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INHIBITION OF ANAEROBIC DIGESTION CAUSED BY HEAVY METALS

R. F. Mueller* and A. Steiner**

**Department of Civil and Agricultural Engineering, Engineering Research Center at Montana State University, Bozeman, MT 59717, USA*
***Bayerisches Landesamt fuer Umweltschutz, Rosenkavalierplatz 3, 8000 Muenchen, Germany*

ABSTRACT

The severity of heavy metal inhibition on anaerobic digestion is dependent on the metal species and their dissolved concentration in the digester. The general sequence of inhibition on anaerobic digestion of municipal sewage sludge was found with Ni>Cu>Cd>Cr>Pb. Metal immobilization affinity in the sludge followed the reverse sequence. Due to sulfide production during digestion high quantities of heavy metals are precipitating as highly insoluble sulfide salts.

Nickel was immobilized to 94 % in the digester and indicated the most dramatic effect on anaerobic digestion. At a concentration of 250 to 300 g Ni m^{-3} toxicity occurred. Lower nickel concentrations resulted in reversible process inhibition. Copper up to 1000 g Cu m^{-3} caused reversible inhibition of acid producing, fermentative, and methanogenic bacteria. The time necessary for recovery of the process was dependent on the initial copper concentration in the digester. The organisms indicated capability of adaptation to copper. The copper uptake in the digester was 97 %. Cadmium inhibited digestion of sewage sludge up to approximately 50 % at 650 g Cd m^{-3}. For long durations of acclimation a tendency toward recovery was observed. The cadmium uptake in the digested sludge was 99 %. Chromium and lead were uptaken at 99.9 % during digestion. Hence, the addition of these metals up to 1000 mg Cr/l and 600 mg Pb/l showed only little effect on anaerobic digestion.

KEYWORDS

Anaerobic digestion, toxicity, inhibition, heavy metals, methanogenic bacteria, nickel, copper, cadmium, chromium, lead, biosorption.

INTRODUCTION

Heavy metals are found in high concentrations in waste water of various industries, e.g.chemical and electroplating industries.

Since heavy metals are removed efficiently from the water phase due to aerobic waste water treatment, heavy metals accumulate in primary and secondary sewage sludge of industrial or municipal treatment plants. High concentrations of heavy metals can be found in the digester and can cause damage to the anaerobic bacteria (Scherb and Steiner, 1982; Parkin *et al.* 1983; Loll, 1986).

The goal of this study was to determine toxic or inhibiting effects of nickel, copper, cadmium, chromium, and lead at various metal concentrations.

Toxicity or inhibiting effects of heavy metals on anaerobic digestion are independent of the total metal concentration in the digester, but depend on the concentration of free metal species in the sludge (Lawrence and McCarty, 1965). In sewage systems many organic and inorganic materials build complexes or precipitates with metal ions, hence free metal ions in such systems are rare. Cyanide, chloride, fluoride, ammonium, and hydroxide build a variety of metal complexes.

Fletcher and Beckett (1988) investigated the chemistry of complex building of heavy metals and soluble organic matter and described the form of binding for Ca(II), Mg(II), Cu(II), Zn(II), Co(II), Mn(II), Cd(II), Pb(II), Fe(III) on two different groups of ion exchange sites of soluble organic material using ion selective electrodes. The general affinity sequence was given with: $H >> Pb > Cu > Cd > Ni > Zn;Fe > Co;Mn > Ca > Mg$. The complexation of all metals was pH dependent. For instance 99 % of all Cu(II) ions build organocomplexes at pH 7, whereas only 14 % bonded to dissolved organics at pH 5. The dissolved organic substances with a high tendency for metal complexation are humic acids and polysaccharide.

Active as well as inactive, dead biomass is capable of binding and accumulating high quantities of heavy metals (Volesky, 1988). This biosorption is based on the chemical composition of the cells especially the cell walls.

Sulfide builds extremely insoluble metal sulfide salts with most heavy metals (Lawrence and McCarty, 1965). During the course of anaerobic digestion there are two major pathways of sulfide production. Sulfide is produced by sulfate reduction (SRB), and protein degradation. HgS, PbS, CuS, and CdS precipitate at pH values as low as pH1. NiS, CoS, MnS, and ZnS precipitate at pH values above pH7. In addition many metals precipitate with hydroxide at neutral pH. Chloride and sulfate ions precipitate with lead at high concentrations (9900 and 40 gm^{-3}, respectively). Metal precipitates are generally pH sensitive, resulting in increased solubility with lower pH values.

