The Role of Particulate Matter in the Mobilization of Trace Metals during Anaerobic Digestion of Solid Waste Material*

Die Bedeutung der partikulären Substanz für die Mobilisierung von Spurenmetallen beim anaeroben Abbau fester Abfallstoffe

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Keywords: Particulate Matter, Adsorption, Trace Metals, Anaerobic Digestion, Wastewater

Summary: Metal ions bound to particulate matter represent the greatest portion (i.e. $>95\%$) of the total metal content found in leachate from reactor experiments where solid waste material was anaerobically digested. This seems true even though strong complexing agents are in solution which increase the solubility of Pb and Cu by a factor up to $10^4 \dots 10^5$ over that theoretically predicted according to the solubility of the corresponding sulfide mineral. A titrimetric characterization of the metal ion binding sites of the particulate matter suggests that the metal binding properties of the particulate matter are mainly due to organic, amino-acid-type compounds (amines, thio groups, carboxylic groups) probably of bacterial origin. The change of the concentration of the binding sites with time, together with the change of the composition of the particulate matter indicates that bacterial flocs are suspended in the leachate during the switch from acidogenic to methanogenic conditions – either due to the detachment of bacterial films from the solid material by the intensive gas production or due to the formation of syntrophic methanogenic bacterial associations or a combination of both. A combination of the two factors, strong affinity of bacterial mass to metal ions on the one hand, and suspending of the bacterial mass in the leachate on the other hand, will therefore imply a great mobilizing potential for trace metals. Consequently, the highest concentrations of particulate bound Cd were found in reactor experiments where sewage sludge contaminated with Cd was added to the waste material. An increase of the concentration of dissolved cadmium over the solubility of cadmium sulfide, however, could not be observed.

Schlagwörter: Partikuläre Substanz, Adsorption, Spurenmetalle, Anaerober Abbau, Abwasser

Zusammenfassung: Metallionen, die an partikuläre Substanz gebunden sind, machen den größten Teil (mehr als 95%) des Gesamtmetallgehalts im Sickerwasser aus Reaktorexperimenten aus, bei denen feste Abfallstoffe anaerob abgebaut wurden. Dies gilt auch, obwohl sich in Lösung Komplexbildner befinden, die die Löslichkeit von Pb und Cu um den Faktor 10^4 bis 10^5 über die theoretische des korrespondierenden Sulfidminerals erhöhen. Die titrimetrische Charakterisierung der Metallbindungszentren des partikulären Materials ergibt, daß dessen Metallbindungseigenschaften hauptsächlich auf organische, aminosäurebürtige Komponenten zurückzuführen sind (Amine, Thiogruppen, Carboxylgruppen), die wahrscheinlich bakteriellen Ursprungs sind. Die Änderung der Konzentration der Bindungszentren mit der Zeit ebenso wie die Änderung der Zusammensetzung der partikulären Substanz weisen darauf hin, daß bakterielle Flocken während der Umstellung von Azidogenese auf Methanogenese im Sickerwasser suspendiert werden – entweder durch Ablösung bakterieller Filme auf Grund der intensiven Gasproduktion oder durch Bildung syntropher, methanogener bakterieller Assoziationen. Die Kombination der beiden Faktoren – hohe Affinität der bakteriellen Masse zu Metallionen einerseits und Suspendierung eben dieser bakteriellen Masse andererseits – impliziert demnach ein hohes Mobilierungspotential für Spurenmetalle. Dementsprechend wurden auch die höchsten Konzentrationen partikulär gebundenen Cadmiums in Reaktorexperimenten gefunden, bei denen Cd-kontaminierter Klärschlamm dem Abfallmaterial beigemischt wurde. Ein Anstieg der Konzentration an gelöstem Cadmium über die Sulfidlöslichkeit hinaus konnte jedoch nicht gefunden werden.

1 Introduction

The mobility of trace metals in aquatic systems is commonly predicted using equilibrium models. Inherent in such an approach is the assumption of equilibrium between a solid phase, i.e. a sparingly soluble metal salt, and dissolved metal compounds. A number of computer programs are available to model such a chemical system as a function of pH and the concentration of ligands which either precipitate metal ions from solution or complex metal ions and keep them in solution. The latter fraction is usually termed as the dissolved fraction, dissolved being operationally defined as filterable with a filter of 0.2 μm pore diameter.

Such a definition may be adequate in systems low in colloidal matter content. However, recent studies point to a much more important role of colloidal or particulate matter in sequestering metal ions. With respect to aquatic systems very rich in particulate matter, such as wastewater, an im-

