste.

5. Discussion

It is assumed that the major phenomenon identified during Ex. 1 and 2 are caused by the oxidation of reactive sulfide phases and perhaps organic matter. The results indicate that protons produced by oxidation reactions are consumed by dissolving carbonates (CaCO_3). The content of carbonates in the degraded waste was estimated to be at least 150 mmole CaCO_3/kg dry waste (Flyhammar, 1997). During the oxidation experiments, only a small proportion of the content of CaCO_3 seems to be dissolved (Table 7). A quite different development can be expected during the oxidation of poorly buffered sediments, such as the one presented in table 7. During an oxidation experiment carried out on another poorly buffered sediment, the pH of the solution decreased from 8 to 3-4 during the first oxidation phase (Calmano et al., 1993). However, during succeeding redox cycles the pH changed between 5.0-5.5 and 3.0 during anoxic and oxic phases, respectively.

Table 7. Relations between the amount of buffering substances (CaCO_3) and the proton production potential in anaerobic wastes and sediments (Flyhammar, 1997; Förstner, 1995; Kersten and Förstner, 1991).

	Ex. 1	Ex.2	Sediment
Consumption of CaCO_3			
Sulfides + Organic acids	≤ 35 mmole/kg	≤ 31 mmole/kg	840 mmole H^+/kg †
dominate phase	sulfides \gg org. acids	org. acids $>$ sulfides	AVS $>$ pyrite
Content of CaCO_3			
CaCO_3	150 mmole/kg		360 mmole/kg

† acid production potential

Table 8. The released amount during different oxidation experiment. Total rel. = the total proportion released, Net rel. = the proportion released after scavenging (Håkasson et al., 1996; Calmano et al., 1994; Calmano et al., 1993; Mårtensson et al., 1998).

	Zn				Pb			
	total	available	Net rel. (ox)	Total rel.	total	Available	Net rel. (ox)	Total rel.
Ex. 1	1006		1.2 %		252		0.3 %	
Sediment 1	538		1.0 %	1.5 %	65		0.1 %	0.7 %
L. sedim.	5690		1.1 %		37.5		0.2 %	
MSW 1	2980				538			
Sediment 2			23 - 38 %	18 - 20 % †			0 - 6 %	0 % †
	Cu				Cd			
	total	available	Net rel. (ox)	Total rel.	total	Available	Net rel. (ox)	Total rel.
Ex. 1	202		1.4 %		5.8		< 0.3 %	
Sediment 1	87		0.5 %	1.0 %	2.6		3.5 %	5.0 %
L. sedim.	42.3		2.6 %		1.8		0.7 %	
MSW 1	179				9.7			
Sediment 2			3 - 7 %	0 % †			0 - 6 %	0 % †

† net release under reduced stages

In table 8, the amounts of Zn, Pb, Cu and Cd released during different oxidation experiments are summarized. The pH in the pore water increased from 7.6 to 7.6-7.8 during

two oxidation experiment going on for 24 hours on a leachate pond sediment (L. sedim.), while the concentrations of heavy metals such as Zn, Pb, Cd and Cu increased almost one order of magnitude (Table 9). During an oxidation experiment carried out on partly stabilized waste (MSW 1) for 83 days, it was found that approximately 6 % of the organic carbon was oxidized and released as CO₂ during the experiment. Indications of decreasing pH buffer capacity were also noticed. The concentrations of heavy metals in artificial leachates produced after the experiment were higher than in similar leachates produced before the experiment (Table 9), while the pH decreased from 8.6 to 8.0. Results from experiments carried out on anoxic river sediments under buffered near neutral conditions (Sediment 1) and acidic conditions (Sediment 2) are presented for comparison (Table 8).

Table 9. The change in concentration (mg/L) before and after oxidation experiments (Håkasson et al., 1996; Mårtensson et al., 1998).

	Zn		Pb	
	anoxic	oxic	anoxic	oxic
L. sedim.	0.165 - 0.183	2.2 - 2.3	0.0042 - 0.0072	0.074 - 0.079
MSW 1	0	1.15	0.000392	0.000641
	Cu		Cd	
	anoxic	oxic	anoxic	oxic
L. sedim.	0.0169 - 0.0171	0.183 - 0.299	0.0006 - 0.0007	0.0047 - 0.0054
MSW 1	0.040	0.71	0.00008	0.001

The release of heavy metals, especially Zn and Cd, during oxidation experiments is extremely sensitive to pH (Table 8). During neutral to weak alkaline conditions only a few percentage of the total amount is released, while up to 30 % of the total content can be dissolved during acidic conditions. Increased concentrations of heavy metals in table 9 can be explained by increasing concentrations of dissolved organic complexing agents, produced by oxidation reactions.

The long term development of the leachate pH will depend on the ability of the waste to produce acidity and to neutralize acid constituents. Belevi and Baccini (1989) found that a partly stabilized MSW could neutralize (pH of leachate \geq 7) 6 mole H⁺/kg dry waste. By assuming that half of the content of organic carbon in partly stabilized MSW can be oxidized to CO₂, less than 4 mole H⁺/kg dry waste can be produced. This is up to two orders of magnitude higher than the supply of protons by acid rain (pH 4) during thousands to a landfill (20 meter of waste).

The continuous depletion of the acid consumption capacity (ACC) in partly stabilized MSW has been estimated in figure 6. An open landfill containing 10 m of waste (field capacity = 41 % (Benz, 1998) and density = 1 kg/dm³ (Baccini et al., 1987)), which permit the infiltration of acid rain (pH 4), have been used in the calculations. It is also assumed that a constant partial pressure of CO₂ (p_{CO2}) prevails within the waste.