MATERIALS & METHODS

Experimental Procedure

It was desired to simulate full scale digester operation in the experiments. A series of 5 1.3 l completely mixed digesters were operated with a 10 day detention time at 35°C. The gas produced was collected and expelled daily. The digesters were fed daily (0.1 of the reactor volume) with a mixture of municipal primary and secondary sludge, identical to the incoming sludge of the full scale anaerobic digesters at the waste water treatment plant München I (Table 1).

Table 1. Chemical composition of the undigested sludge

pH	COD $g\ m^{-3}$	VSS $g\ m^{-3}$	protein $g\ m^{-3}$	vol.fatty acids $mol\ m^{-3}$	N-org. $g\text{-}N\ m^{-3}$	NH_4^+ $g\text{-}N\ m^{-3}$	SO_4^{--} $g\text{-}SO_4\ m^{-3}$	$P_{tot.}$ $g\text{-}P\ m^{-3}$
5.9	50000	32000	13700	13.2	2530	250	46.2	210

The sludge was homogenized and stored at -20 °C. Metal additions were made after the digesters run approximately 14 days under steady state conditions. Metals were added as metal chloride to the sludge fed.

The metal concentrations were determined by using AAS as well as ICP (Table 2), sulfate was determined by ion exchange chromatography, and other analysis were conducted as described previously (Müller and Steiner, 1988).

Table 2. Heavy metal concentration (g m^{-3}) in the undigested sludge

Ni(II)	Cu(II)	Cd(II)	Cr(III)	Pb(II)
6.0	20.0	0.1	15.0	5.5

RESULTS

Nickel

When feeding sludge continuously with a concentration of 300 g Ni m^{-3} the gas production rate (GPR) decreased with the daily increasing nickel concentration in the fermenter (Figure 1). The mean gas production rate (MGPR) before nickel addition was 1396 ml gas l^{-1} d^{-1}. After 14 days of acclimation the fermented sludge contained 245 g Ni m^{-3} and methane production stopped completely. Hence, all of the methane producing bacteria were killed or severely inhibited as microscopic examinations indicated. The slow accumulation of volatile fatty acids caused a lowering of pH in the fermenter a few days after nickel addition started.

Simultaneously, other fermenters were shock loaded with an increase from 6 g Ni m^{-3} (base level) to 300, 150, and 75 g Ni m^{-3}, respectively, in the digester (Figure 2a,b,c). After shock loading, the nickel concentrations in the sludge decreased continuously. The fermenter shock loaded with 300 g Ni m^{-3} stopped methane production and no recovery of the process occurred. The concentration of volatile fatty acids increased exponentially after nickel addition and the pH dropped down to pH 6.5 8 days after the loading and remained constant until the experiment was terminated. Shock loading with the lower nickel concentrations reduced VSS degradation from 54% to 25% (resulting from a 150 g Ni m^{-3} shock), and reduced the gas production rate for a short period of time but inhibition was reversible for 150 and 75 g Ni m^{-3} additions. The concentration of volatile fatty acids increased up to 55 and 90 mol m^{-3} for 75 and 150 g Ni m^{-3} loadings, respectively. In either case the concentration of fatty acids in the fermenters decreased to a normal level after 4 and 20 days, respectively. The pH value dropped from pH 7.6 to pH 6.9 10 days after a 150 g Ni m^{-3} shock but increased back to the normal level 10 days later. pH was not sensitive enough to monitor any effect of a shock of 75 g Ni m^{-3}.

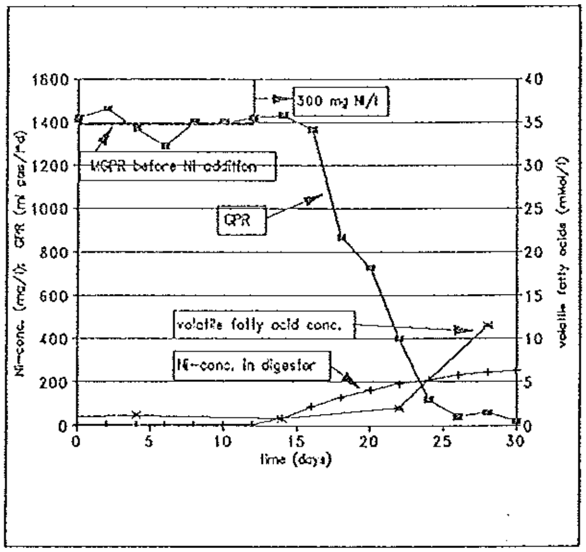

Figure 1. Continuous addition of 300 mg Ni/l started at day 14 and continued until the experiment was terminated