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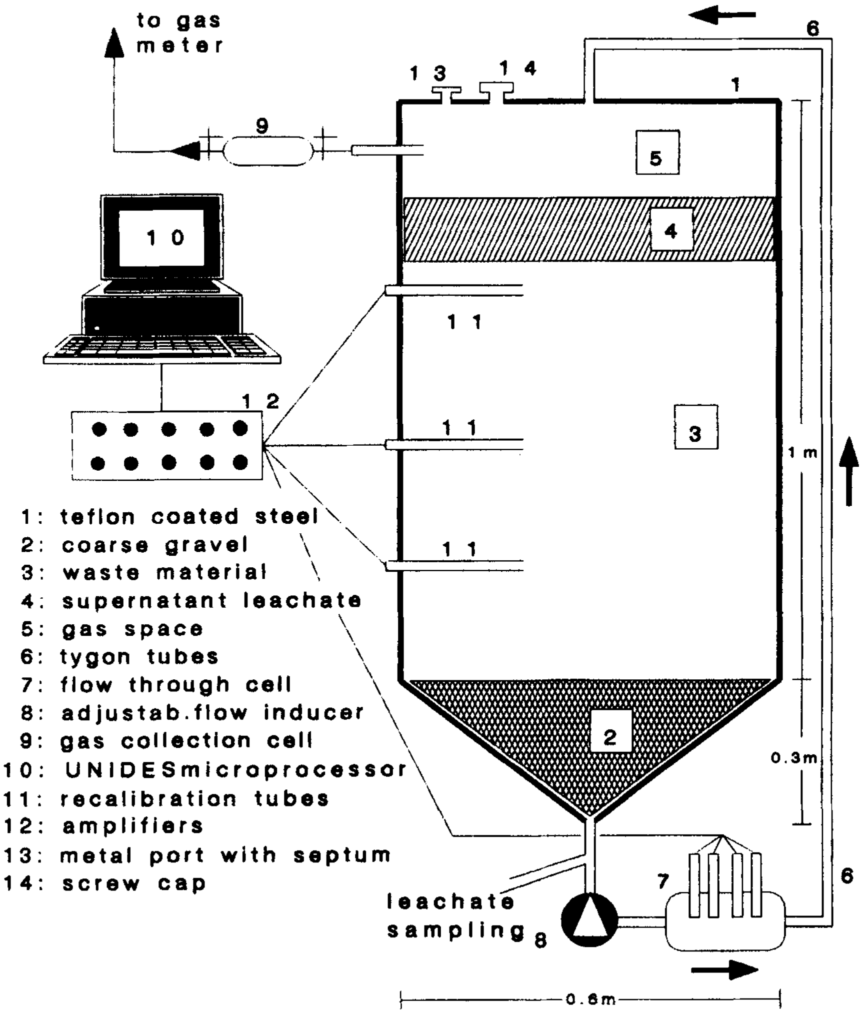

Fig. 1: Scheme of experimental reactor (steel version)

Schema des Reaktors (Edelstahlversion)

proved understanding of its interaction with metal ions seems therefore critical. Recently, we presented results from reactor experiments about the chemical speciation of dissolved metal ion compounds during anaerobic digestion of solid wastes [1, 2]. Additionally, we investigated the metal binding properties of particulate matter [3] found in the leachate. In this paper we want to discuss the dynamics of the composition of particulate matter during the anaerobic digestion process, and how the quantity of metal ions bound to particulate matter is influenced by its binding properties.

2 Materials and Methods

2.1 Experimental Design

The experiments were performed as reactor experiments (Figure 1, for more details see Peiffer [2]). The reactors were filled with shredded solid waste (∅ < 4 cm) from a municipal solid waste composting plant mixed with pure organic substances (e.g. vegetables) in a ratio of 2:1. Sewage sludge, contaminated with trace metal ions (metal content: 2024 ppm Zn, 75 ppm Cd, 318 ppm Pb and 3803 ppm Cu), was added to reactor 5 (30 % of total substrate weight, i.e. 3 kg).

After filling, the waste was saturated with water, and a small volume of water was allowed to overlay the solid material. The water was continuously circulated in order to maintain a steady state with respect to the chemical conditions in the reactors. Theoretical retention times of 3...4 h (larger high-grade steel reactor with a volume of 0.283 m^3, reactor 1 and 3), and 0.3 h (perspex reactor of 0.031 m^3, reactor 2 and 5) were calculated.

2.2 Sample Treatment

About 400 mL of the leachate were sampled under nitrogen and filled in N_2-degassed centrifuge tubes of inert material (tetrafluoroethylene-hexafluoropropylene (FEP) tubes, Kontron) with gas-tight caps. Centrifugation speed was 18000 rpm which corresponds to a separation limit of 0.4 μm particle diameter at a density difference of 0.1 g/cm^3 between solution and solid. With greater density differences, the particle diameter decreases, and therefore 0.4 μm can be regarded as an upper limit. Separation between particulate and dissolved matter is therefore operationally defined according to this centrifugation procedure.

The supernatant was poisoned with sodium azide and stored in polyethylene flasks at 4°C until further treatment.