An infiltration rate of 200 mm/year has been used, which is assumed to represent the infiltration rate at a covered landfill (Nilsson et al., 1991). Two different p_{CO2} have been used, 10^{-3.5} (partial pressure in air) and 10^{-1.5} (the maximum pressure measured in soils). The

content of CaCO_3 in table 7 has been used as the carbonate ACC, while the total neutralization capacity is assumed to be almost two orders of magnitude higher and comparable to the capacity presented by Belevi and Baccini (1989), see above. In this calculation, it is assumed that every mole of protons supplied by acid rain will react with 1 mole of CaCO_3 under alkaline conditions according to $\text{H}^+ + \text{CaCO}_3 = \text{Ca}^{2+} + \text{HCO}_3^-$. The dissolution of calcite under constant p_{CO_2} is based on the equilibrium concentration of Ca^{2+} in reaction:



It is also assumed that the most reactive sulfides and organic matter, which were oxidized during our experiments, react instantaneously.

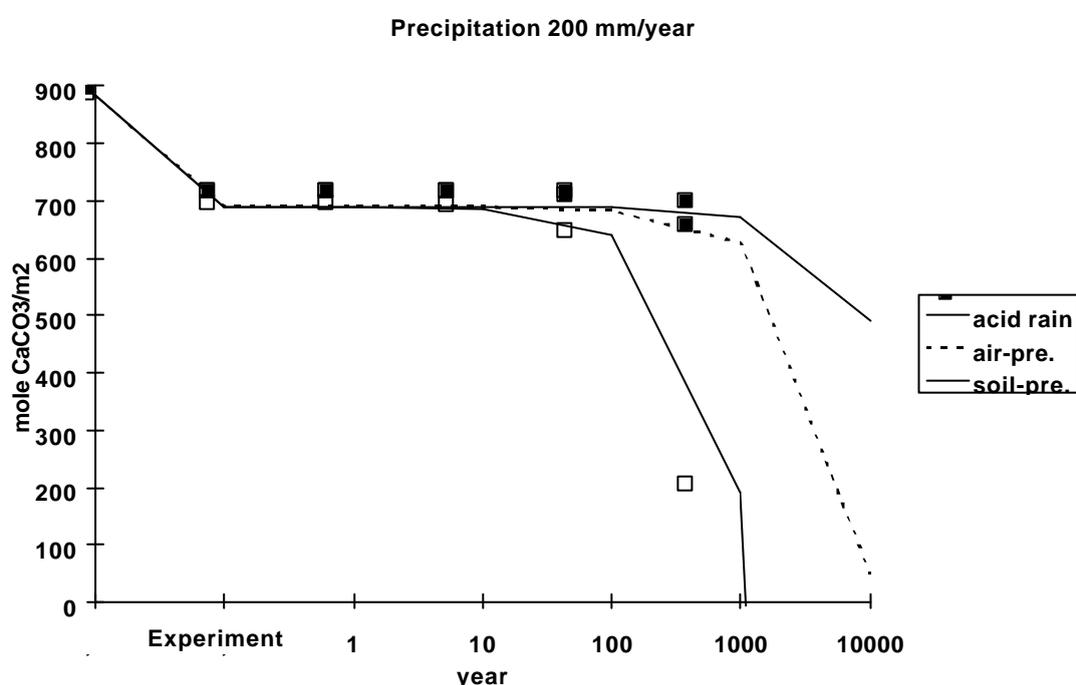


Figure 6. The calculated consumption of the carbonate ACC due to the initial oxidation of reactive sulfides and organic matter (experiment), the continuous infiltration of acid precipitation (200 mm per year) and constant p_{CO_2} .

The development in figure 6 suggests that the content of carbonate ACC is enough to consume the supply of protons for a long period of time, while the total buffer capacity is even much higher. Therefore, acid conditions will not be expected for a long period of time. However, the formation of organic acids and the oxidation of less reactive sulfides can affect the consumption of the buffer capacity.

The time to deplete all the organic matter that remain after the anaerobic degradation phases during different conditions has been estimated by Bozkurt (1998) based on the oxygen intrusion rate (Table 10). The most rapid degradation was identified in a partially water saturated landfill without a cover.

Table 10. Estimated time to deplete all organic matter during different condition, in a 10 m thick landfill.

Case	Time
Diffusion - partially saturated	
with a cover	30 000 years
with a cover (10 % function)	3 000 years
without a cover	600 years
Fully saturated	> 500 000 years
Forced convection	20 000 years
Natural convection	300 000 years

6. Conclusions

This and other similar experiments indicate that the initial oxidation of the most reactive reduced compounds in partly anaerobically stabilized MSW will not mobilized large amounts of the total amount of heavy metals. However, the concentration might increase up to one order of magnitude due to complexation with dissolved organic matter. The mobilization is restricted by the presence of buffering substances in the waste, which are able to buffer neutral to weak alkaline leachates. The high buffer capacity of partly stabilized MSW suggests that acid leachates and a heavy metal chemical time bomb (CTB) will be avoided for a long period of time (hundreds, perhaps thousands of years). However, acid leachates might be recognized earlier than expected due to a unevenly distributed buffer capacity within the waste and a preferential flow of acid leachate in channels, while the main part of the buffer capacity is located within stagnate parts of the waste.

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