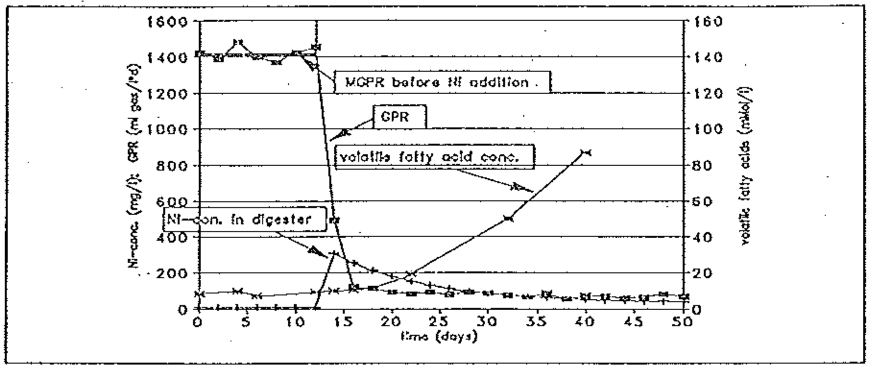

Figure 2a. The nickel concentration in the digester was increased to 300 mg/l on day 14. GPR, and volatile fatty acid concentration was monitored, the metal concentration was calculated.

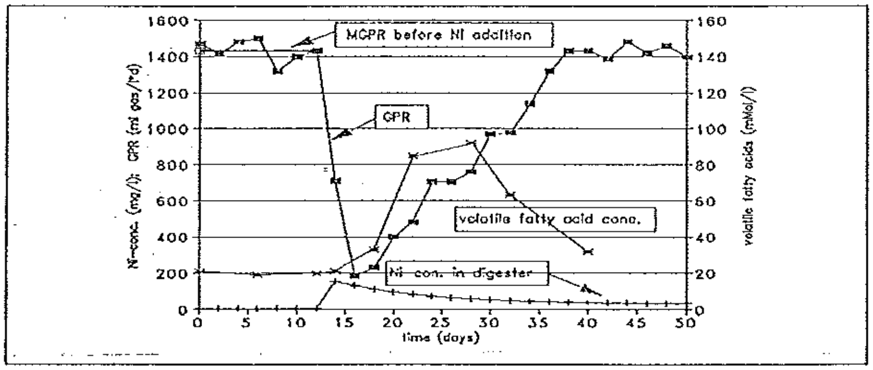

Figure 2b. Shock loading 150 mg Ni/l on day 14.

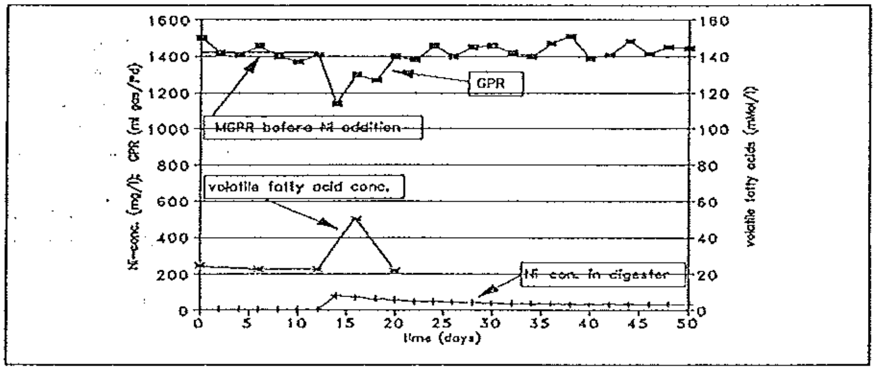

Figure 2c. Shock loading 75 mg Ni/l on day 14.

Copper

The sludge added to the fermenter contained 300 and later 500 g Cu m^{-3}. The gas production rate was inhibited relative to the copper concentration added to the fermenter (Figure 3).

300 g Cu m^{-3} resulted in a 40% lower MGPR than the control
500 g Cu m^{-3} resulted in a 64% lower MGPR than the control

The methane content in the produced gas decreased from 64% to 51% when adding copper to the fermenter. There was no significant difference in methane content between adding 300 or 500 g Cu m^{-3}. The concentration of volatile fatty acids increased steadily up to 30 mol m^{-3} and remained relatively constant. Correspondingly the pH decreased from pH 7.3 to pH 6.7. The degradation of VSS decreased from 53 % to 44 % and remained constant at that level.