For most of the parameters to be analyzed in the supernatant (metal ions), it was necessary to eliminate the high concentrations of dissolved organic matter prior to the analysis. Therefore, a HNO_3/pressure digestion procedure [4] was applied to both the dissolved and particulate fraction of a sample. Before digestion, 20 mL of the supernatant had to be concentrated to about 1 mL. After diges-

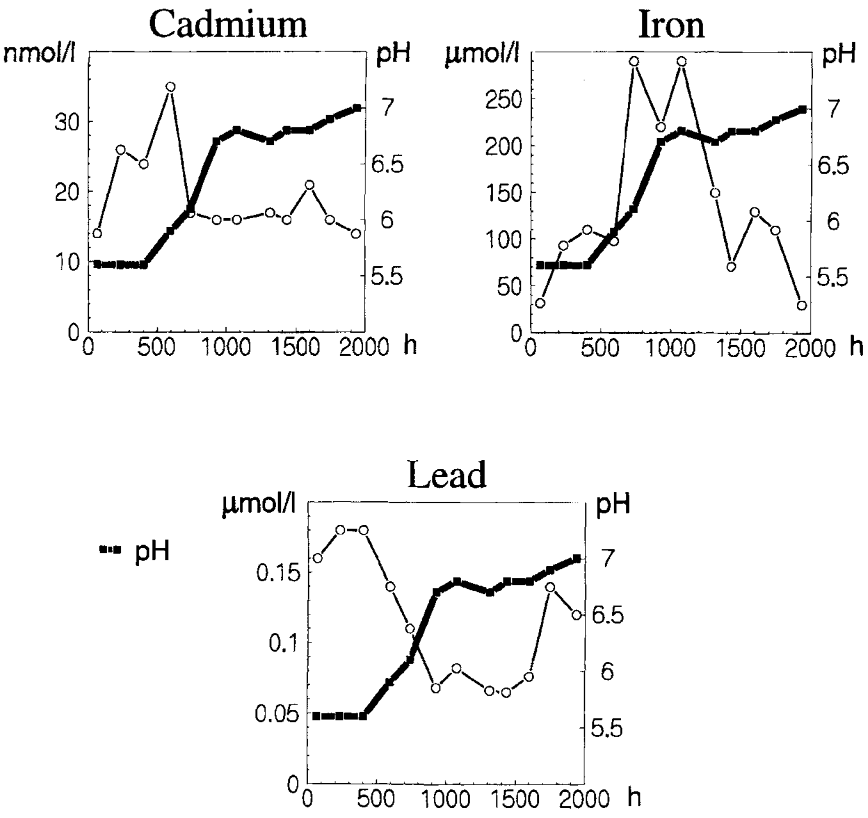

Fig. 2: Total dissolved metal concentration and pH plotted as a function of time for reactor 5

Gesamtgehalt an gelösten Metallen und pH-Wert im Reaktor 5, aufgetragen gegen die Zeit

tion, the samples were filled up to 20 mL and stored at 4°C until measurement. All vessels used were pre-conditioned with HNO_3 (1 vol %, suprapure).

2.3 Analytical Methods

For details concerning analytical methods of dissolved substances, the reader is referred to [2]. The particulate matter content was determined gravimetrically. The metal content of the particulate matter was determined using atomic absorption spectroscopy. The same analytical procedure was applied as described in Peiffer [2]. The protein content was photometrically determined using the biuret method [5].

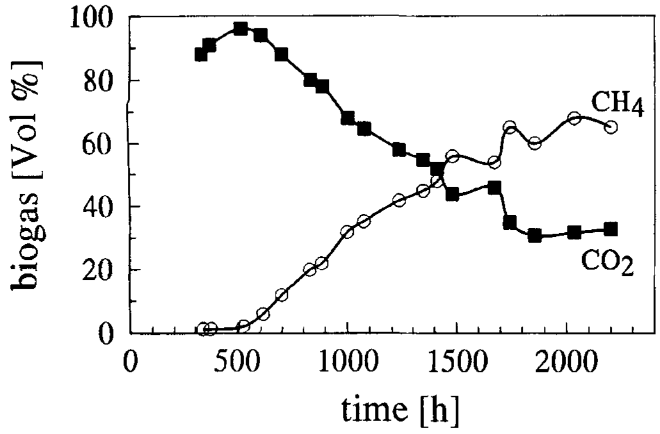

Fig. 3: The relative gas compostion measured in reactor 3 as a function of time. It clearly indicates the change from acidogenesis to methanogenesis

Die relative Gaszusammensetzung in Reaktor 3 als Funktion der Zeit

2.4 Metal Titrations of the Particulate Matter

After the first centrifugation step, the particulate matter was resuspended in 0.01 molar KNO_3. This suspension was then used to perform five different titration techniques, both, continuous and discontinuous. Each of these titration procedures provides different information about the metal-ion particle interaction. Advantages and disadvantages of each method are discussed in [3]. For the evaluation of the titration curves, the discrete ligand model [6, 7] was used. The concentrations and the stability constants of individual binding sites of the particulate matter were obtained by optimization of the parameters of this model [3]. In the following, the various titrimetric approaches are briefly described.