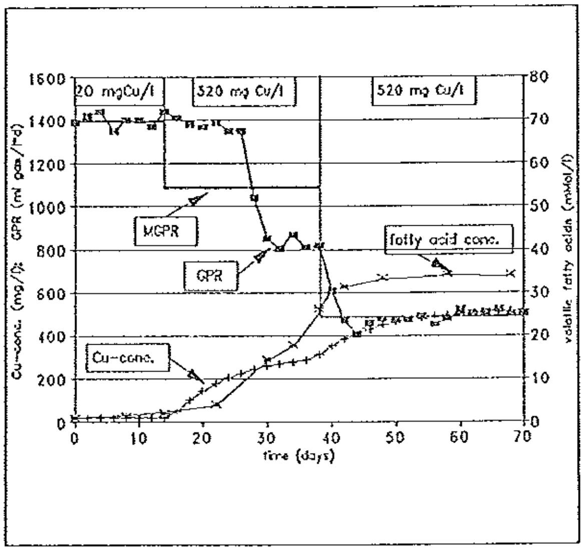

Figure 3. Continuous addition of 320 mg Cu/l from day 14 to day 37. From day 38 to day 70 the copper conc. in the sludge fed was 520 mg/l. GPR and volatile fatty acids were monitored and the copper concentration was calculated.

Shock loading the fermenters with copper (250, 300, 700, and 1000 g Cu m^{-3}) led to a temporary breakdown in gas production (Figure 4). The methane content in the produced gas decreased from 65 % to 35 % (300 g Cu m^{-3}). The concentration of volatile fatty acids increased after a shock of 300 g Cu m^{-3} from 3.5 to 70 mol m^{-3} but decreased later. The pH values dropped in all fermenters exposed to copper down to the lowest value measured of pH 6.6 (700 g Cu m^{-3}). However, at all tested copper concentrations the pH values returned to their initial values. The VSS degradation changed as a result of a 300 g Cu m^{-3} addition from 57 % to 32 % VSS degradation but showed an VSS degradation of 58 % 28 days after the metal was added. The time for total recovery from of the process was dependent on the initial copper concentration added.

18 days for addition of 250 g Cu m^{-3}
26 days for addition of 300 g Cu m^{-3}
33 days for addition of 700 g Cu m^{-3}
43 days for addition of 1000 g Cu m^{-3}

22 days for addition of 700 g Cu m^{-3} (preexposed to Copper)

An experiment was designed to test the adaptation capability of the anaerobic bacteria to copper. In one fermenter shock loading with 700 g Cu m^{-3} occurred 2 days after complete recovery from a former shock of 300 g Cu m^{-3}. The decrease in GPR was less and the time for a total recovery was shorter in the acclimated fermenter than in the fermenter with the same loading but no preexposure to copper. A kinetic study on GPR was performed for the adaptation experiment. One hour after the shock, GPR of the preexposed digester was 20 % below the control value, whereas in the digester without preexposure, the GPR was 90 % below the control value. After 24 hours both digesters produced at a similar level (78 % below control).

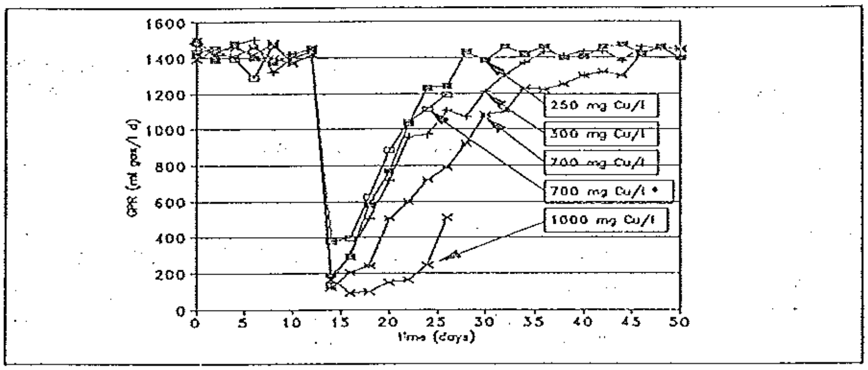

Figure 4a. Shock loading copper at various concentrations (250, 300, 700, and 1000 mg/l). One digester was loaded with 700 mg Cu/l* after preexposure to 300 mg Cu/l.

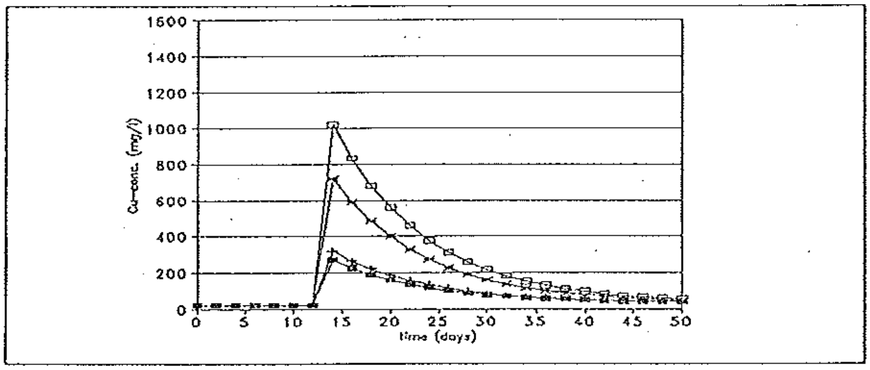

Figure 4b. Copper concentration in the digester during the shock loading experiment.

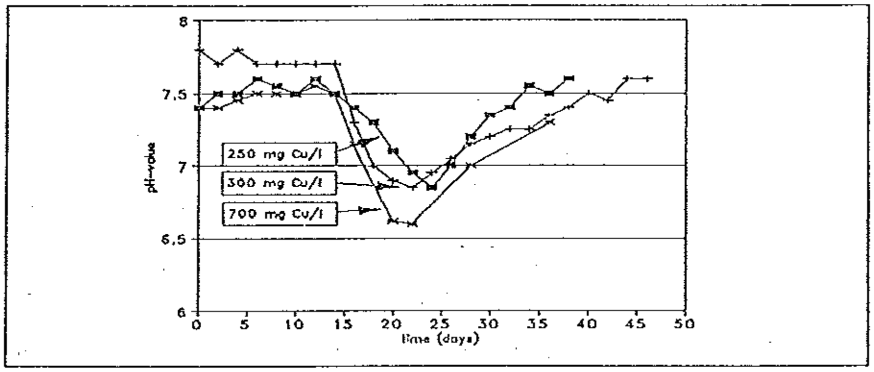

Figure 4c. Monitoring pH during the shock loading experiment with copper.

Cadmium

Cadmium caused a decrease in MGPR proportional to the total cadmium concentration added to the sludge (Figure 5). The methane content of the gas produced decreased from 71 % to 59 % at a continuous dosage of 650 g Cd m^{-3}. A dosage of 155 g Cd m^{-3} did not alter the gas composition significantly. Volatile fatty acids did not accumulate before 650 g Cd m^{-3} were dosed on day 50. Despite a temporarily high acid level, most of these acids were depleted within a few days, but the average acid concentration remained at a higher level. As a result pH decreased from pH 7.4 - pH 7.5 (during day 0 to day 50) to pH 6.9 - 7.0 (during day 53 - 70). The degradation of VSS decreased from 52 % without cadmium addition to 30 % on day 60 (650 g Cd m^{-3}).

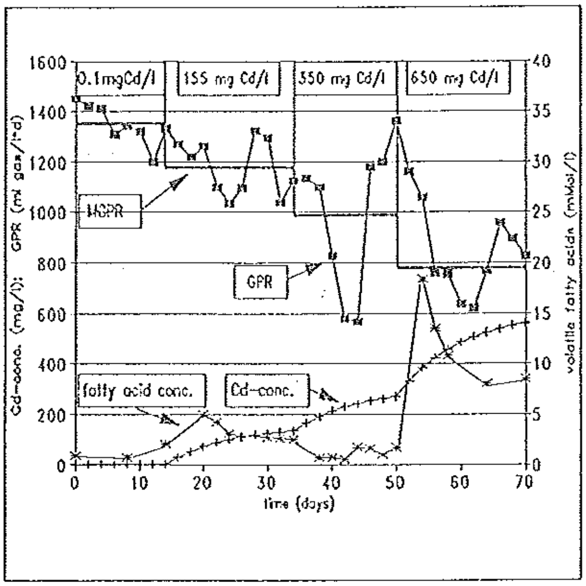

Figure 5. Continuous addition of 155 mg Cd/l (day 14-33, 350 mg Cd/l (day 34-49), and 650 mg Cd/l (day 50-70). Monitoring GPR, and volatile fatty acid conc. and calculating the Cd conc. in the digester.

Chromium

Chromium addition caused little effect on the process of anaerobic digestion, e.g. the gas composition, the concentration of volatile fatty acids, pH value, and VSS degradation did not indicate an excessive response even when adding 1000 g Cr m^{-3} (Figure 6). The MGPR decreased 7 % compared to the control level when continuously adding 500 g Cr m^{-3} and 27 % when adding 1000 g Cr m^{-3}. The variance of GPR increased from 11 to 18 % after addition of chromium. The volatile fatty acids content did not change significantly during the experiment (1 - 6 mol m^{-3}). Consequently pH in the fermenter did not change during the experiment and remained at a neutral level of pH 7.1 - 7.3. The degradation of VSS decreased from 50 % (control level) to 44 % (day 60; 1000 g Cr m^{-3}).