2.4.1 Continuous Titrations Using a Cd^{2+} Sensitive Electrode Cell

The most important advantage of this method is the measurement of the activity of free metal ions. Additionally, a quasi-continuous titration curve is obtained by continuously monitoring the e.m.f. of the electrode cell which is necessary for a precise data fitting at different concentration levels. The continuous titrations were performed using a commercially available titrimetric device (METROHM Dosimat 655). 20 mL of the suspension which contained the particulate matter were acidified with HNO_3 (suprapure) to a pH ≈ 4. We applied three different kinds of continuous titrations:

Titrations with a Cd^{2+} standard solution: Continuous titrations with a 50 ppm Cd^{2+} standard solution ($CdCl_2$) were performed with two samples at two different initial pH values using a Cd^{2+} sensitive electrode cell as the indicator electrode. pH and pCd (i.e. $-\log a(Cd^{2+})$) values as well as the volume of the added titration solution were recorded

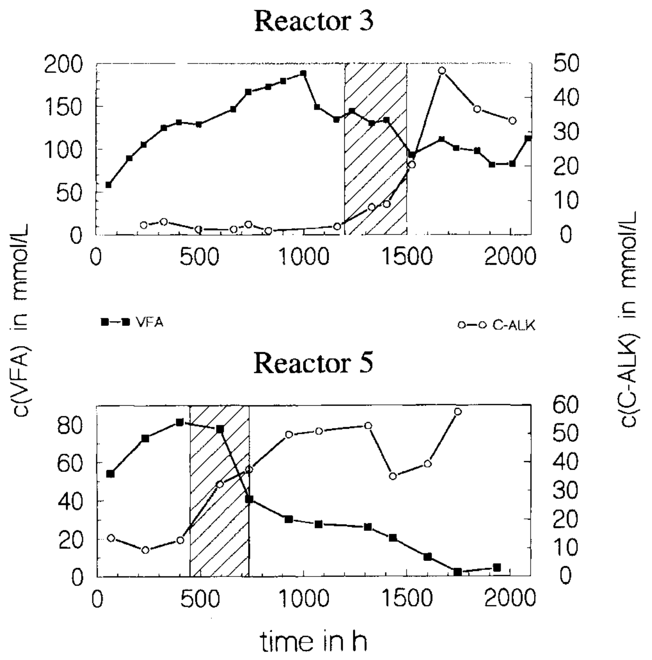

Fig. 4: Concentration of volatile fatty acids (VFA) as a function of time. VFA accumulate during acidogenesis in the reactor. Switching into methanogenesis leads to an increase of the pH (hatched area) and a subsequent increase in carbonate alkalinity (C-ALK).

Konzentration an flüchtigen Fettsäuren (VFA) als Funktion der Zeit. Die VFA reichern sich während der Azidogenese im Reaktor an. Der Wechsel zur Methanogenese führt zu einem Anstieg des pH-Werts (schraffierte Fläche) und einem Anstieg der Carbonatalkalinität (C-ALK).

every ten seconds by an A/D data acquisition system (UNIDES).

Acid/base titrations.: The samples were titrated with NaOH (Titrisol 0.002 mol/L or 0.02 mol/L) to a pH ≈ 10.5. The slowest titration velocity was chosen in order to approximate equilibrium conditions at each titration point as close as possible. The pH values and the volume of the added titration solution were recorded every ten seconds.

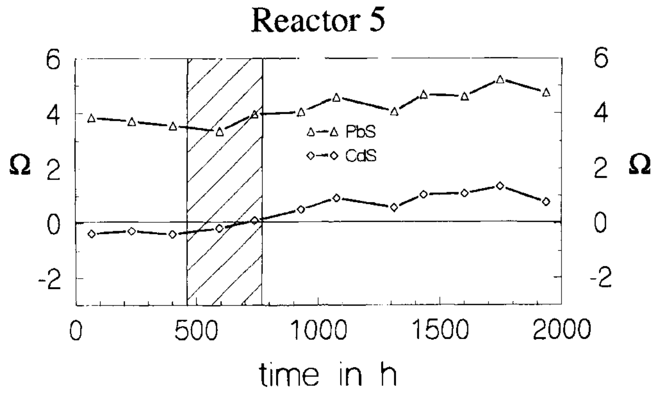

Fig. 5: Saturation indices Ω for PbS and CdS plotted as a function of time

Sättigungsindizes für PbS und CdS, aufgetragen als Funktion der Zeit. Sie dokumentieren eine starke Übersättigung des Sickerwassers aus Reaktor 5 (zu dem cadmiumkontaminierter Klärschlamm gegeben wurde) mit Pb^{2+}. Nur eine leichte Übersättigung besteht mit Cd^{2+}.

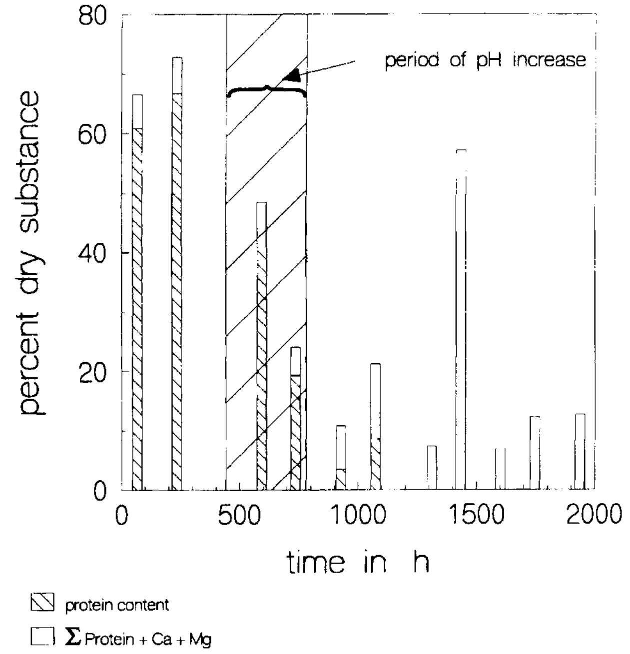

Fig. 6: The composition of suspended particulate matter plotted as a function of time