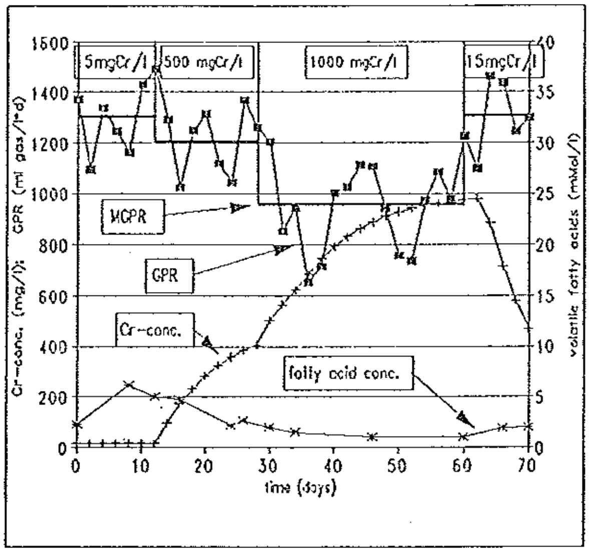

Figure 6. Continuous addition of 500 mg Cr/l (day 14-27) and 1 g Cr/l (day 38-62). After day 62 the addition of Cr was stopped and the Cr conc. decreased in the digester.

Lead

Continuously feeding a sludge containing 600 g Pb m^{-3} had no significant effect on the process of anaerobic digestion (Figure 7). The daily measured gas production rate dropped shortly after the lead addition started but recovered the next day and returned to the same level as measured without lead addition. Hence, the variance in GPR increased from 8 % (before lead addition) to 13 % (with lead addition). The methane content of the gas produced remained constant during the experiment between 67 and 70 % methane in the gas phase. Volatile fatty acid concentration and pH did not respond to the lead addition, and remained at 2 mol m^{-3} and pH 7.3 to pH 7.4, respectively.

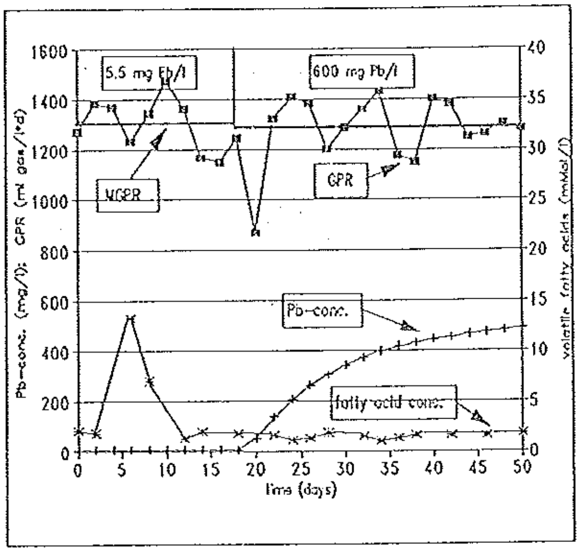

Figure 7. Continuous addition of 600 mg Pb/l (day 18 - 50). Monitoring GPR and volatile fatty acid conc., the Pb concentration in the digester was calculated.

Distribution Characteristics of Ni, Cu, Cd, Cr, and Pb in Digested and Undigested Sewage Sludge

Since toxicity of heavy metals depends on the metal concentration in a soluble, ionic form and not simply on the total metal concentration in the digester, the distribution characteristics of the metals during digestion become a crucial importance. The concentration of dissolved metal ions (or metal complexes) of all tested metals was small compared to the total amount of metal added. Immobilization was assumed for simplicity to be a first order reaction with respect to the metal concentration in the sludge. This assumption will fail for high metal concentration above the binding capacity of the sludge. The concentration of dissolved metal species in the digested sludge is plotted versus the total metal concentration added (Figure 8). The less metal immobilization, the steeper the corresponding line. All heavy metals tested were immobilized to a high degree in the sewage sludge. Metal immobilization was significantly higher after digestion for nickel, copper, and chromium, whereas the concentration of dissolved cadmium and lead seemed unaffected during

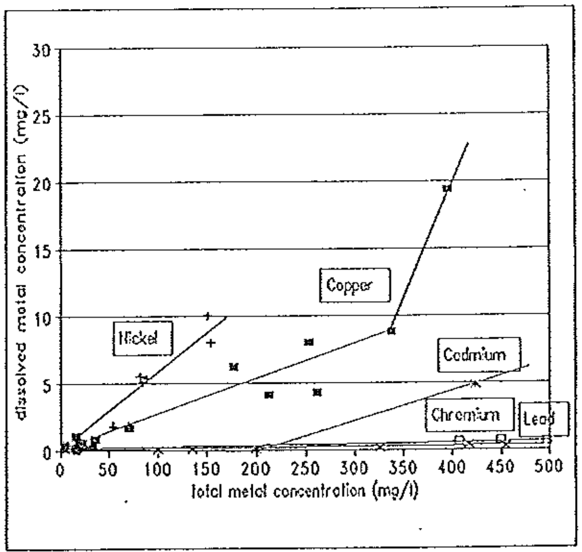

Figure 8. Metal distribution characteristics, plotting dissolved metal concentration versus the total metal concentration in the digested sludge.

digestion. Lead showed very high degrees of immobilization (> 99.9 %) in the undigested as well as in the digested sludge. With the exception of chromium in the digested sludge, the degree of metal immobilization increased with increasing atomic weight of the element.

Table 3. Metal distribution in undigested and digested sludge

metal	Ni	Cu	Cr	Cd	Pb
atomic weight	58.71	63.55	52.00	112.40	207.20
tot. metal conc. [g m^{-3}]	500	500	1000	600	500
diss. metal conc. [g m^{-3}] (undigested sludge)	44	27	29	6	0.5
diss. metal conc. [g m^{-3}] (digester)	28	17	0.7	5	0.3
metal immob. [%] (undigested sludge)	91	95	97	99	99.9
metal immob. [%] (digested sludge)	94	97	99.9	99	99.9

Sulfide

The sulfide production rate in the digester was calculated as follows:

protein content (undigested sludge) [g m^{-3}]:	13,700
sulfur content (undigested sludge) [g m^{-3}]: (assuming 1 g-S in 100 g protein)	137
sulfate concentration (undigested sludge) [g SO_4-S m^{-3}]:	16
protein degradation during anaerobic digestion [%]: (averaged for uninhibited digestion)	55
sulfate conversion during anaerobic digestion [%]: (averaged for uninhibited digestion)	90
sulfide production rate [g H_2S-S $m^{-3}d^{-1}$]: (protein degradation)	75
sulfide production rate [g H_2S-S $m^{-3}d^{-1}$]: (sulfate reduction)	14
total sulfide production rate [g H_2S-S $m^{-3}d^{-1}$]:	89
total gas production rate [m^3 gas m^{-3} sludge d^{-1}]: (averaged for uninhibited digestion process)	14
sulfide content in the gas produced [%]: (no metals present)	0.42

The stoichiometric (maximum) amount of metal precipitating with the produced sulfide (89 g m^{-3} d^{-1}) was calculated according to (Lawrence and McCarty, 1965):

163 g Ni m^{-3} d^{-1}

176 g Cu m^{-3} d^{-1}

312 g Cd m^{-3} d^{-1}

576 g Pb m^{-3} d^{-1}

Since chromium sulfide follows an aquatic hydrolysis chromium precipitates as chromiumoxydehydrate.

DISCUSSION

The severity of inhibition caused by heavy metals was dependent on metal species and concentration in the digester. In general, a larger amount of metal added resulted in a higher degree of inhibition.

Nickel was immobilized to the lowest degree (91 and 94 % before and after digestion), hence the concentration of nickel free ions or nickel complexes in the aqueous phase was high.

From all metals tested, nickel indicated the most dramatic effect on anaerobic digestion (Figure 1 and 2). At a concentration of 250 to 300 g Ni m^{-3} (10.70 g Ni kg^{-1} VS) methane production stopped completely and no recovery of the process occurred. The corresponding concentration of dissolved nickel in the aqueous phase was 26 - 28 g Ni m^{-3}. This toxic effect was observed for a continuous addition of nickel (the daily fed sludge contained 300 g Ni m^{-3}) as well as for a shock load to the fermenter (the nickel concentration in the digester was increased from 7 to 300 g Ni m^{-3} within a few minutes). The initial low level of volatile fatty acids increased exponentially at longer acclimation time, hence methanogens were unable to metabolize fatty acids. This indicates a reversible inhibition for the acid producers but toxicity for the acid consumers, the methanogens.

Lower nickel concentrations caused temporary inhibition depending on the nickel concentration in the digester (86 % and 16 % lower GPR for 150 and 75 g Ni m^{-3}). In either case inhibitory effects were reversible, with a longer recovery time for higher nickel concentrations. Acid producing bacteria indicated immediate inhibition when adding 150 g Ni m^{-3}, however, they recovered faster than the volatile fatty acid metabolizing methanogens which caused an temporary accumulation of fatty acids. A shock of 75 g Ni m^{-3} did not result in significant inhibition of acid producers and the methanogens recovered within a few days of acclimation.