Die Zusammensetzung der suspendierten partikulären Substanz, dargestellt als Funktion der Zeit

Acid/base titrations after adding an aliquot of Cd^{2+}: Additionally, acid/base titrations were performed with all samples after adding different amounts of Cd^{2+} standard solutions.

2.4.2 Discontinuous Titrations

In these experiments, metal ions were added into separate reaction flasks, and the measurements were performed after 24 h equilibration time.

Cadmium titrations as detected by means of differentially pulsed anodic stripping voltammetry (DPASV): Aliquots of a Cd^{2+} standard solution ($CdCl_2$) were added to 5 mL of the particulate matter suspension to obtain total metal concentrations between 10^{-4} and 10^{-8} mol/L. The pH was adjusted by adding HNO_3 (suprapure) or NaOH (p.a.). The flasks were filled with degassed 0.01 molar KNO_3 (suprapure) up to exactly 25 mL and then equilibrated for 24 h on a shaker. After equilibration, the pH was measured again. Zn^{2+}, Cd^{2+}, Pb^{2+} and Cu^{2+} were detected by DPASV (METROHM Polarecord 626, largest drop size, deposition potential: -1.3 V); pH values were measured simultaneously. A shift of the half-wave potential due to complexation of the metal ions provided information about electrochemical lability and therefore about the nature of the complexing ligands.

Cadmium titrations as detected by means of atomic absorption spectroscopy (AAS): In contrast to the DPASV experiments described above, the suspension was centrifuged again after addition of Pb^{2+}, Zn^{2+} and Cd^{2+} and subsequent equilibration. Since the metal content was analyzed in both phases, the supernatant and the remaining particulate matter, this approach allowed the study of competition between several metal ions. For this purpose, 10 mL of the supernatant were removed and preserved by adding 100 μL of HNO_3 (65 vol %, suprapure, MERCK). The remaining 15 mL were also acidified (200 μL of HNO_3) and then put into an ultrasonic bath for 4 h in order to completely dissolve metal ions bound to the particulate matter. Cd, Cu, Pb, and Zn were measured in both fractions by AAS after a third centrifugation step.

3 Results and Discussion

Figure 2 shows the time dependent curves of the total dissolved concentration for iron, cadmium, and lead together with pH in reactor 5. Zinc and copper were detectable only in some samples of reactor 5 and are therefore not presented in Figure 2. Included in the plots is the pH. The pattern of the pH is characteristic for the anaerobic digestion of solid wastes [8]: in a first stage, the acidogenic phase, the complex organic material is hydrolyzed into volatile fatty acids (VFA) accompanied by a drop of pH. In a second stage, the methanogenic phase, the accumulated fatty acids are fermented via acetic acid to methane and CO_2 as the final mineralization products ([9], cf. Figure 3). This phase is accompanied by an increase of pH and carbonate alkalinity, and a consumption of volatile fatty acids (Figure 4).

The pattern of the trace metal dynamics seems to be rather scattered. Lead is higher concentrated during acidogenesis than during methanogenesis, although its concentration increases again towards the end of the experiments; the inverse is true for iron. The behaviour of cadmium is completely different from that of lead and iron. Although contaminated material was added to reactor 5, no increase in metal ion concentration was observed which points to a mechanism retaining the metal ions in the solid phase.

Indeed, equilibrium between solid CdS and the dissolved Cd species is indicated by the saturation index of CdS which is close to zero (Fig. 5). The saturation index Ω can be calculated by comparing the activity product AP:

$$AP = \frac{a(\mathrm{Me}^{2+}_{\mathrm{WATEQ}})\,a(\mathrm{H_2S})}{a^2(\mathrm{H}^+)} \qquad (1)$$

with the constant K_{s2}:

$$K_{s2} = \frac{a(\mathrm{Me}^{2+})\,a(\mathrm{H_2S})}{a^2(\mathrm{H}^+)} \qquad (2)$$

K_{s2} is the equilibrium constant for the twofold protonation of the sulfide group of a metal sulfide [2]:

$$\mathrm{MeS} + 2\,\mathrm{H}^+ \rightleftharpoons \mathrm{Me}^{2+} + \mathrm{H_2S} \qquad (3)$$

The saturation index Ω is then derived as:

$$\Omega = \log\left(\frac{AP}{K_{s2}}\right) \qquad (4)$$

$a(\mathrm{Me}^{2+}_{\mathrm{WATEQ}})$ reflects that part of the total dissolved metal concentration in solution which the computer code WATEQ4F [10] predicts not to be bound to dissolved ligands such as fatty acids. Note that AP is thus derived from measured variables, i.e. total metal concentration, pH and the H_2S activity, while K_{s2} refers to a theoretical value.