Continuous copper addition (up to 500 g Cu m^{-3}) resulted in inhibition of acid producing, fermentative, and methanogenic bacteria in a similar manner (Figure 3). This was indicated by: a slight increase of volatile fatty acids; a decrease of VSS degradation; a decreasing GPR; a decreasing methane content of the gas. The MGPR reduction was related to the copper concentration added (40 and 64 % MGPR, feeding the digesters with a 300 and 500 g Cu m^{-3}, respectively). Shock loading copper up to a concentration of 1000 g Cu m^{-3} in the digester did not result in irreversible inhibition of the process (Figure 4). The immediate decrease in GPR (90 % reduction, one day after the shock) was similar for every tested copper concentration (250, 300, 700, 1000 g Cu m^{-3}), but the time necessary for recovery of the process was linked to the total metal concentration when the shock occurred. Generally, a higher copper shock demanded a longer period of time until curing of the digester was reached. The organisms responsible for anaerobic digestion indicated the capability of adaptation to copper, which was tested in a parallel shock loading experiment of 700 g Cu m^{-3} with two fermenters of different histories. The fermenter which was preexposed to 300 g Cu m^{-3} indicated less immediate inhibition and an almost two times faster recovery than the fermenter without preexposure. This was recognized from the daily measured parameters as well as from the kinetic study on GPR immediately after the shock. Copper uptake in the sludge was 95 and 97 % before and after digestion, respectively.

Cadmium inhibited the process of anaerobic digestion depending on the cadmium concentration in the sludge (Figure 5). A cadmium concentration of 155 g m^{-3}, 350 g m^{-3} and 650 g m^{-3} resulted in 14%, 27%, and 43% reduction of MGPR, respectively. For longer durations of acclimation, a tendency of recovery was observed. The relatively constant level of fatty acids indicated the inhibition of acid forming- and acid metabolizing bacteria to a similar degree. Fermentative bacteria were inhibited at a similar level. The capability of immobilizing cadmium in the sludge was high (99%) and did not differ before and after digestion significantly.

Chromium showed little effect on anaerobic digestion (Figure 6). A continuous addition of 500 g Cr m^{-3} resulted in a 7 % lower MGPR. After increasing the chromium concentration to 1000 g Cr m^{-3} the MGPR was reduced 27 %. All three groups of organisms (fermentative, acid producing-, and methane producing bacteria) were inhibited. A low short chain fatty acid production and a lower methane production rate were observed. After chromium addition stopped, the initial GPR was restored within a few days resulting from an already indicated tendency toward adaptation. Since chromium indicated a high uptake under anaerobic conditions, the concentration of chromium ions in the digester was low (0.7 g Cr(diss) m^{-3} at 1000 g Cr(tot) m^{-3}). The degree of immobilization in the undigested sludge was significantly lower (97 % Cr removal).

Lead addition of 600 g Pb m^{-3} did not indicate any significant long term inhibiting effect (Figure 7). The removal of lead ions by the sludge was very efficient (99.9 %). Hence, the lead ion concentration in the digester was always below 0.3 g m^{-3}.

As described above the presence of sulfide has a major influence on toxicity or inhibiting effects of heavy metals during anaerobic digestion. Sulfide reduces the effect of a toxic heavy metal by precipitation as metal sulfide salt. Many of these highly insoluble metal sulfides precipitate very rapidly even at low pH values. Also, all investigated metals build hydroxide complexes to various degrees depending mainly on pH. In all cases investigated (except chromium) the metal removal from the aqueous phase had a higher efficiency with increasing atomic weight of the metal. This indicates a stoichiometry dependent precipitation and might be caused by the production of metal sulfide salts. This hypothesis is also supported by the low sulfide content in the produced gas for high metal concentrations (0.01 - 0.03 %). The remaining dissolved metal species were not differentiated, but simply determined as dissolved metal.

CONCLUSIONS

Based on the results from this work there are two different mechanisms of similar importance for investigating inhibiting effects on anaerobic digestion.

1) The metal binding characteristics in a sludge. This might change with the treatment of the sludge (e.g. aerobic thermophile stabilization, anaerobic mesophile digestion, etc.), the chemistry (e.g. sulfate and sulfide concentration, pH, etc.) and its concentration and composition of the VSS (e.g. protein- and biomass contend).

2) Toxicity or inhibiting effect on the process caused by dissolved metal species. The severity of the inhibition depends on the metal species and the concentration.

Only a combination of these points provides sufficient information for prediction (or simulation) of toxicity or process inhibition in a specific treatment system.

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