Inherent in such a calculation is the assumption that the number of ligands to react with a certain metal ion are completely considered in the computer program. Consequently, we explain the high supersaturation in case of PbS (cf. Fig. 5) with the existence of organic (sulfur) compounds which could not be considered in WATEQ4F [2]. In other words, the activity of the free, uncoordinated metal ion was overestimated in the calculation procedure for unknown organic ligands solubilized the metal ion to an unknown extent.

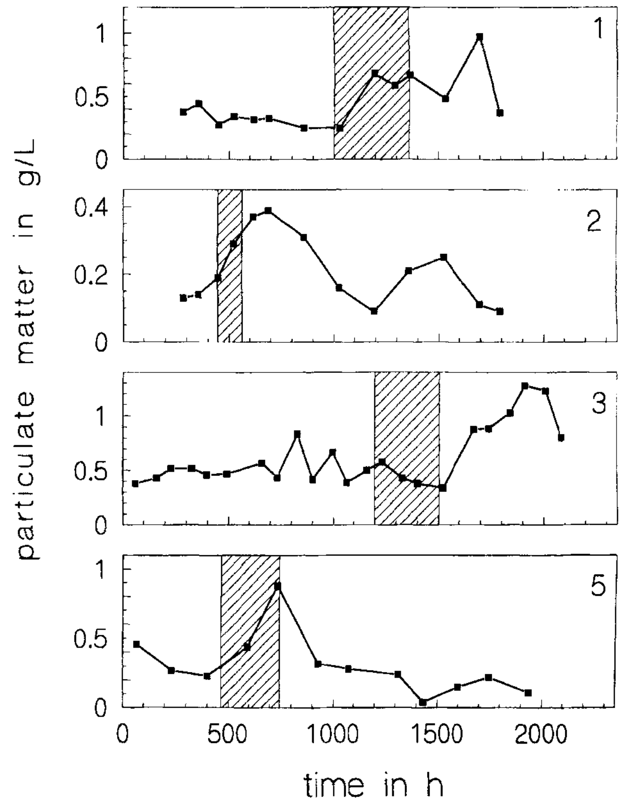

Fig. 7: Change of particulate matter content of the leachate with time in all reactor experiments. The hatched area denotes the increase of the pH during the anaerobic digestion process. The numbers in the upper right corner of each plot refer to the reactor.

Änderung des Gehalts an partikulärer Substanz im Sickerwasser mit der Zeit für alle Reaktoren. Die schraffierte Fläche markiert den Anstieg des pH-Wertes während des anaeroben Abbauprozesses. Die Zahlen in der rechten oberen Ecke jeder Ganglinie beziehen sich auf die Reaktornummer.

This example illustrates the problems arising from the existence of dissolved and particulate organic matter in solution and its operational separation. There is a broad continuum of organic molecule sizes existing in solution, which may have a high but different affinity to metal ions [11, 12].

3.1 The Composition of Particulate Matter

Figure 6 shows how the composition of particulate matter in reactor 5 varies with time. During acidogenesis and in the initial stage of methanogenesis, the particulate matter consists mainly of protein-like material, while the relative portion of Ca and Mg increases with time. Figure 7 shows that a maximum of the particulate matter concentration can be observed in all four experiments either in the period of increase of the pH (reactors 1, 2 and 5) or shortly after (reactor 3) when methanogenic activity is highest. This maximum can be explained either by detachment of bacterial films from the solid material due to intensive gas production during the change from acidogenesis to methanogenesis. A second possibility is the formation of bacterial

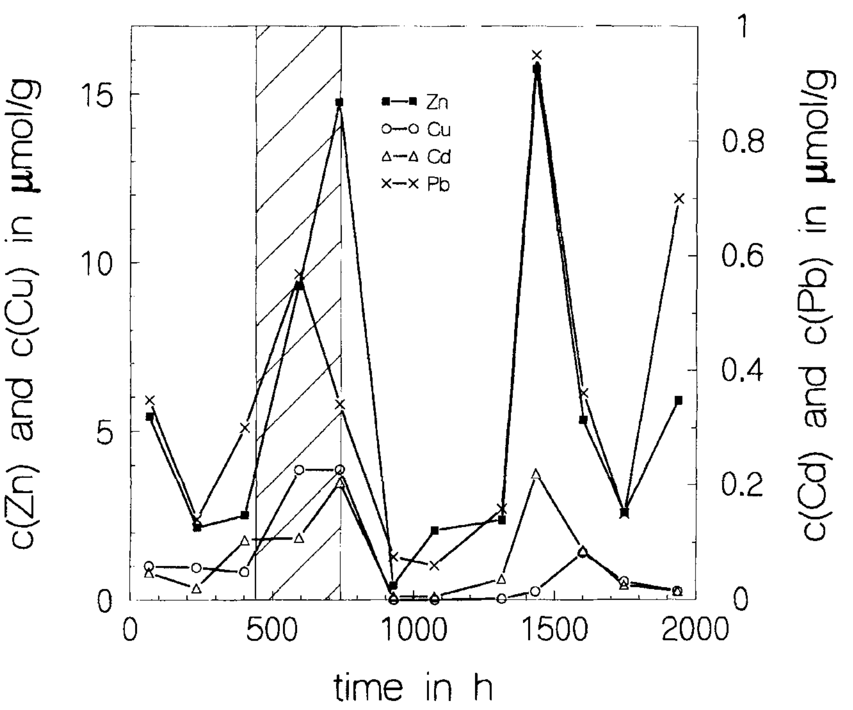

Fig. 8: Trace metal content of the particulate matter from the leachate of reactor 5 as a function of time
hatched area: period of pH increase

Gehalt an Spurenmetallen der partikulären Substanz aus dem Sickerwasser aus Reaktor 5 als Funktion der Zeit
schraffierte Fläche: Periode des pH-Wert-Anstiegs

colloids, a phenomenon very often observed in the methanogenic phase of anaerobic digestion [13]. Such colloids consist of syntrophic associations of a number of bacteria which are able to metabolize organic matter during methanogenesis. After a certain period of growth, the colloids flocculate and therefore disappear from solution. The high Ca and Mg content (which is accompanied by high contents of Fe and Mn, not shown here) may stem from formation of inorganic colloids such as $CaCO_3$ or $MgNH_4PO_4$. (The phosphate content ranged between 0.5...8 weight percent [14].)

A look at the trace metal content of particulate matter reveals two adsorption maxima (Fig. 8): one in the period of pH increase and one which corresponds to the maximum Ca and Mg content at 1450 h (cf. Fig 8). It is interesting to note that all trace metals show the same adsorption pattern. Table 1 demonstrates that the concentration of trace metals bound to particulate matter exceeds that of the dissolved fraction, in case of Cu by a factor of ten. When adding Cd-contaminated sewage sludge to the substrate, particulate matter has a distinct mobilizing effect for Cd: the concentration of particulate bound Cd is five times higher then that of dissolved Cd.

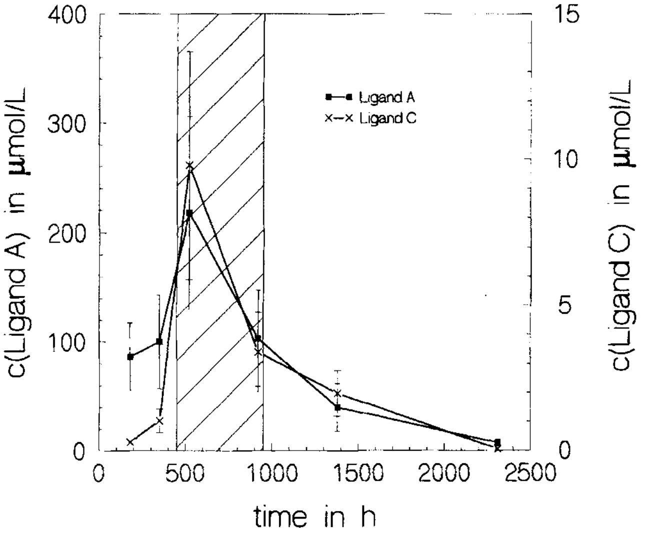

Fig. 9: Concentration of ligands A and C vs. time
hatched area: period of pH increase

Konzentration der Liganden A und C als Funktion der Zeit
schraffierte Fläche: Periode des pH-Wert-Anstiegs

Table 1: Range of dissolved and particulate matter bound metal concentrations in leachate from anaerobically digested solid waste (all concentrations in µmol/L)

Konzentrationsbereich gelöster und partikulär gebundener Metallionenverbindungen im Sickerwasser anaerob abgebauten festen Abfalls (alle Konzentrationsangaben in µmol/L)

solid matter composition	dissolved	particulate bound	metal
municipal waste household waste (Reactor 3)	0.0...0.31	0.4...3.2	Cu
	0.0...0.18	0.0...0.28	Pb
	0.0...0.034	0.015...0.09	Cd
municipal waste household waste Cd-contaminated sewage sludge (Reactor 5)	0.0...0.2	0.0...3.4	Cu
	0.07...0.18	0.02...0.3	Pb
	0.014...0.034	0.0...0.018	Cd

3.2 Binding Properties of Particulate Matter

Becker and Peiffer [3] titrimetrically identified seven individual binding sites of particulate matter, of which the change of concentration with time was determined in reactor experiments as described above. Based on acidity constants, metal binding stability constants, electrochemical behaviour, and reaction kinetics, the following functional groups were attributed to the binding sites [3]:

Ligand A: Mercapto groups (-SH) with a maximum concentration of 200 µmol/L at the beginning of the pH increase;

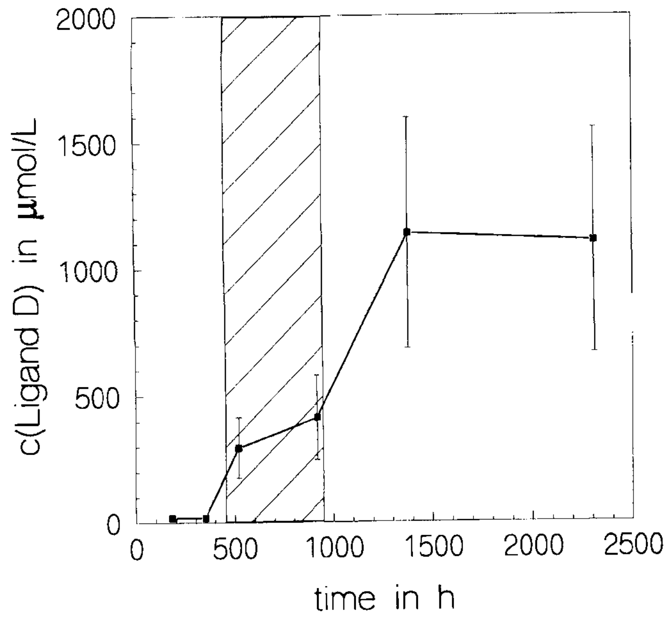

Fig. 10: Concentration of ligand D vs. time
hatched area: period of pH increase

Konzentration des Liganden D als Funktion der Zeit
schraffierte Fläche: Periode des pH-Wert-Anstiegs

Ligand B: Ligand which forms complexes with Cd, Pb or Zn with two or more carboxylic groups with a maximum concentration at the end of the pH increase;

Ligand C: Complexation of Cd or Pb at cell walls or within the cell of (probably methanogenic) bacteria;

Ligand D: Primary amines in the neighbourhood of oxo groups, whose concentrations were still increasing at the end of the experiment after 2500 h;

*Ligand E(*a,b*):* Ligands which could only be measured with metal ion titrations at very high pH values ($pH > 9.5$), namely phosphate (a) and SH-groups in the neighbourhood of amino groups (b);

Table 2: Logarithm of acidity (K_a) and metal stability constants (K_{Me}) of the metal binding sites of particulate matter from leachate from anaerobically digested solid waste as determined by Becker and Peiffer [3]. The symbol ≈ denotes that analytical problems did only allow an estimate of the constants.

Dekadischer Logarithmus der Aziditäts- (K_a) und Metallstabilitätskonstanten (K_{Me}) der Metallbindungszentren partikulärer Substanz, bestimmt von Becker und Peiffer [3]. Die partikuläre Substanz stammt aus dem Sickerwasser anaerob abgebauter fester Abfallstoffe.
Symbol ≈: Analytische Probleme erlauben nur die Angabe eines Schätzwertes.

Ligand	log (K_a)	log (K_{Cd})	log (K_{Pb})	log (K_{Zn})
A	−9.2	7.0	7.5	
B	≈ −5	≈ 5	≈ 6.0	≈ 5
C	≈ −6	≈ 13	≈ 14	
D	−7.7	4.0	5.4	≈ 3
E. a	−12.0	9.1	9.9	
E. b	≤ −9.0	−log(K_a) + (0.4±0.3)		
F	≥ −1.5		4.3±0.5	

Ligand F: Special Pb binding sites which were observable at very low pH values ($pH < 2$). These ligands could not be classified as a certain functional group.

Table 2 summarizes the acidity and stability constants of the various ligands. The highest affinity for metal ions can be observed with ligand C. However, the concentration of this ligand is not very high (1...10 µmol/L) compared to that of ligand A (Fig. 9). Ligand C was related to intracellular binding sites, for no release of a certain metal ion due to addition of other competing metal ions could be observed [3]. Such a criterion was applied by Brown and Wells [15] to distinguish between extra- and intracellularly bound metal ions. In contrast, SH-groups may be responsible for the binding of metal ions with ligand A. The maximum concentration of both ligands can be observed when the pH increases in the experimental system (Fig. 9). This maximum coincides with the sorption maximum of trace metals described above. Therfore, it may be concluded that methanogenic bacterial associations have a great capacity to (actively) sequester metal ions and keep them in solution.

In contrast to ligand A and C, ligand D which is attributed to amino groups [3] accumulates towards the end of the experiment (Fig. 10). Such a behaviour can also be observed for ammonium (not shown). Both compounds are decomposition products from the mineralization of amino acids which were degradated during acidogenesis and the initial phases of methanogenesis (cf. Fig. 6).

4 Conclusion

The discussion suggests that the colloidal fraction provides a great portion to the trace metal loading of leachate from anaerobic digestion processes. The contribution of typical anaerobic digestion products, such as volatile fatty acids, to metal solubilization is important only for Fe, to a lower extent for Zn but not for Cu, Pb and Cd [2]. Obviously, bacteria play an active part in the formation of particulate matter during anaerobic digestion and are also responsible for the particulate matter concentration to be found in leachate. Due to the high binding capacity of such colloidal matter, trace metal export from anaerobically treated solid wastes via this way may be the result. Therefore, problems may arise if wastewater is treated which stems from contaminated sites. A separate analysis of the dissolved and particulate matter fraction for its trace metal content seems strongly recommendable.

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